SUPPLEMENT TO THE CHEMICAL NEWS, JULY 3, 1891.

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IN ALL ITS APPLICATIONS TO

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No. 1623.—JANUARY 2, 1891.

ON A
DETERMINATION OF THE BOILING-POINT OF SULPHUR,
AND ON A
METHOD OF STANDARDISING PLATINUM RESISTANCE THERMOMETERS BY REFERENCE TO IT.*

By HUGH L. CALLENDAR, M.A., Fellow of Trinity College, Cambridge, and E. H. GRIFFITHS, M.A., of Sidney Sussex College, Cambridge.

EXPERIMENTS by different observers have shown that electrical resistance thermometers afford the most convenient and accurate method of measuring temperature through a very wide range. By selecting a particular thermometer as the standard, and directly comparing others with it, it has been found possible to attain a degree of accuracy of the order of 0·001° in the relative measurements between 0° and 100° C., and of the order of 0·01° at 450° C.

In a previous communication† it has been shown that, if t be the temperature by air thermometer, and if pt be the temperature by platinum resistance thermometer, the difference between them is very closely represented from 0° to 700° C. by the formula—

$$d=t-pt=\delta\left\{\overline{t/100}|^2-t/100\right\} \quad .\ .\ .\ .\ (d).$$

The value of the constant δ for a particular wire was found to be 1·570.

The object of the present paper is to describe a method of finding the value of this constant for any such thermometer, by means of a single observation at some known fixed point other than 0° or 100° C.

The boiling-point of sulphur happens to be the most convenient for this purpose. We have therefore made a careful determination of this point by reference to the standard air thermometer, and have given a full description of the method and apparatus which we have found most suitable for standardising platinum thermometers by means of it.

The paper is divided into three parts.

Part I. contains a description of the method and apparatus employed in comparing the platinum thermometers used in this investigation with the air thermometer at a temperature very near the boiling-point of sulphur.

Part II. contains the determination of the actual boiling-point of sulphur by means of the thermometers thus standardised, and a description of the method and apparatus to be used in standardising other platinum thermometers. A table is also given reduced from a previous series of observations of other fixed points which may be used for the same purpose.

Part III. contains a comparison of the platinum and air thermometers between 0° and 100°, and shows that the δ-formula holds accurately between those limits.

The determination of the boiling-point of sulphur was made by means of three platinum thermometers, L, M_1, and M_2, constructed out of the wire used in the experiments of 1887, before referred to.

Full descriptions of these thermometers are given in the paper. They were furnished with double electrodes for measuring the resistance of the connecting wires at each observation, their insulation was carefully tested, and all due precautions were taken to guard against thermal effects and other sources of error.

Thermometers M_1 and M_2 were standardised by direct comparison with an air thermometer at the boiling-point of sulphur. Full particulars are given of the details of the observations and calculations, showing the limits of error of the experiments.

The expansion of the glass forming the bulb of the air thermometer was determined both by the method of linear expansion, and also by using the bulb itself as a mercury weight thermometer. The values found by the two methods agreed very closely.

The small changes of the volume of the bulb were determined from time to time during the progress of the experiments. The final observations were not taken till the thermometer had reached a fairly steady state.

The limit of accuracy attainable with this air thermometer was found to depend chiefly on that of the barometric readings. The barometer used was therefore verified by a careful comparison with the standard metre scale.

The iron-tube apparatus in which the platinum and air thermometers were compared was so constructed as to be capable of being maintained at a constant temperature by a steady flow of sulphur vapour for any length of time.

Observations were taken with it on two separate days. On each occasion the temperature was kept steady to 0·1° for about two hours. Allowing for the difference of the atmospheric pressure, the temperature attained was the same on both days.

The results of the comparison were in perfect agreement with the experiments of 1887, and showed that the δ-coefficient of the wire had not altered appreciably in the interval.

The apparatus which we have found most convenient for standardising platinum thermometers by means of the boiling-point of sulphur consists of a wide glass tube, 40

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* Abstract of a Paper read before the Royal Society, Dec. 18, 1890.
† Callendar, *Phil. Trans.*, A., 1887, p. 161.

c.m. long and 4 c.m. in diameter, with a spherical bulb at the end. Tubes of this kind are commonly used to heat Victor Meyer's vapour-density apparatus. For brevity we have called it a "Meyer" tube.

The outside of the tube is thickly padded with asbestos wool, with the exception of the lower half of the bulb, and of a short length of 3—5 c.m. at the top, which serves as a condenser. The tube is filled with sulphur to a level of 3 or 4 c.m. above the bulb, and is heated by a Bunsen burner. The gas is adjusted so as to keep the level of the vapour near the top of the tube, which is covered with asbestos card to prevent the sulphur catching fire.

Our experiments have shown that a thermometer inserted in an apparatus of this kind will not attain the actual temperature of the vapour, unless it is protected from radiation to the sides of the tube, and from the condensed liquid which runs down the stem. The lowering of temperature due to radiation, &c., may readily amount to upwards of 2° at the boiling-point of sulphur.

The method which we have adopted for screening the thermometer is to bind an umbrella of asbestos card on to its stem a short distance above the bulb. Two coaxial tubes are hung on to this umbrella to screen the thermometer from radiation. We have found that glass is not sufficiently opaque to heat radiation at this temperature. The inner tube at least should be of metal.

To avoid superheating of the vapour, it is necessary to make sure that the level of the liquid sulphur stands well above that part of the bulb which is exposed to the flame.

Using these precautions, we have found that the temperature by normal air thermometer at constant pressure of the saturated vapour of sulphur, boiling freely under a pressure of 760 m.m. of mercury at 0° C. and $g = 980{\cdot}61$ C.G.S. (sea level in lat. 45°), is—

$$t = 444{\cdot}53^\circ \text{ C.}$$

The value given by Regnault[*] is nearly 4° higher than this; but in the account which he gives of his experiments he has pointed out several sources of error, and it is evident that he did not place much confidence in his results.

The close agreement between the air thermometer experiments of 1887 and the present series leads us to conclude that the number above given is probably correct to a tenth of a degree, and that it may be safely used for standardising platinum thermometers.

The method which we recommend for standardising platinum thermometers is briefly as follows:—Observe the value R_s of the resistance in sulphur vapour in an apparatus such as we have described. Calculate the value of pt_s by the formula—

$$pt_s = 100\,(R_s - R_0)/(R_{100} - R_0).$$

Find the temperature t of the sulphur vapour, corresponding to the corrected barometric pressure H_0, from the formula—

$$t = 444{\cdot}53 + 0{\cdot}082\,(H_0 - 760).$$

The appropriate value of δ is then given by the equation—

$$t - pt = \delta\left\{\overline{t/100}|^2 - t/100\right\}.$$

We have made use of this method to reduce the results given in a previous communication,[†] "On the Determination of some Boiling and Freezing Points by means of the Platinum Thermometer," and we find that the values of t deduced from the observations with several thermometers of different patterns and with very different coefficients, are in remarkably close agreement. The results found with the three best thermometers are given in the following table:—

Table of Boiling and Freezing Points Reduced by Formula (d).

Nature of experiment.	Thermometers used.			
	E.	F.	G.	Mean.
Boiling-point of—				
Aniline .. .. (760 m.m.)	184·11	184·13	184·14	184·13
Naphthalene.. ,,	217·88	217·96	217·98	217·94
Methyl salicylate ,,	222·98	223·08	—	223·03
Benzophenone ,,	305·82	305·87	305·78	305·82
Triphenyl methane (770·8 m.m.)	356·47	—	356·41	356·44
Mercury.. .. (760 m.m.)	356·74	356·82	356·71	356·76
Freezing-point of—				
Tin	231·66	231·66	231·73	231·68
Bismuth..	269·18	—	269·25	269·22
Cadmium	320·70	—	320·66	320·68
Lead	327·66	—	327·71	327·69
Zinc	417·55	—	417·59	417·57

The fixed points given in the above have not been so carefully determined as the boiling-point of sulphur. They rest entirely on the assumption of the accuracy of the δ-formula, and have not been directly referred to the air thermometer. We believe, however, that they are probably correct to 0·1° C., and that they may be safely used to standardise thermometers of limited range, in cases where it may happen to be inconvenient to make use of the sulphur point.

In comparing the platinum and air thermometers between 0° and 100° C., observations were taken at intervals of 5° all the way up. The mean deviation of the observations from the parabolic formula (*d*) is only 0·006°. This corresponds to the limit of accuracy of the barometric readings, and there is no reason to suppose that the δ-formula may not represent the difference even more closely than this.

The same platinum thermometer has been compared with several mercury thermometers standardised at Kew.[*] The result seems to show that the Kew standard reads 0·1° C. lower than our air-thermometer at 30°.

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[*] *Mémoires de l'Institut*, vol. 26, p. 526.

[†] Griffiths, *Phil. Trans.*, A, 1890.

[*] Griffiths, "Brit. Assoc. Report," 1890.

THE VARIATIONS OF ELECTROMOTIVE FORCE OF CELLS CONSISTING OF CERTAIN METALS, PLATINUM, AND NITRIC ACID.[†]

By G. J. BURCH, B.A., and V. H. VELEY, M.A., the University Museum, Oxford.

The description of the apparatus, the capillary electrometer, and the method of working are given fully in the paper. The following conclusions are drawn from the results of the experiments:—

I. When the metals copper, silver, bismuth, and mercury are introduced into purified nitric acid of different degrees of concentration, and a couple made with platinum, the electromotive force of such a cell increases considerably until it reaches a constant and (in most cases) a maximum value. The rise of E.M.F. is attributed to the production of nitrous acid by the decomposition of the nitric acid, and the final value is considered to be due to the former acid only, while the initial value is due for the most part to the latter acid, though it is affected to a remarkable degree by the amount of impurity of nitrous acid, either initially present or produced by minute and unavoidable uncleanliness of the metallic strip and the containing vessel.

II. If nitrous acid has been previously added to the nitric acid, then the maximum E.M.F. is reached *at once*.

III. If the conditions, namely, increase of temperature, of impurity, and of concentration of acid, are such as

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[†] Abstract of a Paper read before the Royal Society.

would favour a more rapid solution of the metal, and consequently a more rapid production of nitrous acid, then the rise of E.M.F. is concomitantly more rapid.

IV. Conversely, if the conditions are unfavourable to the production of nitrous acid, the rise of E.M.F. is less rapid.

V. If any substance, such as urea, be added which would tend so destroy the nitrous acid as fast as it may be formed, then the rise of E.M.F. is extremely slow, being dependent upon the number of molecular impacts of the nitrous acid upon the surface of the metal.

Thus the results obtained by the electrometer and by the chemical balance are in every way confirmatory the one of the other.

The authors propose to conduct further investigations on cells containing other acids, to determine whether the action of them upon metals is conditioned by the presence of their products of electrolysis.

THE CONDITIONS OF CHEMICAL CHANGE BETWEEN NITRIC ACID AND CERTAIN METALS.*

By V. H. VELEY, M.A., the University Museum, Oxford.

This paper is in continuation of a preliminary communication on the same subject; the main points contained in it are as follows:—

I. The metals copper, mercury, and bismuth do not dissolve in nitric acid of about 30 per cent concentration (the acid commonly employed for the preparation of nitric oxide gas) and heated to a temperature of 30° C., provided that nitrous acid is neither present initially nor formed subsequently. To prevent this it is necessary in the cases of copper and bismuth to add a small quantity of some oxidising substance, such as hydrogen peroxide or potassium chlorate, or, as less efficacious, potassium permanganate, or to pass a current of air or, lastly, such a substance as urea, which destroys the nitrous acid by its interaction.

II. If the conditions are such that these metals dissolve, then the amount of metal dissolved and the amount of nitrous acid present are concomitant variables, provided that the nitric acid is in considerable excess. Change of conditions, such as concentration of acid and variation of temperature, which increase the former increase also the latter.

III. If the conditions are such that these metals dissolve, it would appear that the metallic nitrite is at first formed, together with nitric oxide; the former is decomposed by the excess of nitric acid to liberate nitrous acid, while the latter reduces the nitric acid to form a further quantity of nitrous acid.

Eventually the net result is the product of two reverse chemical changes represented by the equations—

$$\text{(i.)}\ 2NO+HNO_3+H_2O=3HNO_2,$$
$$\text{(ii.)}\ 2HNO_2=2NO+HNO_3+H_2O.$$

The nitrous acid is thus destroyed as fast as it is generated.

IV. If the conditions are such that metals dissolve in nitric acid, then nitrous acid is invariably the initial product of reduction.

V. The metals copper, mercury, and bismuth dissolve very readily in a 1 per cent solution of nitrous acid; under these conditions nitric acid present in slight excess interferes with, rather than promotes, the chemical change. This result is probably due to the greater stability of nitrous acid in the presence of nitric acid.

VI. Hydrogen gas reduces nitric to nitrous acid in presence of cupric or lead nitrate; it also converts mercuric into mercurous nitrate, but does not produce any change in solutions of bismuth and zinc nitrates dissolved in nitric acid.

FRICTION OF GASES IN PIPES.

By Dr. L. C. LEVOIR, Polytechnicum, Delft.

The introduction of gaseous fuel in factories compels lecturers in technical colleges to discuss a series of quite new laws. In all the old treatises on Physics and Chemistry no experiment is related that might give a large audience an idea of the diminution in pressure on conducting gases through tubes. In the Chemical News for August 3rd, 1861 (vol. iv., p. 60), and *Dingler's Polytechnisches Journal* (German), 1861, I described an experiment to show that friction of smoke in a chimney is higher in a conical one when the widest end is used as inlet.

Two small gas-flames on the same T-shaped gas-pipe, with very low pressure of the gas, gave me an opportunity to show that one of the flames was nearly invisible on the opposite side from where the chimney (1 metre in length, and 2 and 5 centimetres in diameter) drew with the highest force.

But there is a still more sensitive test for difference in exhausting power,—that is, in every Bunsen's burner of great size the inlet for the air must be regulated in the stand, that the flame cannot burn on the top, but detonates always downwards from too great admixture of air. A small end of tube placed in the air-holes directly stops that explosion, by causing friction therein and diminishing the quantity of air admitted.

Evidently this is a way to show to a large audience the friction of smoke in chimneys and gas in tubes, which is so difficult a point both in the education of physicis and engineers.

ON GASEOUS ILLUMINANTS.*

By Professor VIVIAN B. LEWES.

I.

Just 200 years after Van Helmont (in the seventeenth century) first used the term "gas" to describe aëriform bodies, Faraday defined a gas as being the vapour of a volatile liquid, existing at a temperature considerably above the boiling-point of the liquid, and that the condensing-point of the gas was merely the boiling-point of the liquid producing it. This definition was contested at the time, as several of the gases had not then been condensed; but now it is known that the condensation of any gas to the liquid form is merely a question of sufficiently intense cold, and pressure.

Hydrogen and the gaseous compounds of carbon and hydrogen have so strong an affinity for the oxygen contained in the atmosphere, that the heat emitted by a burning match is generally sufficient to determine combination between the gases; and where the heat evolved by the combination is sufficient to raise the gases or vapour to incandescence, the phenomenon of flame is the result. Some flames have the power, under certain conditions, of emitting light, while others have no photometric value; and it is a matter of the gravest importance to the gas world that as clear a conception as possible should be obtained of the conditions and cause of luminosity in flames. A visible flame may either be solid—that is to say, composed of a solid mass of incandescent particles—or it may have a distinctive internal structure, and show zones in which varying phases of combustion are taking place; and it is to this latter class

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* Abstract of a Paper read before the Royal Society.

* Abstract of the Cantor Lectures delivered at the Society of Arts Communicated by the Author.

that all flames produced by a gas issuing from a burner belong.

In the *Philosophical Magazine* for 1817 Sir Humphry Davy says, while alluding to a paper published in one of the early numbers of the *Journal of Science and Arts*: "I have given an account of some new results on flame which show that the intensity of the light of flames depends principally upon the production and ignition of solid matter in combustion."

His theory, however, has gradually been altered by frequent quotation, until it is more often given as "the presence of solid particles suspended in the flame (or in immediate contact with the burning gas) is essential to its luminosity"—an idea which Davy never had, as is shown by him later in the paper defining flame as follows:—"Flame is gaseous matter heated so highly as to be luminous;" and again: "When in flames, pure gaseous matter is burnt, the light is extremely feeble." Moreover, he alludes to "common flames"—evidently meaning the flames of candle, lamps, or gas; in all which cases I think it can be proved beyond a doubt that his theory, as expounded by himself, was perfectly correct. On June 11, 1868, Professor E. Frankland read a communication before the Royal Society, in which he described experiments which led him to doubt Sir Humphry Davy's theory. He points out that the deposit of soot formed when a cold surface is held in a gas or candle flame is not pure carbon, but contains hydrogen, which can only be got rid of by prolonged heating in an atmosphere of chlorine. Also that many flames possessing a high degree of luminosity cannot possibly contain solid particles. Arsenic burnt in oxygen gives a bright white light; yet as arsenic volatilises at 180° C., and the arsenic trioxide forms at 218° C., it is evident that at the temperature of incandescence (which is at least 500° C.) there can be no solids, but simply vapours present in the flame; and for the same reason, the intense light resulting from the burning of phosphorus in oxygen cannot be explained by the solid particle theory. From these results Dr. Frankland considers that "incandescent particles of carbon are not the source of light in gas and candle flames, but that the luminosity of these flames is due to radiations from dense but transparent hydrocarbon vapours;" and he further shows that non-luminous flames, such as that produced by carbon monoxide and hydrogen, can, when burning in an atmosphere of oxygen, be rendered luminous if the ordinary atmospheric pressure is increased to 10 atmospheres, so as to prevent or retard as far as possible expansion during combustion. From Dr. Frankland's experiments, there is no doubt that the luminosity of a flame is increased by pressing around it the atmosphere in which it is burning, and also that rarefaction has the opposite effect—a point also worked at by Davy; but his experiments do not show that incandescent particles of carbon are not the principal source of luminosity in a gas flame. He also shows that the higher the density of the vapours present in a flame, the more likely is it to be luminous.

In 1874, Soret attempted to demonstrate the existence of solid particles in a luminous hydrocarbon flame, by focussing the sun's rays on the flame, and examining the reflected light by means of a Nicol prism; but neither his research nor that of Burch, who repeated his experiments, using the spectroscope instead of the prism, showed more than that solid particles are present. Herr W. Stein, in considering Dr. Frankland's objections to Davy's theory, pointed out that the soot which is deposited from a candle or gas flame, and which Frankland looked upon as a condensed hydrocarbon, contains 99·1 per cent of carbon and only 0·9 per cent of hydrogen, which is about the quantity of hydrogen one would expect to be occluded by carbon formed under these conditions, and he also pointed out that if the soot were a heavy hydrocarbon condensed by a cold surface, cooling the vapour present in the flame, it ought to again become volatile at a high temperature, which it does not. The next steps in the controversy were the attempts made by Hilgard, Landolt, and Blochman to trace the actions taking place in various flames by withdrawing the gases from different parts of the flame and determining their composition. Experiments which show that with ordinary gas it is the hydrogen which burns first, whilst the heavy hydrocarbons become gradually reduced by the heat of the flame into simpler compounds until in the luminous zone of the flame they are broken down into carbon and methane, and it is the carbon in excessively minute particles which at the moment of liberation is heated to incandescence, and "principally" gives the light of the flame—the marsh gas originally present, and also that formed from the heavier hydrocarbons, adding its quota to the luminosity by still further decomposition during combustion, and finally becoming carbon dioxide and water. In 1876, Dr. Karl Heumann made a most important contribution to the theory of luminous flames in some papers published in Liebig's *Annalen*, in which he carefully went over the work of previous observers, and, by a large number of original experiments, proved that Davy's theory was correct, but that other causes also affected the degree of luminosity in a gas or candle flame.

In the ordinary atmospheric burner in which a mixture of coal-gas and air burn with a non-luminous flame, it was supposed that the admixture of air, by supplying oxygen to the inner portion of the flame, caused immediate and complete oxidation of the hydrocarbons, without giving time for the liberation of carbon in the flame, and consequently luminosity. More modern researches, however, have proved this to be utterly wrong. The loss of luminosity is due to two causes—first, to the diluting action of the air introduced; secondly, to the fact that when a gas is so diluted it requires a far higher temperature to break up the hydrocarbons present than when the gas is undiluted, and therefore the temperature which serves to liberate carbon and render the undiluted gas-flame luminous, is totally insufficient to do so in the diluted gas. Consequently the hydrocarbon burns to carbon dioxide and water without any such liberation, and hence with a non-luminous flame. The truth of this theory can be easily proved by the fact that diluting the gas with nitrogen, carbon dioxide, or even steam, serves to render it non-luminous, and therefore more rapid oxidation has very little or nothing to do with it, while the non-luminous flame can again be rendered luminous either by heating the mixture of air and gas just before combustion, or by heating the air with which the gas is diluted. This being so, it is evident that in the non-luminous flame we have the same hydrocarbon present as in the luminous flame; and anything that will tend to break them up, and liberate the carbon before the hydrocarbons are consumed, should again make the flame luminous. That heat will do this has been already shown; but it can be demonstrated in a still more striking way. It is well known that chlorine gas and bromine vapour will both support the combustion of a gas containing much hydrogen, but that the combustion is very different from that of the same gas burning in air, as the chlorine or bromine, having no affinity for the carbon, combines with the hydrogen only, and deposits the carbon in clouds of soot; in other words, at the temperature of flame, chlorine will break up the hydrocarbons and liberate solid carbon. If now a small quantity of chlorine is led into the non-luminous Bunsen flame, it at once becomes luminous; proving conclusively that luminosity is due to solid particles of carbon liberated in the flame. Again, Heumann points out that a small rod held in the luminous flame becomes rapidly covered on its lower side with a deposit of soot; that is to say, the soot is present in particles in the flame, and the uprush of the gas drives it against the rod and deposits it there. If the soot were present in the flame, as Frankland supposed, in the state of vapour, and the rod merely acted by cooling and condensing it, the soot should be deposited on all sides of the rod; while a still further proof is that if the soot existed as vapour in the flame, then if the rod were heated to a high temperature no soot should be deposited on it, whereas the soot deposits on a heated surface just as well as on a cool one.

It has been objected to the "solid particle" theory that, if it were true, solid carbon particles introduced into a non-luminous flame should render it luminous and make it look like an ordinary gas-flame, whereas it simply gives rise to a cloud of sparks. But it must be remembered that the "nascent" carbon, as it is liberated from the decomposing hydrocarbons, is in the molecular condition, and has a very different degree of coarse-grainedness to any preparation of charcoal or lampblack we can make; and that, although our finest particle is a mass which takes so long to burn that it leaves the flames only partly consumed, and is projected into the air as a spark, the molecular particles of carbon are consumed as soon as they are rendered incandescent, and a steady luminosity, free from sparks, results. It is possible, however, to make the particles in a luminous flame roll themselves together, when they can be either deposited in a very coarse kind of soot, or be seen as glowing sparks and particles in the mantle of the flame. This can be done when two luminous flames are allowed to rush against each other or against a heated surface. Heumann also shows that the luminous mantle of a flame is not altogether transparent, and that the thicker the flame-layer, and the greater the number of solid particles contained in it, the less transparent does it become. If a non-luminous flame—say hydrogen—is charged with the vapour of chromyl dichloride (CrO_2Cl_2), chromic oxide is produced; and this flame, which undoubtedly contains solid particles, is quite as transparent as the hydrocarbon flame. Finally, those flames which undoubtedly owe their luminosity to the presence of finely divided solid matter produce characteristic shadows when viewed in sunlight; the only luminous flames which do not throw shadows being those which consist of glowing vapours and gases. Luminous gas-flames, oil-lamp flames, and candle flames produce strongly-marked shadows in sunlight, and therefore contain finely-divided solid matter; and that this can be nothing but carbon is evident from the fact that all other substances capable of remaining solid at the temperature of the flames are absent.

From the foregoing considerations, it must be admitted that Sir Humphry Davy's statement that the intensity of the light of flames (such as those produced by candles, oil, or gas) depends principally upon the production and ignition of solid matter in combustion, was undoubtedly the true one; and it must also be borne in mind that the degree of luminosity of a flame is affected by the constituents of the gas other than the heavy hydrocarbons—some, like marsh-gas, although ordinarily burning with an apparently non-luminous flame, and separating no soot, adding considerably to the luminosity at the temperature of the flame, while others, like carbon monoxide, reduce it.

The luminosity of a flame is increased by an increase of density in the media in which it is burning, and is decreased by rarefaction—an effect supposed by Dr. Frankland to be owing to the alteration of density and alteration of the mobility of the oxygen molecules in the air. This view, however, had been contested by Wartha, who concluded that it was due to the effect of pressure on the dissociation point of the hydrocarbons burning in the flame; this taking place more rapidly under increased pressure, and therefore liberating the carbon more quickly. However this might be, the effect of pressure on luminous flames was very marked, even under ordinary atmospheric pressure; the difference of an inch in the barometric column making 5 per cent difference in the luminosity. A burner giving 100 units of light with the barometer at 30 inches would only give 95 units if it fell to 29, while a rise to 31 inches would mean an increase of the luminosity to 105 units.

NOTES ON A RED SEDIMENT FORMED IN A RAFFINOSE SOLUTION.

By F. G. WIECHMANN, Ph D.

While engaged in the isolation of raffinose from a low beet-sugar, the writer incidentally obtained from the raffinose solution a precipitate, bright red in colour, and of peculiar properties, which he has so far been unable to identify as one of the numerous substances whose occurrence in saccharine solutions has been established.

The incident seemed sufficiently curious to merit recording, and although the amount of the substance secured was, unfortunately, too small to permit of ultimate analysis or of an exhaustive investigation, a brief history of the case, and a description of the properties of the body, as far as determined, may prove of interest.

The raw material used for the preparation of the raffinose was an after-product from a German beet-sugar factory employing the strontianite process.

The sugar presented a highly crystalline appearance, and exhibited in profusion the needle formation characteristic of products containing raffinose. In colour it was of a dark brown. The analysis, made in duplicate, showed:—

Polarisation	93·6	93·7
Sucrose	88·2	88·3
Raffinose	2·9	2·9

Work was commenced on November 23, 1888. The different steps taken were as follows:—

To 6000 grms. of raw sugar there were added 6000 c.c. methyl alcohol.

The solution was after some time drained off, and the sugar treated with an additional 4000 c.c. of methyl alcohol.

From the 10,000 c.c. alcohol added, about 7400 c.c. were recovered.

This solution was placed on a water-bath and the alcohol evaporated completely.

When this had been accomplished, and while the solution was still warm, ethyl alcohol was added until a *permanent* turbidity was caused.

This precipitate was allowed to settle, and was then separated from the clear solution.

This operation was performed six times; the time allowed for settling being in each instance about two days.

Then the raffinose syrup, perfectly free from alcohol, was drawn off.

This syrup amounted to 200 c.c., and was divided into three portions.

As the coloured sediment was produced in only one of these portions, a brief statement of the treatment which each of these portions received is given.

Part I.—20 c.c. were devoted to a trial of Scheibler's method for preparing raffinose.*

Treatment was commenced January 16, 1889, and by September 5, 1889, the separation of the raffinose crystals seemed complete.

Part II.—50 c.c. were treated as follows:—

The specific gravity of the syrup was determined to be 1·4022.

To the 50 c.c. (70·11 grms.), there were added 140·22 grms. acetate of lead. Then absolute ethyl alcohol was added, and the solution heated on a water-bath.

The precipitate which formed was filtered out, suspended in water, and sulphuretted hydrogen was passed in until complete precipitation of the lead had been accomplished.

The sulphide of lead was filtered out and thoroughly washed with water. The filtrate was evaporated on a

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* *Zeitschrift des Vereines für Ruben-zucker Industrie*, 1888, p. 337.

water-bath to the consistency of a thick syrup. This was dissolved in very little water, and when cold ethyl alcohol was added, drop by drop, until the turbidity just continued to disappear. The flask into which the solution had been placed was well corked and set aside to allow the crystallisation of its contents. On March 28, 1890, there was considerable of a white crystalline deposit in the bottom of the flask, and the sides of the flask were completely studded with warts of raffinose.

Part III.—On March 28, 1890, work was commenced on the balance of the 200 c.c. previously referred to, and it was in this portion that the coloured sediment was developed.

The specific gravity of the solution was 1·30642. To 97 c.c. of this solution (126·7227 grms.), 253·4455 grms. of acetate of lead were added. Ethyl alcohol was then added and the solution was heated on a water-bath.

This treatment was repeated until all of the raffinosate of lead had been precipitated.

This precipitate was then filtered out, suspended in water, and sulphuretted hydrogen gas was passed in until all of the lead had been thrown down.

The sulphide of lead was filtered out and was thoroughly washed with cold water. This was continued until the washings no longer polarised.

To the filtrate blood-carbon of the best quality was added; this was thoroughly shaken up with the solution, allowed to remain in it for about 12 hours, and then filtered off from the then almost colourless liquid. The blood-carbon was then washed with water until the washings no longer polarised.

The washings were added to the filtrate and the whole evaporated at a temperature of about 70° to 75° C., under partial vacuum, to the thickness of a syrup.

This syrup reacted decidedly acid, and upon testing, sulphuric acid was found to be present. This acid was exactly neutralised with barium hydrate, and the precipitate of barium sulphate was filtered out. The filtrate, which was of a light amber colour, was concentrated to a thick syrup by evaporation in partial vacuum.

The solution again turned dark and again reacted slightly acid. Barium hydrate was once more added to neutralisation; an additional quantity of the best blood-carbon was also placed in the liquid, and the whole was allowed to stand at rest for four days.

The solution was then filtered through asbestos, washed slightly with water, and set aside.

It would now have needed only the addition of ethyl alcohol and a leaving at rest to secure the crystallisation of the raffinose.

When set aside the solution was perfectly clear and of a light brownish colour. After allowing it to stand well corked for 24 hours, on close inspection it was found to contain a bright red sediment, in colour not unlike red sealing-wax. On moving the solution the sides of the glass vessel were seen to be coated with a beautiful rose-coloured film.

The solution looked at by transmitted light was of a brownish yellow colour; by reflected light the solution was opaque and of a very dark green colour, resembling in appearance the heavy oils of petroleum; looking across the surface films of emerald-green and rose were visible.

The solution was allowed to stand well corked, and at rest, for seven days, during which period the sediment increased.

At the end of this time the sediment was filtered out, the filtrate being passed into a covered flask in order to avoid exposure to the atmosphere.

This filtration yielded a perfectly clear brownish yellow solution which had lost every trace of fluorescence. This filtrate, well corked, was set aside (June 18th), in order to learn whether any more of the coloured sediment would be developed in it.

This solution will hereafter be referred to as specimen A. The sediment, all of which had been retained by the filter-paper, was of a bright red colour, resembling in tint, as already stated, ordinary red sealing-wax. By reflected light it exhibited an emerald-green sheen.

This sediment will hereafter be referred to as specimen B.

To remove all raffinose solution adhering to the filter-paper the sediment B was washed moderately with distilled water. The washings were caught and kept in a separate flask.

These washings were preserved for three months and no sediment having formed in them they were then discarded.

The filtrate (A) was inspected from time to time. The following are some of the entries recorded:—

June 18th.—Solution perfectly clear; colour brownish yellow, no fluorescence.

June 19th.—No change.

June 20th.—Distinct though thin layer of sediment has formed, adhering uniformly to all parts of the glass in contact with the liquid.

June 21st.—Sediment slightly increased. A green fluorescence of the solution is noticeable.

June 23rd.—Sediment increasing. Distinct rose layers on sides of vessel. The solution is brownish yellow by transmitted light and dark green by reflected light.

These observations were continued through July and August. The rose-coloured sediment in the solution gradually changed in colour to a rich brown. At the beginning of September it was noticed that white round disks, which seemed to be mould formations, appeared floating on the surface of the solution. Fearing a possible destruction of the coloured precipitate at the bottom of the flask, these disks were removed and the sediment filtered out.

This sediment was marked specimen C.

The solution after the sediment had been filtered out was of a dark brown colour, and without any fluorescence.

It was treated with absolute ethyl alcohol, and after standing a few hours yielded a copious brownish grey precipitate, which should, and probably will, prove to be raffinose. This precipitate, however, yet awaits purification and re-crystallisation from alcohol.

The red sediment first obtained, specimen B, was for months preserved practically unchanged. It was kept on the original filter-paper, of course carefully protected from the dust.

Examined under the microscope with low powers (3·4 and 1·5 objectives with respectively the A, B, and C eye-piece), the substance exhibited an appearance like scales, partly round, partly angular; no crystalline system could be distinguished.

When submitted to examination by a Zeiss immersion lens the sediment was found to consist of small plates and rod-like formations.

It was impossible to determine with certainty whether the rod-like formations were bacteria or of crystalline structure.

The deposit is, however, probably a chemical precipitate. Dr. A. A. Julien, who also kindly examined the specimen, expressed this view, which is strengthened by the following considerations:—

1. The sediment was formed in the liquid, preferably on the sides and bottom of the flask, whereas most chromogenic bacteria are aërobic, and hence would display greatest activity at the surface of the solution.

2. The sediment is insoluble in alcohol, whereas bacteria colours are soluble in this reagent.

3. The rods vary considerably in size, whereas bacteria would exhibit fairly uniform dimensions.

As this coloured sediment was not formed in either of the two preceding portions of the raffinose solution, but only occurred in that portion which was decolourised with blood-carbon, it was natural to suspect that this reagent might have been the source of the sediment in question.

Hæmatin was looked for in a hydrochloric acid solution by the spectroscope (absorption bands), but with negative result.

Attempts were then made to obtain hæmatin from some of the blood-carbon by treatment with acetic acid and ether. This also failed to yield even a trace of the substance sought.

The supposition that this sediment is hæmatin will, therefore, have to be abandoned, although some of the reactions given further on would point to a body of this nature.

Subjecting the blood-carbon to treatment with twenty times its volume of 75 per cent alcohol, and subsequent addition of barium hydrate—a repetition of the conditions of the experiment, but in the *absence* of the raffinose syrup —also failed to produce the coloured sediment, thus proving that these reagents alone could not have given rise to its existence.

Various reagents were tried in the attempt to find a solvent for the sediment. It was found to be:—

Soluble in hydrochloric acid, concentrated.
Soluble in nitric acid, concentrated.
Soluble in sulphuric acid, concentrated.
Insoluble in acetic acid, concentrated.
Insoluble in turpentine.
Insoluble in ethyl alcohol.
Insoluble in methyl alcohol.
Insoluble in water.
Insoluble in sucrose solution, concentrated.
Insoluble in ether.
Insoluble in ammonic hydrate, concentrated.

A test made with a hydrochloric acid solution of the sediment showed it to be inactive to polarised light.

On burning some of the substance on platinum foil a small residue remained; this gave a distinct reaction for iron, an impurity introduced by the barium hydrate which had been used for neutralisation.

Tests made on the hydrochloric acid solution of the sediment proved the presence of barium and iron, and the absence of calcium, potassium, and sodium.

In the absence of data obtained by ultimate analysis it would be idle to speculate on the nature of this substance, remarkable for its fluorescence and brilliant colour. As, however, its properties seem to differ from those of any body known to occur in saccharine solutions, it seems permissible to assume that it is either some substance hitherto entirely unknown, or else a new derivative or compound of raffinose.—*School of Mines Quarterly*, New York, vol. xii., No. 1.

PROCEEDINGS OF SOCIETIES.

FRANKLIN INSTITUTE.

(Chemical Section.)

Tuesday, November 19, 1889.

Mr. T. C. Palmer, Vice-President, in the Chair.

The nomination of officers for the ensuing year was taken up. The following nominations for President were made:—Mr. T. C. Palmer, Prof. S. P. Sadtler, Prof. R. L. Chase. On motion, the nominations for President were closed.

Nominations for two Vice-Presidents were then made. The following gentlemen were put in nomination:—Dr. H. H. Keller, Mr. W. L. Rowland, and Prof. Henry Trimble. On motion, the nominations for Vice-Presidents were closed.

Dr. W. C. Day was nominated for Secretary, Dr. H. W. Jayne for Treasurer, and Dr. William H. Wahl for Conservator.

Mr. W. W. McFarlane gave a description of some new dyeing materials, in which he explained the use of a number of dyes which have recently been introduced into this country by the representatives of Fried. Bayer and Co., of Elberfeld; samples of dyed products were also exhibited.

Among other interesting matters, the speaker stated that "carmine blue" is dyed with the use of Glauber's salt and sulphuric acid, in the same way as indigo carmine or extract, and further, that the carmine blue will probably displace the indigo extract at no distant period in the future. "Sulphon Azurin" is also used in dyeing cotton, using a boiling bath and some alkaline salt, such as borax, sal-soda, sodium phosphate, or silicate. The blue produced is similar in shade to that of indigo, and is said to withstand the action of light and of dilute acids as well.

Benzo-black-blue is dyed in cotton in the same way as other benzo-colours, and very dark shades are the result. There are two shades of this colour, designated respectively as G and R.

The paper was discussed by Messrs. McFarlane and Palmer.

Dr. Wahl, from whom a paper was expected, announced that he must defer, until a later meeting, his paper on "a new gold-like alloy;" and gave in place of this a statement of further results obtained by him in the electrolytic deposition of platinum, exhibiting specimens of work. As the investigation is not yet entirely completed, and certain details of the mode of procedure are to be made the subject of letters-patent, the speaker preferred, for the present, to withhold the same from publication.

Dr. Wahl also made some critical remarks on statements made in a paper by A. J. Rogers, on "Experimental Researches in the Reduction of the Difficultly-reducible Metals," which was published in the *Proceedings of the Wisconsin Natural History Society*, April, 1889, expressing doubts, based on theoretical considerations, as to the accuracy of one of the results announced by the author; namely, that he had obtained "a yield of aluminium six times greater than had ever been obtained by electrolysis."

Mr. F. Lynwood Garrison presented some remarks on the Paris Exposition, with special reference to Metallurgy and Fuels. As these remarks will be embodied later on in a full and comprehensive report to the Institute, they are omitted here; this paper was followed by a general discussion of some of the statements it included.

Prof. E. F. Smith read a paper on the "*Occurrence of Vanadium in Caustic Potash.*" This paper was referred for publication. He then presented another on the subject of nitration by the use of nitrogen trioxide as obtained by the action of nitric acid on arsenic trioxide. This paper was also referred for publication.

Professor Smith next presented the following results of further work in the electrolysis of metallic sulphocyanide solutions. His object in presenting these results was to reserve for the future the field upon which he has entered. In addition to the results already reported in a former paper, it was observed that iron, cobalt, and nickel in sulphocyanide solutions were fully deposited by weak currents, and that the presence of a sulphocyanide in manganese solutions prevented the formation of the dioxide, and when the latter had already precipitated the addition of KCNS would effect its re-solution. To these facts may be added that mercury, cadmium, bismuth, and lead deposit from sulphocyanide solutions. With lead, a behavior analogous to that noted with manganese was observed.

Approximate quantitative separations were made in several cases, but the complete development of these observations requires further study. Another line of experiment has been the electrolysis of metallic phosphates in the presence of free phosphoric acid. Mercury, silver, copper, cadmium, lead, iron, zinc, cobalt, and manganese have given interesting results qualitatively and quantitatively. Separations seem possible when regard is had to the proper condition of the current. The speaker stated that although in possession of quantitative figures in some of these cases, he preferred to postpone their publication until a careful examination has been made with each metal. Curiously enough, with manganese phosphate dissolved in phosphoric acid there is no separation of dioxide; the solution slowly acquires a red tint, and in time becomes turbid, although the addition of more acid causes the turbidity to disappear.

Dr. Warwick, at the request of Professor Smith, has begun an electrolytic study of the metallic formates; the results obtained will be communicated later.

Tuesday, November 18, 1890.

Mr. T. C. Palmer, President, in the Chair.

The report of the Committee on the Publication of the Paper by Dr. Masser, of Los Angeles, Cal., on "The Curve of the Elements," and also another by Dr. Hans von Strombeck, of New York, on "The Constants of Ammonia" was accepted, and the committee was discharged.

On motion of Dr. **Wahl**, it was voted that a committee be appointed to prepare a circular-letter addressed to chemists at large, setting forth the facilities possessed by the Section to receive, examine, and publish promptly papers of meritorious character on chemical subjects.

In this circular-letter, he proposed also to call attention to the fact that a number of printed copies of an accepted paper would be returned to the author, within two weeks of the date of its acceptance by the Section; and furthermore to the fact that the publications of the Section are forwarded promptly, as advance sheets, to the leading chemical journals at home and abroad.

The following nominations of officers for the ensuing year were then made:—For President, Dr. Wm. H. Wahl; for Vice-Presidents, Mr. H. Pemberton, Jr., and Dr. Wm. H. Greene: for Secretary and Treasurer, the present incumbents in each case; for Conservator, Dr. Wahl.

Dr. **Greene** then presented a paper by himself and Dr. **Wahl**, on "*Alloys of Sodium and Lead.*" It was referred for publication in the *Journal*.

Dr. **Greene** also stated that he would submit a number of specimens of new alloys proposed by the authors at the next meeting.

Dr. **Wahl** then read an abstract prepared by Prof. C. F. Himes, of Carlisle, describing a new photographic process without the use of metallic salts, based on the light sensitive properties of primuline. It was referred for publication. In connection with this paper Mr. Macfarlane stated that the active substance of the process known as "primuline" and the primuline dyes in general had been abandoned in dyeing, because of the fact that they would stand exposure to direct sunlight for only a short time before fading out.

Dr. **Jayne** called attention to a chart illustrating clearly the details of the new process for manufacturing nitric acid, invented by Oscar Goodman, and recently described in various journals.

Mr. **Palmer** exhibited a piece of logwood which was unusual in presenting a bronzy green surface, such as is commonly found only in chipped wood that has been put through the process of curing. This fragment was part of a log six feet in length, taken from a wind-shaken tree through which rain-water had percolated. The rain-water, probably by the action of the ammonia contained it, had produced a result analogous to that secured by the usual curing process.

On Di-isobutylamine Ethyloxalate.—H. Malbot.—The substance obtained has a composition corresponding to the formula $C_{12}H_{25}O_4N$.—*Bull. de la Soc. Chim. de Paris*, Vol. iv., No. 8.

NOTICES OF BOOKS.

Researches on Micro-Organisms: Including an Account of recent Experiments on the Destruction of Microbes in certain Infectious Diseases, Phthisis, &c. By A. B. Griffiths, Ph.D., F.R.S.E., F.C.S., &c. London: Baillière, Tindall, and Cox.

Bacteria and their doings figure as prominently in our medical literature as ever did the "Solar Myth" in the lucubrations of historians and archæologists, though with much better reason. The work before us is not a formal manual of bacteriology, but an account of some recent researches in that department, chiefly in connection with infectious diseases. The part played by microbia in the chemistry of agriculture and of fermentation is not overlooked, but forms a less prominent feature.

Dr. Griffiths gives a significant hint in his introduction. "It must not be supposed because the blood and tissues of animals suffering from contagious diseases contain certain microbes that these microbes are necessarily the cause, even indirectly, of the disease. Not until the investigator has obtained by pure cultivations in an artificial sterilised medium, the microbes in a perfectly pure state, and then, by injecting into the blood, &c., of an animal, the disease is reproduced, can one say that a particular disease is the result of the life history of a certain microbe." Thus the physiologists and chemists of Britain, whether they are medical men or not, find themselves practically excluded from this department of research by the deplorable Anti-Vivisection Act.

For bacteriological work the author recommends the microscopes of Zeiss, of Jena. Sterilising appliances are brought into due prominence. Indeed, the student who enters upon such researches will find his attention called at every step to the necessity of sterilisation.

In the classification of microbia we find them arranged as micrococci, bacteria, bacilli, vibriones, spirilla, and spirochætæ, all being now fully recognised as plants. The rate of increase of these beings is truly terrible. A single bacterium will, in the course of a week, have multiplied to a number which can only be expressed by figures of fifty-one places. Hence, ultra-microscopical as they are, we need not wonder at the part which they play in Nature.

The author regards air, water, and soil as means of distributing pathogenic microbia, and human intercourse as a still more powerful factor. It is a painful fact—to which Dr. Griffiths does not refer—that Australia, South Africa, and temperate South America, which once ranked among the healthiest countries of the world, have within the last 25 years acclimatised diphtheria and typhoid fever.

The author admits that flies may convey poison from a diseased to a sound animal. But he scarcely lays sufficient weight on the agency of two-winged insects, including both the blood-suckers and those which merely settle upon man and domestic animals—as the colporteurs of zymotic affections. What is the poison of the Tzetse?

The remark that moderately high-lying places are particularly liable to the attacks of Oriental plague is perfectly justified by history. In the north of Derbyshire the tourist is even yet shown "the graves of Eyam"—a mountain village which lost practically its entire population in a visitation of the plague.

The author is convinced that the mischief effected by pathogenic microbia is not so much due to their vital activity as to their power of manufacturing poisonous products. Of these substances there are three classes—ptomaines or putrefactive alkaloids; leucomaines, which are produced in health as well as in disease; and "extractives." The latter class, though nitrogenous, are not basic and are incapable of crystallising. One of the authorities quoted makes use of the term "toxic" to express the quantity of any poison capable of killing

1 kilo. of living animal matter. But as different animals are unequally susceptible to the action of different poisons the "toxic" ought to be referred to some one species—say the rabbit.

The properties of many ptomaines are most remarkable. Some of them give off very offensive odours. Others, poisonous all the same, have the fragrance of orange flower, of cinnamon, syringa, the rose, or other flowers.

Probably the most formidable body of this class is hydrocollidine, which is regarded as "nearly as poisonous as the venom of the cobra."

Some of the non-poisonous microbes have the power of forming a variety of pigments from the matter in which they live. Indigo itself is the product of a bacillus, which, however, is pathogenic. *Micrococcus prodigiosus* has been known to appear on bread, which it turned of a blood-red. In the middle ages such phenomena were ascribed to sorcery, and sometimes served as a pretext for the persecution of the Jews.

A very interesting chapter is devoted to the action of heat, light, electricity, gases, &c., on microbia. It is found that certain lower organic forms, both animal and vegetal, can retain their vitality for years; in one case given by Mr. W. Carruthers, F.R.S., of the British Museum, some specimens of *Tylenchus* were re-vivified after they had been in the National Collection for upwards of thirty years.

No species of microbe experimented on by the author was able to resist an electric current of 3·34 volts.

We regret that we are not able to carry further our examination of this most interesting and suggestive work, which deserves our warmest recommendation.

The Physical Properties of Gases. By ARTHUR L. KIMBALL. London: Heinemann.

THIS work is one of the series of Scientific Hand-books now being issued by the publisher. The author, who appears to hold a chair at the "Johns Hopkins" University, here undertakes to give a general view of our present knowledge concerning gases adapted to the requirements of the non-specialist. No attempt is made, of course, to teach anything not fully known and acknowledged in the scientific world, but our present state of knowledge is very fully and clearly expounded.

After an introduction the author discusses pressure and buoyancy, elasticity and expansion with heat, gases and vapours, with a notice of the recent experiments of Caillelet and Pictet on the liquefaction and solidification of gases; air-pumps and high vacua, under which head we find an illustrated account of the mercurial air-pumps of Geissler and Sprengel; diffusion and occlusion; the thermodynamics of gases; Avogadro's law, and the kinetic theory, and Geissler tubes and radiant matter. The author admits that "the phenomena of the radiant condition of matter as developed by Crookes, furnish, perhaps, the strongest experimental evidence of the truth of the kinetic theory of gases in its essential features."

In a concluding chapter the author quotes the opinions of the late Clerk Maxwell, against the formation of the various kinds of molecules by evolution. None of the arguments brought forward, however, seem conclusive, and we may venture to think that if Professor Maxwell had lived to follow the results of recent experiments, *e.g.* on the rare earths, he would have modified his opinions.

Although this book has been printed in England, we regret to see that the American orthography has been adopted. Thus potassium nitrate is spoken of as "niter." If so, why not on the same principle write "possibel," &c.? There is no foot-hold between our ordinary English orthography with all its anomalies and the wholesale innovations of the "Fonetic Nuz."

In a general preface to the entire series of works, for which Mr. Kimball is evidently not responsible, we find a very objectionable expression.

The writer aims at explaining "the most important inventions and practical discoveries of the present day." This is part and parcel of that confusion between art and science against which we, in common with not a few men of wider influence, have all along protested. An invention always is or aims at being "practical," whether for good or evil.

A discovery cannot be practical; it is simply the announcement of some truth, old as Creation, but hitherto overlooked.

The atomic theory, the periodic law, the persistence of energy are discoveries; photography, the telephone, the spectroscope are inventions.

The man of culture who wishes for a general and accurate acquaintance with the physical properties of gases will find in Mr. Kimball's work just what he requires. We hope we are within measurable distance of the time when such knowledge will be demanded as imperatively as classical lore has been in the past.

A Systematic Handbook of Volumetric Analysis; or the Quantitative Estimation of Chemical Substances by Measure Applied to Liquids, Solids, and Gases. By FRANCIS SUTTON, F.I.C., F.C.S. Sixth Edition, enlarged and improved. London: J. and A. Churchill.

THIS work evidently increases at once in bulk and in value, and certainly holds its place in the estimation of chemists.

A few points only, and those of subordinate interest, seem to call for remark. Looking over the table of abbreviations we regret to find that gramme is contracted into "gram," which, if not carefully written, may easily be mistaken for grain. Nor do we see what is to be gained by writing "liter," "centimeter," &c.

Heretical as it may seem, we cannot help doubting whether chemists have not been too precipitate in abandoning the so-called "empirical" standard solutions which express the proportion of a constituent at once in percentages without any calculation. This advantage will, to many persons, more than compensate for the trouble of keeping a greater variety of standard solutions.

On the subject of normal solutions there is unfortunately no small confusion. The author, like Mohr, Fresenius, and Classen, follows the equivalent system. Pattison Muir in his version of Fleischer's *Maasanalyse*, and Muter in his "Manual of Analytical Chemistry" seem to be inconsistent.

The analysis of water is explained at great length, especially as far as the Frankland and Armstrong process is concerned. The microscopical and cultural examination is of course only slightly touched upon as not strictly belonging to the subject of the work.

CORRESPONDENCE.

OUTLINES OF GENERAL CHEMISTRY.

To the Editor of the Chemical News.

SIR,—To-day I received the last number of your valuable journal, containing the favourable account of my little book.

In your commencement you give a quotation from my preface, which contains just the opposite to my meaning; for I have not written "the necessity of the *employment* of higher mathematics," but "the necessity of *avoiding the employment*," &c.

Further, I have expressly stated that the *understanding* even of the new development of chemistry is possible without higher mathematics; only for useful work in this branch it is indispensable. I am quite aware that there exist broad districts in chemistry, where great discoveries can be made without this most useful means.

W. Ostwald.

December 21, 1890.

[The passage on which our comments were founded is in the Author's Preface (English translation), lines seven to five from bottom :—"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."—*Ed.* C. N.]

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

Sir,—We have striven in our letters on this subject on the 28th ult. and 12th inst., to be, above all things, plain in our statements. It appears, however, that we have failed to be sufficiently explicit for certain correspondents who seem scarcely to have grasped the ideas we endeavoured to convey.

"A Contributor to the *Journal of the Chemical Society*" deprecates the "Chemical Society of London advertising itself." Such deprecation cannot but command sympathy; it is, however, to be feared that the word "advertise" has been understood in its modern and limited sense, and that the phrase "advertise itself" has been considered equivalent to "indulge in self-laudation." A re-perusal of our last letter will probably suffice to dissipate this idea and to restore the Society's equanimity by leading to the withdrawal of the threat of resignation, under which it has doubtless quailed.

We will ask you to accord us a little further space in which to reply to Mr. Friswell, who has hinged a second protest from himself upon our last letter.

We were not aware that we had any "difficulties" in the matter; in our first letter we asserted that we believe the Chemical Society to be in a dilemma, in our second we stated what appear to us the only possible issues therefrom.

The Society is certainly not responsible for the erroneous tendency of the public to confer a professional status upon its members, but to accept passively the advantages accruing from that tendency is scarcely consistent with self-respect. Nor will the charter serve as a refuge; such a crisis was not foreseen fifty years back, and charters are not unalterable.

We have never recommended *wild* black-balling under any circumstances; we have never even advocated the *vigorous* black-balling mentioned in the first alternative set forth in our last letter, merely indicating it to be a logical necessity for those who adopted that alternative. We asserted that *all* or *no* candidates must be admitted while this question is *sub judice*, because we were fully conscious both of the incapacity of a meeting (as at present constituted) of the Chemical Society to act in any sense as a qualifying body, and of the invidious distinctions that would be—we had almost said, were being—made by those scarcely qualified to judge.

The present system will undoubtedly be sufficient if those who uphold it will take steps to rectify the public estimate of the value of the letters F.C.S.; otherwise we repeat that they will convict themselves of being either illogical or dishonest.—We are, &c.,

A. G. Bloxam.
Bertram Blount.

ALLOYS OF SODIUM AND LEAD.

To the Editor of the Chemical News.

Sir,—The report of Messrs. Greene and Wahl's paper on "Alloys of Sodium and Lead" given in last week's Chemical News contains wrong densities for certain mixtures of those metals. By calculation a mixture containing 10 per cent of sodium has a density 10·36, one containing 19·5 per cent a density 9·36, and one containing 31·7 per cent a density 8·1. The authors give the respective densities of such mixtures as 5·6, 3·7, and 2·7, figures which it is difficult to see how they obtain. If the observed densities of the alloys are given correctly, they are considerably lower than those of mixtures of the same composition, not higher as is stated in the paper.—I am, &c.

W. J. A. B.

December 27, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 24, December 15, 1890.

On the Detection and the Determination of Very Small Quantities of Aluminium and Cast-Iron in Cast-Irons and Steels.—Adolphe Carnot.—Aluminium has been used of late in some works to impart to cast-irons and steels special properties which are particularly appreciated in casting. Its introduction, even in very small proportions, appears to exert a great influence; but its manner of action has not yet been properly determined, and we do not know with certainty if a part of the aluminium exists in the state of an alloy in the cast-iron or the steel, or if it disappears entirely in the state of oxide, though still preventing the formation of carbon monoxide and the production of blow-holes in the metal. For the thorough study of this question it is necessary that metallurgists should possess an accurate and simple method of analysis, enabling them to recognise and determine very small quantities of aluminium in iron. He purposes here to make known a method which he uses and which he has taught for eight years at the Paris School of Mines. His researches date back to July, 1882; they were undertaken at the request of M. Lan, then Professor of Metallurgy at the School of Mines. He considered that the presence of minute quantities of aluminium or of the alkaline earthy metals might have a great influence on the quality of cast-metal, of iron, and steel. He sent the writer specimens of cast-irons from the different works of the Châtillon-Commentry Company, with the request to determine the small quantities of aluminium, which he suspected might be present in some of them, obtained from the very aluminiferous ores of Berry. The results of the analyses were almost absolutely negative for the cast-irons, in which there were found only doubtful traces of alumina, which might be due to small inclosed particles of slag. Such researches had then merely a theoretical interest, and the author had neglected to publish them. Since that time aluminium has been purposely introduced into irons and steels intended for casting, and the question of the determination of this metal thus acquired a greater importance. The method in question is founded upon reactions which the author pointed out in the *Comptes Rendus*, July 18, 1881, May 8, 1882, and April 7, 1884. The alumina may be completely precipitated as a neutral phosphate on boiling in a slightly acetic liquid. This precipitation succeeds equally well in presence of a considerable quantity of iron, which is not thrown down if the precaution has been taken of reducing the ferric salt to the ferrous state by means of sodium thiosulphate. The author takes about 10 grms. of the metal, and treats it with hydrochloric acid in a platinum capsule. He avoids, as far as possible, the use of glass or porcelain vessels to prevent the accidental introduction of alumina from this source. When the metal is entirely dissolved without allowing the solution to become peroxidised in the air, it is diluted with distilled water and put in a flask or a beaker of Bohemian glass, washing several times by decantation, and retaining the insoluble matter, such as silica and graphite, upon a filter. A small quantity of silica may remain in solution, and must be eliminated subsequently, but it is convenient not to make this elimination at the outset by evaporating the solution to dryness, as an excessive quantity of ferrous salt is present. The bulk of the free acid is then neutralised with ammonia and then with sodium carbonate. Sodium thiosulphate is then added. When the violet colour has disappeared, and there no longer remains any ferric salt in the colourless solution, there are added 2 to 3 c.c. of a saturated solution of sodium phosphate and about 20 c.c. of a solution of sodium acetate. The mixture is then heated to ebullition, which is kept up for about forty-five minutes as long as the slightest odour of sulphurous acid is perceptible. There is formed a precipitate, generally not bulky, of aluminium phosphate mixed with sulphur and containing a little ferric phosphate. This precipitate is collected on a filter, washed with a little boiling water, and then placed over a platinum capsule and treated in heat with 10—15 c.c. of hydrochloric acid diluted with water. The solution is evaporated to dryness, and the residue is kept at 100° for one hour, so that the silica may become entirely insoluble in acids. The residue is then taken up in a little dilute hydrochloric acid, which dissolves all the aluminium and iron phosphates. The liquid is then filtered to remove silica, diluted with 100 c.c. of cold water, and the precipitation is repeated in the same manner as before, *i.e.*, almost complete neutralisation with sodium carbonate, addition (in the cold) of thiosulphate, and subsequently of a mixture previously prepared of 2 grms. acetate and an equal weight of thiosulphate, boiling for half an hour, and filtration through a small paper filter which has been washed with acids and which leaves no ash. The silica and any iron which remained in the first precipitate are thus completely eliminated from the second, which after washing with boiling water is dried, ignited, and weighed. The aluminium phosphate thus obtained contains 22·45 per cent of alumina.

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Bulletin de la Société Chimique de Paris.
Series 3, Vol. iv., No. 10.

Researches on Dispersion in Organic Compounds (Ether Oxides).—Ph. Barbier and L. Roux.—The specific dispersive powers of the alcoholic oxides are of the same order of magnitude as those of the alcohols from which they are derived. In the series of oxides—

$$\begin{array}{l}(C_nH_{2n}+1)\\(C_nH_{2n}+1)\end{array}>O$$

the dispersive powers vary regularly with the molecular weights and increase with them. In the series of oxides—

$$\begin{array}{l}(C_nH_{2n}-7)\\(C_nH_{2n}+1)\end{array}>O$$

they decrease regularly as the molecular weights increase. In the series of oxides—

$$\begin{array}{l}(C_nH_{2n}-1)\\(C_nH_{2n}+1)\end{array}>O$$

the specific dispersive powers have a value which is approximately constant in the different terms of the series. The specific dispersive powers of isomeric compounds are sensibly the same, and the addition of CH_2 in the molecule occasions a variation of the specific molecular dispersive power equal to about 8. Lastly, the specific molecular dispersive power of an alcoholic oxide is equal to the algebraic sum of the specific molecular dispersive powers of its components.

Researches on Dispersion in Organic Compounds (Fatty Acids).—Ph. Barbier and Roux.—The specific dispersive powers of these bodies increase regularly with the molecular weights. The specific dispersive powers of isomeric compounds are nearly the same, those of the abnormal acids being slightly inferior to those of the corresponding normal acids. The introduction of CH_2 into the molecule occasions a variation of the specific molecular dispersive power, which is constant for the different terms of the series, and is about equal to 7·8.

Essays on the Laws of Berthollet.—A. Colson.—The author proposes to apply these laws to the alkaloids.

Action of Hydrofluoric Acid upon Diastase.—Dr. Effront.—The author has stated that hydroflouric acid acts more energetically than the other mineral acids upon the lactic and butyric ferments. The temperature is most favourable to fermentation, but much lower.

Action of Isopropyl Iodide upon Aqueous Ammonia in Equimolecular Proportions at 100°.—H. and A. Malbot.—The principal products of the reaction are di-isopropylamine and propylene.

Action of Isopropyl Chloride upon Aqueous Ammonia in Equimolecular Proportions at 140°.—H. and A. Malbot.—There is formation of mono- and di-isopropylamine, partly free and partly combined.

General Process for the Synthesis of the β-Acetonic Ethers.—L. Bouveault.—Not adapted for useful abstraction.

Action of Phenylhydrazine upon the β-Ketonic Nitriles.—L. Bouveault.—It may be said that the tertiary β-acetonic nitriles yield with phenylhydrazine true hydrazides, whilst the secondary β-ketonic nitriles produce amidopyrazols.

MISCELLANEOUS.

Recovery of Uranium Residues.—Laube (*Zeit. Angewandte Chemie*) recommends a modification of the Reichardt process. The residues from titrations are collected together, and the clear liquid is decanted off from time to time. When a sufficient quantity has been collected the pasty mass is either heated in the pot by introducing steam, or in an iron pan over an open fire. Soda crystals are then added until the precipitate appears chiefly dissolved. It is let cool, mixed with a sufficiency of ammonia, and the phosphoric acid is precipitated with magnesia mixture. After standing for 12 hours the supernatant liquid is syphoned off, and the precipitate is washed with ammoniacal water. The alkaline liquids are neutralised either with hydrochloric or sulphuric acid, heated to expel carbonic acid, and the uranium is precipitated at a boiling heat with ammonia as uranium oxide ammonium. The precipitate is washed by decantation. A small quantity of some ammonium salt must be added to the last washing-waters, as the precipitate otherwise does not settle well. For obtaining uranium nitrate the precipitate is dissolved in excess of nitric acid and concentrated by evaporation.

Detection and Determination of Yolk of Egg.—S. Bein (*Berichte der Deutsch. Chem. Gesellschaft*).—The colouring-matters of egg yolk are exposed to changes on exposure to the air which render its identification in articles of food practically impossible. In particular Thudichum's reaction (a blue colouration with nitric acid) cannot be obtained. The author founds a process for the determination of yolk upon the determination of the phosphorus present in the substances which are extracted by ether, especially the glycerin phosphoric acid and the lecithine. He makes an ethereal extract of the substance in question, evaporates and incinerates at a gentle heat with the addition of a little saltpetre, and obtains in the ash the phosphorus which was present in the glycerin phosphoric acid and in the lecithine. By operating cautiously so as not to destroy the lecithine 1·12902 grms. of phosphoric acid obtained in the ash proves the presence of 100 grms. yolk of egg.

Messrs. Dunn and Co.—This old-established business has been purchased by Mr. Thomas Tyrer, of the firm of Messrs. May and Baker, of Battersea, now dissolved. The business will be continued under the title of Thomas Tyrer and Co., Stirling Chemical Works, Stratford, E.

The Clothworkers' Technical Scholarship.—This valuable scholarship (value £240) has again been taken by a pupil (aged 13) of the St. Thomas Charterhouse Schools. Notwithstanding the competition for this great prize becoming keener year by year, so far this school produces the winner. The subjects of Examination were mathematics, drawing, science, and the usual English subjects.

A Contribution to the Valuation of Zinc Powder.—G. Klemp.—Of the numerous methods proposed for ascertaining the value of zinc powder, the only one which has come into general use is that of Drewsen, depending on the reductive action of metallic zinc in an acid solution. The author shows that the results of this method are discordant and too low. In all the methods proposed the presence of lead or iron must interfere with the results. The author has sought for a method permitting the determination of the metallic zinc in zinc powder by ascertaining its reductive power in alkaline solutions. After having tried potassium ferricyanide in an alkaline solution unsuccesfully he took up potassium iodate, which is converted by reducing agents into the corresponding iodide. If potassium iodate is used in excess on acidifying the solution, iodine is liberated, the quantity of which bears a definite proportion to the metallic zinc contained in the zinc powder used. 15 Zn correspond to 6 I and 0·1 grm. Zn to 0·407799 I or to 0·1356 grm. KIO_3 and 0·086 KOH. In ascertaining the conditions of the reaction, he finds that if dilute lye is used, and in theoretical quantities, only the decomposition of the zinc powder is slow and imperfect. If a more concentrated solution is used, and in greater quantity, the decomposition is more complete and more rapid. If no excess of potassium iodate is present hydrogen escapes. The solution of the zinc-powder is accelerated by shaking up with glass beads or other bodies having a comminutive power. In order to absorb the hydrogen evolved the potassium iodate and the zinc powder must be intimately mixed, which can be effected only by the use of strong solutions of potassium iodate; but the concentration must be such that when mixed with concentrated potassa lye there is no separation of potassium iodate. Zinc powder is also decomposed by water, although slowly; hence in quantitative determinations the zinc powder should be placed in dry vessels. The solution used in the author's experiments contained 15·25 grms. KIO_3 in 300 c.c.. In quantitative determinations the author used to 0·1 grm. zinc powder, 3, c.c. of the iodate solution; the total quantity of liquid (solution of potassium iodate, potassa-lye, and any water added) was 13 c.c. to each 0·1 grm. of zinc powder. The determination of the iodine set free is effected by distillation in the Topf apparatus, the iodine being received in a solution of potassium iodide. The solution obtained is titrated with a solution of sodium thiosulphate containing per litre 7 grms. $Na_2S_2O_3+5H_2O$. For titrating back there is used a dilute solution of iodine, of which 2 or more c.c. corresponded to 1 c.c. of the solution of thiosulphate. The author suggests that aluminium may be determined in the same manner, and proposes to examine the subject further.—*Zeitschr. f. Analyt. Chemie*, Vol. xxix., Part 3,

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.

Chloride of Magnesium.—Can any one recommend me to a book or paper that treats on the manufacture of chloride of magnesium?—W. H. B.

MEETINGS FOR THE WEEK.

Monday, 5th.—Medical, 8.30.
—— Society of Chemical Industry, 8. "The Basic Copper Process," by Percy Gilchrist. "On Standard Sperm Candles," by W. C. Young.
Tuesday, 6th.—Pathological, 8.30.
—— Royal Institution, 3. "Frost and Fire," by Prof. Dewar, M.A., F.R.S.
Wednesday, 7th.—Geological, 8.
Thursday, 8th.—Royal Institution, 3. "Frost and Fire," by Prof. Dewar, M.A., F.R.S.
—— Royal, 4.30.
—— Royal Society Club, 6.30.
—— Mathematical, 8.
Friday, 9th.—Astronomical, 8.

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THE CHEMICAL NEWS.

Vol. LXIII. No. 1624.

ON THE SO-CALLED II. OR COMPOUND SPECTRUM OF HYDROGEN ACCORDING TO DR. B. HASSELBERG, AND ON THE STRUCTURE OF HYDROGEN.

By Prof. A. GRUNWALD.

The author has continued the investigation of the second hydrogen spectrum observed by Dr. R. Hasselberg.

Whilst he formerly confined himself to "Balmer Series" of at most four members (wave-lengths): λ_1, λ_2, λ_3, λ_4, and was only able to resolve a part of the hydrogen spectrum of Hasselberg into such series, it now appeared, on extending the consideration to more than 4 members, that with 8 members almost the entire spectrum can be divided into groups whose corresponding wave-lengths, $\lambda_1, \lambda_2, \ldots \lambda_8$ from Balmer series.

The author understands by a "Balmer series of n members" a series of n wave-lengths, $\lambda_1, \lambda_2, \lambda_3, \ldots \lambda_n$, two of which at least belong to the compound hydrogen spectrum, and for which the proportions hold good—

$$\frac{1}{\lambda_1} : \frac{1}{\lambda_2} : \frac{1}{\lambda_3} : \frac{1}{\lambda_4} : \ldots\ldots : \frac{1}{\lambda_{\frac{n}{4}}} = 1 - \frac{4}{3^2} : 1 - \frac{4}{4^2} :$$

$$1 - \frac{4}{5^2} : 1 \quad \frac{4}{6^2} : \ldots\ldots 1 - \frac{4}{(n+2)}{}^2$$

where one value of the magnitude independent of n corresponds to each single series of this kind.

The author has collocated these series and the corresponding mean values of h in an especial table, which we cannot insert here.

Not all the wave-lengths belonging to any given wave-length can be found in the spectrum given by Hasselberg. The gaps which thus occur are due in part to the circumstance that the missing wave-lengths do not fall within the region of the spectrum observed by Hasselberg ($\lambda = 6422{\cdot}67$ to $\lambda = 4412{\cdot}0$ of 1883, or the additional spectrum $\lambda = 4497{\cdot}35$ to λ 4062·07 of 1884), but in part because the electric illumination of the hydrogen contained no rays capable of exciting the vibrations in question with the necessary intensity.

From the above it follows in consequence of the author's theory, and of dynamic-chemical considerations otherwise known, "that the molecule which radiates out the II. or compound hydrogen spectrum consists of two equal secondary atoms H, each of which possesses a stratified structure, and consists of a nucleus of maximum density with a series of forms of condensation of one and the same primary matter "a" surrounding it in strata, or possibly in the form of a ring, and of densities diminishing progressively outwards. If we suppose the nucleus with the immediately surrounding strata, exclusive of the v outermost $= r^{(v)}$ (where v is one of the whole numbers 1, 2, 3, 4), and if we designate the last v strata, or rings, which represent the same number of primary chemical atoms "a" in determinate forms of condensation from the outermost stratum towards the nucleus respectively with $a^{(1)}, a^2, a^3, a^4 \ldots a^{(v)}$, then—

$$H = a^{(1)}, a^{(2)}, a^{(3)}, a^4, \ldots\ldots a^{(v)}, r^v \ (v = 1, 2, 3, 4),$$

the general chemical formula for the simple secondary hydrogen atom H, which according as we put $v = 1$ or $= 2$ or $= 3$ or $= 4$, &c., assumes different special forms. Especially if we put $v = 4$ and $r^{(4)} = b$, we have—

$$H = a^{(1)}, a^{(2)}, (a)^3, a^{(4)}, b, \text{ or more briefly, } H = a_4\, b.$$

In other words, the so-called simple hydrogen atom H can be conceived as a compound similar to ammonium H_4N of an atom "b" with four primary atoms "a" in the different condensations $a^{(1)}, a^{(2)}, a^{(3)}, a^{(4)}$.

The atom "b," which in the author's earlier memoirs was supposed to be quite independent of the primary atom "a," appears now in the light of the most recent results as exceedingly complex, consisting of a nucleus surrounded by strata, all capable of being derived from the primary element "a," so that this seems to be the true "protyle." It becomes at the same time very probable that the remaining chemical atoms, so-called, such as K, Na, &c., are single atoms or systems of single atoms in the stricter sense, each of which possesses a stratified structure resembling that of the simple hydrogen atom, the structural elements of which (nucleus and strata, or possibly rings), can be derived according to a fixed law from the primary atom "a." Thus the atom "a" discovered by the author, and the group of the values of h deduced by him from Hasselberg's hydrogen spectrum, which are simply the wave-lengths of protyle in a certain form of condensation which he names the "central," acquire an extraordinary importance for an understanding of the structure of all the derived chemical elements.—(Reprinted from the *Anzeiger*, No. 19, of the Imperial Academy of Sciences at Vienna).

SEPARATION OF BARYTA, STRONTIA, AND LIME.

By A. RUSSMANN.

The author has subjected a number of the methods proposed for this purpose to a critical examination, the results of which he communicates in an elaborate memoir.

1. *Method of Frerichs.*—Russmann experimented first with this method, precipitating a pure solution of barium with neutral potassium chromate after an addition of acetic acid and ammonium acetate, letting settle completely, filtering, washing with dilute acetic acid, drying at 110°, and weighing. The results were approximately accurate, but though a trace of barium could be detected in the filtrate the amount found was in excess of the truth, as the precipitate always contained small quantities of potassium chromate.

In using this method for the separation of barium and strontium attempts were made to separate varying quantities of strontium from a constant quantity of barium. Russmann took into account the advice of Meschezerski, that the saline solutions should be diluted to 0·5 to 1 per cent. From the experiments it appears that in solutions which contain to 50 parts of barium 10 to at most 15 parts of strontium no strontium is precipitated. In solutions containing relatively larger proportions of strontium appreciable quantities of it are carried down along with the barium chromate.

In separating baryta and lime the quantity of the latter does not interfere, as calcium chromate is not precipitated.

In order to dispense with the use of a weighed filter the author attempted to determine the barium chromate by weighing the precipitate after ignition in a porcelain crucible. The precipitate was first removed from the filter as completely as possible, the portion adhering to the paper was dissolved in dilute nitric acid, the solution evaporated down in the tared crucible, and the main quantity of the precipitate then added. The result was not satisfactory, as portions of chromic oxide were formed by the action of the fibres of the paper.

Russmann also endeavoured to determine barium volumetrically by decomposing the barium chromate with hydrochloric acid and potassium chromate. Experiments of this kind performed in various manners gave results in excess, as the hydrochloric acid of itself liberated iodine from the potassium iodide. The best results were obtained in the simplest manner by dissolving the precipitate of barium chromate in dilute hydrochloric acid, mixing the solution with potassium iodide, and titrating with sodium thiosulphate immediately after dilution.

C. Diehl's Method (*Journ. Prakt. Chemie*).—According to this method a mixture of barium sulphate and calcium sulphate recently precipitated is gently heated repeatedly with a concentrated solution of sodium thiosulphate. The calcium sulphate dissolves, and may be determined with ammonium oxalate, whilst the barium sulphate remains undissolved. Russmann could not obtain accurate results. There always appeared a deficiency of lime, as the barium sulphate retains calcium sulphate, the error becoming more considerable as the proportion of lime is greater. If it is intended to determine the calcium in the filtrate the sodium thiosulphate must first be decomposed by boiling with hydrochloric acid.

The sulphur thus eliminated involves a further source of error, as it incloses small quantities of lime. If we attempt to avoid the separation of sulphur and add to the dilute solution of sodium thiosulphate containing the lime ammonia prior to evaporation, sulphur is still deposited on the dry parts of the capsule, and on precipitating the lime with ammonium oxalate this finely divided sulphate accompanies the precipitate, and on ignition converts a part of the lime into sulphate. The method cannot be recommended on account of the inconvenience and tediousness of repeatedly treating the sulphates with sodium thiosulphate.

Separation of Barium and Calcium by Means of Sulphuric Acid.—This method can be successfully used both in solutions in which small quantities of barium exist along with much calcium, and in such as contain part calcium to 100 parts barium. On using 10 to 20 c.c. hydrochloric acid containing 25·28 HCl, lime never accompanies the precipitate. In very dilute solutions the method certainly requires much time, as the precipitate is not completely deposited within twenty-four hours.

Method of D. Sidersky.—A neutral solution of strontium and calcium compounds being mixed at a boiling heat with the dissolved mixture of ammonium sulphate and oxalate gives a precipitate of strontium sulphate and calcium oxalate. These salts are separated either by treating the filtered precipitate with dilute hydrochloric acid, which dissolves the lime salt, or by mixing the solution at the outset with hydrochloric acid, which keeps the lime salt from being thrown down.

Experiments conducted in the former manner showed that on washing the precipitate with dissolved hydrochloric acid considerable quantities of the strontium sulphate passed into solution, and the time when all the lime is removed from the precipitate cannot be determined. In this form the method is not applicable even for technical purposes.

As regards the second method of execution Russmann concludes that if a very dilute acid is used a little calcium oxalate easily accompanies the strontium sulphate. If a stronger acid is used a part of the strontium sulphate is dissolved. Approximate results may be obtained by working in such a manner that the liquid on precipitation contains at least 8·4266 per cent of hydrochloric acid. For separating barium and calcium the method of Sidersky is applicable.

Method of C. H. Bloxam (See Chemical News, vol. liv., pp. 16 and 168).—On examining this method Russmann arrived at the conclusion that it is very well adapted for the detection of small quantities of calcium in presence of much strontium, as 1 part of calcium can be recognised along with 500 parts of strontium. But the quantitative determination of lime by means of ammonia and arsenic acid presents more difficulties than its determination as calcium oxalate, since in the latter method there is no need for a weighed filter. Besides, the results, although only 20 per cent calcium instead of 20·86 were supposed to exist in the precipitate dried at 100°, are not such as can be recommended.

On attempting to render the precipitate fit for weighing as $Ca_2As_2O_7$ after ignition a considerable loss of arsenic could not be avoided even with special precautions.

The method cannot be used for the quantitative separation of strontium and calcium, since calcium sulphate on precipitation carries down considerable quantities of calcium; the results are fluctuating and very unfavourable.—*Zeitschrift fur Analytische Chemie.*

(To be continued).

NOTES ON KJELDAHL'S PROCESS.

By VINCENT EDWARDS, F.C.S.

Manure works' chemists are so frequently called upon to estimate nitrogen in such substances as dried blood, shoddy, fleshings, soot, &c., of more or less value that it becomes a matter of importance to have some accurate and reliable yet not too costly method within reach. The old soda-lime process is of course a very good one, and comparatively simple, but the chief difficulty is the gas supply, which is not always powerful enough if it exists at all. I have known some works without it. As to the ancient plan of red-hot charcoal, which is still recommended by some chemists of the "old school," I consider it as much out of place as the rack and thumb-screws would be in a court of justice. As the following modification of the apparatus usually said to be required for Kjeldahl's process may be useful to those who work in somewhat isolated places, I venture to submit it.

The digestion of the substance, 1 grm. for ordinary manure, 0·5 grm. for guanos and rich substances, I carry out in the manner recommended in the Chemical News, vol. lix, No. 1525, except that rather less oxide of mercury will answer; about 0·2 grm. is enough. For description see the same Chemical News. Messrs. Mawson and Swan will supply them. The flasks can be supported in any convenient manner over a rose burner, and nothing hardly will break them. A spirit lamp will answer if there is no gas, but the time required will be much longer.

I think the pictures of apparatus given in some books are rather discouraging, as not only are they very elaborate but next to impossible to procure. Very simple forms of condenser and receiver will answer just as well as a metal one; in fact too much condensation delays the process and is entirely unnecessary. I use a 500 c.c. flask on a sand bath, with a rubber cork, through which passes a tube which is carried about three inches into a small tubulated retort holding about 110 c.c. (this quantity of distillate will contain all the ammonia); the stopper of the retort is replaced by a cork, through which passes the bent end of a Will and Varrentrap's nitrogen bulb tube; this contains the standard sulphuric acid, drawn in as usual from a beaker, into which at the end of the operation the whole distillate, acid in bulbs, &c., are emptied. For titration with normal soda diluted to 1 in 3. This may seem a very simple apparatus, but I can confidently assert it will answer as well as many costing five times as much. Certain precautions are necessary with these modifications —the heating of the distilling flask must be gradual and carefully done as the alkali is apt to spray at first; the gas must not pass too quickly through the Will and Varrentrap bulb tube. In fact an eye must be kept on the whole concern during the process. The chemical details will be found in the paper I have mentioned. 35 grms. of caustic soda can be dissolved in 60 c.c. of water; if it is not desirable to make a quantity of saturated solution this is enough, if 20 c.c. of strong acid is used for the digestion. I think a Florence oil flask would answer for this if the others are not at hand. A glass tube about a foot long and 1¼ inch in diameter will do very well for a condenser; there is a cork at each end through which the tubes pass, and which retains the water; this can be run off when it is almost boiling, and cold or moderately warm water run in without fear of breaking the glass or stopping the process. A little ingenuity will enable the analyst to construct a condenser out of appliances which are always at hand.

Dublin, Dec. 26, 1890.

ON GASEOUS ILLUMINANTS.*

By Professor VIVIAN B. LEWES.

II.

In the second Cantor Lecture on the above subject, Professor Lewes pointed out that, in the various analyses of illuminating gases, the heavy hydrocarbons are, as a rule, expressed as "illuminants," and were formerly considered to consist mainly of ethylene. This is an idea which the researches of the last few years have shown to be totally erroneous, as, besides ethylene, there is undoubtedly present benzene, propylene, butylene, and acetylene, and probably such members of the paraffin series as ethane, propane, and butane, while under certain circumstances, crotonylene, terene, allylene, and others, are present. The determination of the illuminants is therefore by no means the simple process one would imagine it to be from the directions given in most text-books on gas analysis.

The illuminants present in any given sample of coal gas depend upon (1) the kind of coal used, (2) the temperature at which it is distilled, and (3) the length of time the gas is in contact with the heated sides of the retort, as well as with the liquid products of the distillation.

Having dealt with this part of the subject at considerable length, the lecturer then went on to consider the methods of analysis which can be utilised in determining the constituents of an illuminating gas, and showed that all analyses of coal gas have hitherto been founded on the idea that the "illuminants"—*i.e.*, the heavy hydrocarbons responsible for the illuminating power—could be absorbed by fuming sulphuric acid, chlorine, or bromine. This, however, he said, is undoubtedly not the case. Mr. Wright has shown that, when coal gas has been treated with this acid, the residual gas still retains from 32 to 55 per cent of its original luminosity; and although this may, to a certain extent, be owing to the methane, which at high temperature becomes slightly luminous, it is certain that a considerable percentage is due to the higher members of the paraffin series which are not absorbed by the acid, and which the methods of analysis usually employed utterly fail to detect. Indeed, given a gas containing any member of the paraffin series other than methane, the analytical results are not only incorrect, but misleading, as the percentages of hydrogen and methane present will be absolutely nullified by a very small quantity of the higher hydrocarbons.

The processes instituted by Bunsen, and used with all forms of mercury apparatus, have several drawbacks; the chief one being that the residue left after absorption with Nordhausen acid was looked upon as hydrogen, methane, and nitrogen, and that these were estimated by explosion with oxygen, and the volume of carbon dioxide formed was taken as representing the volume of methane. All researches on the composition of coal gas point to the presence of ethane, and probably of higher members of the marsh gas series; while in carburetted gases they are undoubtedly present to a far higher extent. Ethane, propane, and butane have all been shown to be present in small quantities; and as ethane gives double, propane three times, and butane four times its own volume of carbon dioxide, it is evident that exploding with oxygen and taking the volume of carbon dioxide as representing marsh gas will undoubtedly give too high results with ordinary coal gas, while with a carburetted gas it will render the whole analysis useless. Moreover, the free oxygen is next absorbed, and the remainder taken as nitrogen; and the volume of gas after absorption by Nordhausen acid, less the marsh gas and nitrogen, is taken as representing the hydrogen in the gas. The result is that the hydrogen is always far too low, not only because the volume of marsh gas is too high, but because the residual nitrogen, having to bear the brunt of all the errors of analysis throughout some seven or eight absorptions, is also nearly always too high. These palpable errors in the quantity of marsh gas and hydrogen also render worthless the calculations of carbon and hydrogen density of the gas, on which great stress has been laid by previous observers. On the whole, therefore, it is not to be wondered at that no relation has been discovered between the carbon and hydrogen density and the illuminating value of the coal gas. With the more rapid methods of technical analysis, it is evident that no explosion over water, and subsequent measurements of carbon dioxide, could give satisfactory or even approximate results, as the pressure at the moment of explosion, and the subsequent reduction of pressure, cause the water to effervesce like soda water from the absorption, and then the liberation of the carbon dioxide; and as this washes out other gases dissolved in the water, leaving an indefinite quantity of carbon dioxide in solution, any such process must be discarded.

These troubles have induced chemists to suggest several modifications in the process, some of which aim at doing away altogether with explosion. Certain of these, like the process of burning hydrogen, but not methane by passage over palladium asbestos, are of great value. The last method proposed for the analysis of coal gas without explosion has been published this year. It consists in absorbing the illuminants by strong alcohol, the carbon dioxide by potash, the oxygen by pyrogallate of potash, the carbon monoxide by cuprous chloride, the hydrogen by alkaline solution of permanganate of potash —calling the residual gas methane and nitrogen. The objections to this process are that alcohol not only absorbs the illuminants, but also a very large percentage—say, 50 per cent—of the methane, with considerable rapidity; that, after washing with water from the alcohol vapours, it would be useless to expect an exact determination of the carbon dioxide, as it has been mostly dissolved; and finally that, as far as Professor Lewes' experiments have at present gone, alkaline permanganate is not a reliable absorbent for hydrogen. He is now working at the various processes of gas analysis, and checking the several methods by the analysis of known mixtures of pure hydrocarbon—work which he expects to have ready for publication early next year. So far, the general scheme of analysis which he is following, and which gives him the best and most instructive results, is as follows.

Two of Stead's apparatus are taken and placed with the entrance tubes end to end, and filled—one with distilled water saturated with air, and the other with clean pure mercury. The gas to be tested is collected in one of the Stead absorbing tubes, over water, so as to be saturated; it is then transferred over mercury in the eudiometer-tube of the second apparatus, and measured and passed into sodic hydrate, in order to absorb the small trace of carbon dioxide to be found in the highly-purified London gas. When present in only small traces, the amount of carbon dioxide lost by water saturation cannot be detected, while a calculation is avoided. After the absorption of the carbon dioxide, the gas is run into the second apparatus, and the oxygen estimated by absorption with alkaline pyrogallate, which must be strong and fresh, containing about 25 grammes of pyrogallic acid dissolved in 50 grammes of sodic hydrate in 200 c.c. of water. It is absolutely essential that the solution should be fresh, as after some time it will evolve a considerable amount of carbon monoxide. The heavy hydrocarbons have now to be estimated; and inasmuch as benzene is one of the most valuable illuminants in the coal gas, it would be of great value if any absorbent could be found that would

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* Abstract of the Cantor Lectures delivered at the Society of Arts. Communicated by the Author.

separate the benzene and ethylene series. Unfortunately this does not exist as far as is known; the usual absorbents having the following drawbacks: (1) Nordhausen sulphuric acid, in which sulphur trioxide has been dissolved until it will solidify on cooling, absorbs both ethylene and benzene, and therefore cannot be used to separate them. (2) Fuming nitric acid is a good absorbent for both series. (3) Bromine water acts far more rapidly on ethylene than on benzene, but undoubtedly does absorb a considerable quantity of the latter if left long in contact with a mixture of the two. (4) None of the foregoing affect methane in diffused daylight. The nearest approximate result is obtained by treating the gas first with strong bromine water, but not leaving it too long in contact with it, and then removing bromine vapour over sodic hydrate—the absorption being taken as the ethylene series; while the benzene is absorbed by fuming nitric acid or saturated Nordhausen acid—acid fumes being removed in the sodic hydrate tube before measurement over water. After absorption with nitric acid gas, it is run back into the eudiometer, and measured over water. It is then passed into an absorption-tube filled with a fresh solution of ammoniacal cuprous chloride. This must not be used for more than six determinations of an ordinary coal gas containing (say) 3 to 6 per cent of carbon monoxide or three of a carburetted water gas, as after much carbon monoxide has been absorbed, the solution has a tendency to again give up small quantities of the gas.

The gas is now returned to the mercury eudiometer-tube; and, after measurement, it is passed into an absorption-tube containing ordinary paraffin oil (previously heated until everything that will distil at 100° C. has gone off), which absorbs ethane, propane, butane, and a good deal of the methane. The residue is then washed and mixed with oxygen, which has itself been analysed, so that the percentage of nitrogen and foreign gases in it are known, and the mixture exploded over mercury. The carbon dioxide formed is estimated; and its volume *plus* the volume of gas absorbed by the paraffin gives the volume of gases in the methane series. A fresh portion of gas is now taken over mercury, and is exploded with excess of analysed oxygen. The carbon dioxide is absorbed by sodic hydrate and the oxygen by pyrogallate; and the residue will be the nitrogen—the hydrogen being determined by difference. In this way an analysis of South Metropolitan gas shows—

	Hydrogen		47·9	
Illuminants	Ethylene series	approx.	3·5	Total Hydrocarbons 45·6 p.c.
	Benzene ,,		0·9	
	Methane series	by paraffin	7·9	
		by explosion	33·3	
	Carbon monoxide		6·0	
	Carbon dioxide		0·0	
	Oxygen		0·5	
	Nitrogen		0·0	
			100·0	

In such an analysis, the lecturer remarked, no pretence was made that the exact percentage of each illuminant was given. But the total of the hydrocarbons were accurate, and their rough subdivision gave a far clearer insight into the characters of the gas than the more pretentious and more faulty analysis upon which it has been customary to argue. He said it must be clearly borne in mind that he only put forward this scheme of analysis to meet the need now rapidly arising for a method which would show whether ordinary coal gas enriched by cannel coal gas carburetted with either gasoline or oil gas, or coal gas enriched by highly carburetted water gas, was being dealt with. In the first case the ethylene and benzene series would be found well represented, while the carbon monoxide was low; in the second, the amount of hydrocarbons in the methane series would have become greater; and if oil gas had been used a small increase in carbon monoxide might also be noticed, while the presence of carburetted water gas at once brought up the quantity of carbon monoxide, and the methane series became more important illuminants.

Professor Lewes went on to show that the light-giving value of the hydrocarbons present in coal gas vary very greatly; the illuminating power increasing very rapidly with the number of carbon atoms in the molecule.

The action of the diluents in coal gas upon its illuminating power has been determined by Dr. Percy Frankland by taking ethylene, with its illuminating value of 68·5 candles, as representing the hydrocarbons in the gas, and diluting with the various diluents present.

The results show that, with the combustible diluents, hydrogen reduces the illuminating power least with large quantities of the hydrocarbons; but that marsh gas is preferable when in excess, as with low percentages of the illuminant, especially when burnt at a high temperature, marsh gas itself becomes a feeble illuminating agent. This is due to the fact that although, when the marsh gas or methane burns at ordinary temperatures, it is non-luminous, at a high temperature some of it is broken up into acetylene, which gives it distinct luminosity. Carbon monoxide is the most injurious of the combustible diluents, 80 per cent mixed with ethylene rendering it non-luminous —a result which would require 90 per cent of hydrogen to bring about.

The influence of incombustible diluents on the illuminating power of flames containing hydrocarbons has been also determined.

Moisture, when present to the extent of 2 per cent (the proportion present in coal gas saturated at 20° C. and 760 m.m.), with ethylene, reduces the illuminating power 3·6 per cent, or in coal gas 3·3 per cent. Of the inert or non-combustible diluents, therefore, carbon dioxide is the most injurious, while atmospheric air is the least harmful. Wurtz has also determined the loss of light incidental to the addition of air to coal gas, and he gives the following results:—

Added Air.	Percentage Loss of Light.
3·00	15·69
4·96	23·83
11·71	41·46
16·18	57·53
25·00	84·00

The addition of oxygen to gases rich in hydrocarbons causes an increase in the illuminating power up to a certain point, by raising the temperature of the flame, by burning up the hydrogen of the hydrocarbons, and rendering the carbon incandescent, without diluting the flame with nitrogen to the extent that would have been necessary had air been used for the purpose. The effect of such gases as hydrogen, marsh gas, and carbon monoxide is simply to dilute the flame, and, by separating the molecules of the hydrocarbons, to make them more difficult to decompose; whereas such bodies as carbon dioxide, nitrogen, air, and water vapour not only dilute, but also cool the flame, as they do not add to the heat by any action of their own, and have to be heated up to the same temperature as the flame itself. Rosette determined the temperature of a gas-flame diluted with air, nitrogen, and carbon dioxide respectively, and found that it was least with the last-named gas, and highest with air—a result which agrees with Dr. Frankland's determination of illuminating power. His figures are as follows:—

Volumes taken.		Temperature.		
Gas.	Diluent.	Air.	Nitrogen.	Carbon dioxide.
1 vol.	1 vol.	—	1180° C.	1100° C.
1 ,,	2 ,,	1260° C.	1150° C.	880° C.
1 ,,	3 ,,	1116° C.	1040° C.	780° C.

Preservation of Flexible Tubing (*Pharm. Zeit. fur Russland*).—The author places the coils of tubing in water containing a little salt.

A NEW METHOD OF MAKING ALLOYS.[*]

By WILLIAM HALLOCK.

While occupied with a careful study of an article by W. Spring[†] on the production of Wood's alloy, and seeking the forces possibly brought to bear in his experiments, the following explanation occurred to me, and was subsequently verified by critical experiments. The method of production used by Mr. Spring was to mix filings of the four metals in the proper proportions, subject the mass to a pressure of 6000 atmospheres, file up the block thus produced and compress it a second time, obtaining as an end result a block of Wood's alloy.

Now, if at any time during the various operations, be it the first compression, the subsequent filing, or the second compression, or if anywhere in the whole mass the original metals came in contact all together, then at that point we should have a particle, a molecule as it were, of Wood's alloy. If thereafter the temperature ever rose to 70° C., that particle would melt and dissolve down its immediate neighbours until finally the whole mass was liquefied and converted into a homogeneous mass of alloy. Without waiting to consider how improbable it was that the three or four metals could be brought simultaneously into perfect enough contact to act as a real alloy, I tried the experiment and it proved an easy success.

The metals were filed to fine grains and mixed in the proper proportions, one part cadmium, one part tin, two parts lead, and four parts bismuth. A glass tube of 5 m.m. inner diameter and 70 m.m. length, sealed at one end, served as containing vessel. About 6 grms. of the mixed filings were placed in this tube and packed down, an iron wire 3 m.m. diameter, held between the thumb and finger, being used as a packer; which certainly eliminated the possibility of any considerable pressure. The tube was thereupon so placed upon the water-bath that the sealed end containing the metals projected downward into the boiling water. In this way the filings remained dry and were kept at a temperature of 98° to 100° C. After remaining in this position for eighteen hours (over night) the filings showed signs of sinking together, which would indicate a beginning of the reaction. The tube was jarred upon the table to assist the condensation and again placed on the bath. Two hours later the tube contained a *homogeneous liquid globule of Wood's alloy*. The experiment was repeated, using two larger tubes, into which the metals were packed with a lead pencil, and producing some 30 grms. of alloy. Of course when the operation is once started there is no limit to the quantity which can be produced. One tube remained on the water-bath over a week without signs of a solution and yet finally dissolved.

In further application of the same principle lead and tin were melted together at 190° to 200° C. by simply laying a piece of tin upon a carefully cleaned piece of lead and placing the whole in an air-bath at 190° C. A few hours suffice for this experiment. The melting points of the above metals are—Cadmium 315° C., tin 230° C., bismuth 267° C., lead 325° C. Potassium and sodium were also used, melting at 62° 5' C. and 95° 6' C. respectively.

A very interesting and striking experiment is the production of the alloy of equal parts of potassium and sodium, which is liquid at temperatures above 6° C. Pieces of the two metals are simply placed with freshly cut surfaces in contact and slightly pressed together; in a few seconds the liquid alloy, which resembles mercury, is visible in drops around the contact surface, and an hour or two suffices to produce several cubic centimetres of the fluid.

It is my intention in the near future to follow up these observations by a series of experiments intended to establish and extend the principle here illustrated. The heat phenomena which doubtless accompany these reactions will also be investigated. Possibly also some electrical manifestations may be discovered, and perhaps some facts bearing upon the origin of contact electricity may be developed. In the meantime I would propose the following law:—An alloy can be produced out of its original constituents without considerable pressure if the temperature be above the melting point of the alloy, even though it be far below the melting point of the most easily fusible constituent.

Probably this law will also be found applicable wherever under the existing circumstances the product is a liquid, even though the original substances be solids.—*Bulletin of the United States Geological Survey*, No. 60.

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[*] Read before the Philosophical Society of Washington, D.C., at the meeting of February 18, 1888.

[†] W. Spring, "*Ber. der Chem. Gesell.*, vol. 15, 1882, pp. 595—597.

COEFFICIENTS OF VOLATILITY FOR AQUEOUS CHLORHYDRIC ACID.

By ROBERT B. WARDER.

The various questions of physical chemistry are claiming more and more attention, and problems relating to states of aggregation seem to have a special interest. The art of fractional distillation on a manufacturing scale has developed a great variety of appliances, but much remains to place the theory on a satisfactory mathematical basis, especially in the case of bodies which exert a mutual affinity.

The term "coefficient of volatility" was introduced by Wanklyn[*] to indicate the relative readiness of different constituents to volatilise. Thus he found that when a very dilute solution of ammonia was distilled until $\frac{1}{10}$ of the water passed over, nearly $\frac{1}{2}$ of the ammonia had distilled with it. He estimated that a given quantity of water in any small fraction of the distillate was accompanied by 13 to 14 times as much ammonia as the same quantity of water in the boiling liquid. Expressed more formally, if a boiling liquid has the composition—

$$H_2O+nNH_3,$$

and yields a mixed vapour represented by $H_2O+vnNH_3$, the factor v is the coefficient of volatility, and in the case cited v equals about 13 or 14. Since this gas may be absorbed in indefinite proportions, of course the coefficients n and vn may be fractional, indicating the number of molecules of NH_3 divided by the number of molecules of H_2O.

In the case of chlorhydric acid, as is well known, when the liquid boils under the ordinary atmospheric pressure, it tends to acquire the constant composition $HCl+8H_2O$, or $H_2O+\frac{1}{8}HCl$. After a stronger or weaker acid has reached this composition, on further boiling $n=vn$ and the factor $v=$unity.

The well-known researches of Roscoe and Dittmar[†] showed that an acid of higher composition will boil unchanged under diminished pressure; a similar result was observed upon evaporation in a current of air of given temperature to supplement the partial pressure exerted by acid and aqueous vapour. Hence it is clear that v depends not only upon the composition of the mixture, but also upon the pressure (or temperature) at which the distillation is conducted. The published data relate to the conditions under which $v=1$, but no attempt has yet been made to show the relation between v and n.

The more recent researches of Roozeboom show certain conditions of equilibrium among solid, liquid, and gaseous phases of aqueous chlorhydric acid[‡] and other compounds which are illustrated by thermodynamical theory;[§] but

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[*] *Philos. Magazine*, [4] 45, 129 (1873). *Pharm. J. Trans.*, [3] 3, 543 (1873).

[†] *Jour. Chem. Soc.*, 12, 128.

[‡] *Rec. Trav. Chim, Pays-Bas*, 3, 84 (1884). Abstract in *Zeitsch. physik. Chem.*, 1, 365 (1887), and 2, 459 (1888).

[§] *Rec. Trav. Chim. Pays-Bas*, 5, 335, (1886). Abstract in *Zeitsch. physik. Chem.*, 2, 463 1888).

the papers do not discuss the ordinary conditions of distillation.

Many operations of manufacturing, geological, and analytical chemistry depend upon the partial or complete separation of volatile constituents. Chloryhdric acid is typical of a large number of substances which have strong attraction for the solvent; and a more exact knowledge of its *volatility* as a function of the *composition* is the object of this research.

Experimental Method.

One hundred cubic centimetres of chlorhydric acid of known strength was subjected to fractional distillation in a boiling flask of 250 c.m.³ capacity. Successive portions of the distillate were conducted through a Liebig condenser and discharged near the bottom of receivers; a loosely fitting cork was used to hinder evaporation. The several fractions, after weighing in well stoppered vessels, were titrated with sodium hydrate, containing a little barium hydrate and carefully protected from the air by soda lime. Phenolphthalein was used as indicator. In some cases very weak distillates were evaporated with excess of ammonia, and titrated with centinormal silver solution and potassium chromate. The water was determined by deducting the acid from the total weight of the fraction. As a rule no reliance was placed upon specific gravity, the ordinary summer temperature of the room being far above that recognised in the tables; hence the acid used for each distillation was weighed. The residues in the boiling flask were also weighed and titrated for control.

When fractional distillation is conducted for the purpose of separating the constituents, this is promoted by some kind of dephlegmation; this may be accomplished by exceedingly simple means, as the walls of an ordinary boiling flask, by the complicated appliances of the manufacturers, or by the many devices for laboratory use. The object of the present work required the exclusion of dephlegmation, since this would introduce an element of great uncertainty. The flask was placed in a cylindrical air bath and covered with a conical hood of sheet copper. By means of a ring burner (as devised by Gibbs), with very gentle air blast, a circle of gas jets was thrown upon the copper cone, so as to keep the upper part of the flask heated far above the boiling point of the fluid, while distillation was effected by a large Bunsen burner under the air bath. A thermometer in the vapour was usually kept at a temperature of 145° to 153°. The boiling point of the liquid was from 100° to 109° C. (varying with the concentration); and from the rate of distillation and the space above the liquid, it was estimated that the vapour would pass from the surface to the condenser in about six seconds; hence it is not to be supposed that the thermometer indicated the actual temperature of the vapour, but something between this and the temperature of the radiating surface of glass or copper. By this means the condensation of moisture upon the sides of the flask was prevented. In a preliminary experiment with

$$H_2O + 0{\cdot}037HCl,$$

the first fifty per cent distilled without the hood and ring burner contained no more acid than the 10 per cent distilled with the precaution described; and this was only one-twentieth as much acid as distilled in the first 50 per cent under the heated cover.

As the distillation proceeded and the volume of vapour increased the temperature had to be moderated by turning down the flame.

In the distillation of strong acid each receiver was weighed with 10 c.m.³ water, to absorb the acid fumes.

Calculation of Results.

The weight of HCl found in each fraction of the distillate subtracted from the total weight leaves the weight of water; and the weights of water and acid thus found in each fraction were subtracted successively from the water and acid taken to find the composition after the removal of this fraction. The mean composition of the boiling liquid during the removal of each fraction was expressed in the form $H_2O + nHCl$, the composition of the distillate being $H_2O + n'HCl$ or $H_2O + vnHCl$. The coefficient v was then found by dividing n' by n. Four distillations gave 25 pairs of values as follows:—

I.		II.		III.		IV.	
n	v	n	v	n	v	n	v
0·0952	0·284	0·0681	0·140	0·0666	0·084	0·1939	5·44
0·1031	0·423	0·0759	0·194	0·0693	0·111	0·1853	3·71
0·1107	0·537	0·0862	0·282	0·0730	0·158	0·1713	2·40
0·1186	0·645	0·0984	0·429	0·0769	0·172	0·1567	1·66
0·1231	0·868	0·1107	0·597	0·0806	0·198	0·1474	1·31
				0·0844	0·243		
				0·0879	0·247		
				0·0911	0·253		
				0·0944	0·300		
				0·0970	0·311		

Discussion of Results.

Two points remain to be considered:—

First. What formula will best express the values found for v as function of n?

Second. Do the relations here determined point to actual equilibrium between liquid and vapour?

No one equation was found to express all the values given above. When dilute acid ($n = 0{\cdot}07$ to $0{\cdot}11$) was boiled rapidly (about one grm. per minute) the results agreed with the equation $v = 445n^3$ as in series II. When strong acid ($n = 0{\cdot}15$ to $0{\cdot}20$) was boiled rapidly, the values of v were somewhat greater than would be indicated by the equation above; approximately, $v = 3063n^4$, as in series IV. These two empirical curves, which occupy different parts of the field, are entirely consistent with each other, but must be regarded as a *first approximation only* to the function sought. When the dilute acid of Series I. and III. was boiled from 20 to 60 per cent more slowly than that of Series II., the values of v were about 10 to 30 per cent less than those indicated by the equation. There can be little doubt that v is a function of the rate of boiling as well as of the composition of the liquid. The problem appears to be dynamical, not a question of equilibrium merely, and I hope to investigate this point further.—*Bulletin of the United States Geological Survey*, No. 60.

AN IMPROVED METHOD FOR THE ESTIMATION OF THEINE IN TEAS.

By G. L. SPENCER.

The estimation of theine has received considerably more attention from analysts than the value of a knowledge of its proportion in teas seems to warrant. The estimation of the percentage of theine in a tea gives little if any information in regard to the commercial value of the latter, though, in general, it may be said the high-priced teas usually contain a large proportion of this alkaloid.

Twenty-five or more methods have been devised for the estimation of theine, though it must be said the later of these methods bear a strong resemblance to one another. In the earlier methods the alkaloid was extracted from the tea leaves by means of ether or acidulated water, the extract purified, and the theine separated by crystallisation from concentrated solutions, or if finally obtained in ether or chloroform solution, by the complete evaporation of solvent. The various methods differ more especially in the purification of the solutions of the alkaloid.

In the method of Blyth the alkaloid is obtained quantitatively directly from the powdered leaves and in a state of great purity, by sublimation. Some of the later methods differ from one another only in slight variations in the manipulations, the object being the reduction of the labour required.

Weyrich (*Ztschr. anal. Chem.*, xii., 104) examined a number of theine methods and rejected all but that of Mulder. His objections to the various methods were based upon either imperfect extraction of the alkaloid, imperfect precipitation, or an impure product. The method of Mulder, which he adopted, consists in evaporating a definite volume of a water extract of the tea with magnesia to dryness; the residue is then digested two days with ether; this latter is occasionally heated and poured off into a tared flask, a fresh portion of the solvent being added. This extraction is continued as long as the residue yields theine. The ether solutions are united, and finally the solvent is removed as usual by evaporation. This is a favourite one of the older methods, and is given to emphasize the simplicity of manipulation required by the method, which I propose to describe below. While the method about to be described is but little shorter than some of the new methods, which it resembles, it has the advantage of very considerable accuracy. This method may be briefly described as follows:—

Transfer three grms. of very finely powdered tea to a 300 c.c. flask; fill the flask with hot water nearly to the neck; add a small fragment of tallow to prevent foaming; heat gradually to ebullition, and maintain this temperature half an hour. Small particles of tea adhering to the neck of the flask should be washed down with a few drops of water. After boiling, cool and add subacetate of lead in slight excess. The amount of the reagent required may be determined by the ease with which the precipitate separates. Approximately 0·3 c.c. concentrated lead solution is required per grm. of tea. After the addition of the lead, complete the volume to 300 c.c. and shake the flask to mix its contents thoroughly; filter off 100 c.c. of the solution into a sugar flask, *i.e.*, a flask graduated to 100 and 110 c.c.; precipitate the excess of lead with hydrosulphuric acid, employing ether to prevent foaming; heat to expel excess of the reagent, cool, and complete the volume to 110 c.c. The extra 10 c.c. permits washing the gas delivery tube. Filter, transfer 55 c.c. of the filtrate, corresponding to 0·5 grm. of tea, to a separatory funnel, and extract seven times with chloroform. The chloroform solution of the theine is collected in a tared flask and the solvent removed by distillation and drying. The temperature at which the latter is accomplished should not exceed 79° C. The theine obtained is very pure and contains one molecule of water of crystallisation.

It may be noticed in the above method that all washings of precipitates is avoided. A slight error is introduced through the non-removal of the tea residue and the lead precipitate, but this will rarely if ever exceed about 0·02 per cent. A second error results from leaving the lead sulphide in the sugar flask, but this is extremely small, if care has been taken in adding the lead subacetate. If preferred, the lead may be removed without the use of the sugar flask, a definite volume of the solution being taken for this purpose. In this case the precipitate requires washing. It is preferable to follow the method as first described, as in this way the volume of the solution in the funnel will not exceed 55 c.c., a large volume being objectionable through the possibility of a portion of the alkaloid remaining in water solution.—*Journal of Analytical Chemistry*, Vol. iv., Part 4.

ON THE METHODS OF ESTIMATION OF THE FATTY BODIES IN VEGETABLE ORGANISMS.

By WALTER MAXWELL.

THESE investigations have been conducted with the purpose of acquiring some further data showing the comparaive proportions of matters which become separated from egetable organisms by extracting with pure ether in variable durations of time. It has further been attempted to determine whether the whole of the substituted glycerides, or lecithines, do become separated by direct extraction with ether only.

The materials used in the work were pulverised to the greatest state of fineness, and the extractions were made with the Knorr extraction apparatus. The calculations are reduced to the standard of water-free material.

a. The preliminary experiments, which were made in order to establish the proportions of the vegetable matters separated by the action of pure ether in different durations of time, are illustrated by the following results:—

Cotton-seed. Time.	Wt. of Material. Grms.	Wt. of Extract. Grms.	Per cent.
8½ hrs.	4	1·472	37·39
10 ,,	4	1·491	37·87
15 ,,	4	1·511	38·38

These results give the average of a great number of analyses. Although an increase of substance becomes separated with an increased duration of the period of extraction, the proportion is small; and it is not apparent that the greater duration of time causes an increase in the fatty bodies only, as other matters can be affected by a very protracted boiling. For these reasons it has been resolved to estimate the amounts of the fatty bodies separated by extraction with pure ether in a duration of 15 hours.

In considering the estimation of the proportion of glycerides and substituted glycerides which are contained in the ether extract, the presence of other bodies, which have been removed with the ether, make it impossible, in the absence of an absolute analysis of the extract, to determine accurately the comparative relations of those fatty bodies. The ether extractions of plant matters contain variable proportions of cholesterin and of, in some instances, solid hydrocarbons, which may constitute several per cent of the extract. However, although the percentage of glycerides cannot be definitely estimated, the lecithines or substituted glycerides may be determined with absolute accuracy, as the estimation of these bodies rests upon the proportion of phosphorus present in the ether extract. The extract is ignited with mixed alkali salts, by which the phosphorus present in the organic form as lecithine becomes fixed as an alkali phosphate and is then determined as magnesium pyrophosphate, and the latter body being multiplied with the known Hoppe-Seyler factor, gives the exact amount of lecithine.

A further series of extractions was made of the pulverised cotton-seed with pure ether for a period of 15 hours and the total extract determined. The proportion of lecithine contained in the extract was estimated by the method already given, the residue of the extract being considered as glycerides and other bodies. The average of eight analyses gave the following results:—

Per cent of extract	38·46
Per cent glycerides, &c.	98·84
Per cent lecithines	1·16

b. It will be shown that the proportion of substituted glycerides stated, 1·16 per cent, does not represent the total lecithines present in the cotton-seed.

The observation was made simultaneously by Prof. E. Shulze, Zurich, and W. Maxwell, of Harvard College, that the substituted glycerides do not become wholly separated by extraction with ether, even in a great duration of time. It was found that if the material which had been already extracted with ether were further extracted with absolute alcohol, another portion of substituted glycerides was obtained, which, in most instances, was greater than the amount separated by the ether. The process of the alcohol extraction consisted in merely extracting the material already treated with ether and evaporating off the alcohol, and re-extracting the alcohol extract residue with ether. The reason for taking up the lechithines out of the alcohol extract was that it has been observed that those lecithines which were originally insoluble in ether became soluble in that menstruum when previously acted upon by alcohol. The use of ether was further made to avoid any small portion of inorganic phosphates which might have been removed from the vegetable material by alcohol. It was found, however, that only a mere trace of mineral phosphates had been separated by the action of the alcohol.

The amount of the ether extraction of the alcohol extract in 100 parts of the vegetable material with the proportion of lecithines was as follows:—

Extract	2·3 per cent
Lecithines in extract ..	16·6 ,,

A further comparison inditates the following:=

	Extract. Per cent.	Lecithines. Per cent.	Glycerides, &c. Per cent.
Ether	38·46	1·16	98·84
Ether and alcohol	40·76	2·30	97·69

The proportion of lecithines to the total fatty bodies contained in the cotton-seed is very small, yet it is seen that about 50 per cent of those substituted glycerides are left in the material after extraction with ether for a period of 15 hours. If certain other varieties of seeds be considered, such as the legumes, pea, vetch, bean, Boston bean, &c., it is found that the total ether and alcohol extracts of those seeds are composed of lecithines varying from 25 to 45 per cent. It is thus apparent that, in the examples of seeds given, as far as 20 per cent to 25 per cent of the total fatty bodies can remain unseparated and undetermined when the material is extracted with ether only.—*Journal of Analytical Chemistry*, Vol. iv., Part 4.

THE ANALYSIS OF CUPRIC BROMIDE, AND THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

The uncertainty of knowledge regarding the atomic weight of copper, owing to the widely different values assigned by various experimenters, led nearly four years ago to the beginning of an investigation, of which this paper is the third publication. The two earlier papers (*Proceedings of the American Academy of Arts and Sciences*, xxii., 342, and xxiii., 177; also *Fresenius's Zeitschrift*, xxviii., 392) described a number of determinations made by a method which had not until then been successfully applied,—the precipitation of metallic silver from neutral silver solutions by means of metallic copper. The results obtained were in themselves very satisfactory, but differed entirely from the value which has hitherto been accepted with little question by chemists; and the desire to discover, if possible, the cause of this discrepancy has finally led to the continuance of the investigation.

It is well known that we can rarely find with regard to any element more than one or two compounds which answer the exacting requirements of atomic weight determination; although others of its definite compounds may by their analysis more or less strongly support the verdict of the more exact results. Disagreement implies constant error in one or other of the disagreeing values, and the detection and correction of this constant error can alone give certainly to our conclusions. Much, however, may be learnt by careful study from a new standpoint, and the first step in the present investigation was to discover if possible such an opening.

The basic tendency of cupric salts, and the ready oxidation of cuprous compounds, complicate to such an extent the relations of copper, that the preparation of any one of its salts in a dry state of perfect purity may be regarded as almost an impossibility. One by one the usual cupric and cuprous compounds were rejected as unsuitable for the foundation of a new research, until finally, after much study, cupric bromide was selected on account of the simplicity and exactness of its analysis, and moreover because by establishing beyond doubt the relation of copper to bromine we connect its atomic weight with precise values previously determined in this laboratory.

The balance used throughout the research was the one used by Professor Cooke in his admirable work upon the atomic weight of antimony, and was kindly loaned by him for the present purpose. A long-armed balance of the best type, manufactured by Becker, of New York, it was very perceptibly turned by one-twentieth of a m.grm. with a load of fifty grms. in each pan, and showed unusual constancy in its indications. It was kept in a large quiet room of nearly constant temperature, and was protected from unequal heating and from air currents by suitable curtains. The weights were made by Sartorius in Göttingen, the larger ones being of gold-plated brass, and the fractions of a grm. of platinum. Three days were spent in their comparison, according to a method somewhat similar to that described by Crookes (*Fresenius's Zeitschrift*, vi., 431), and the very small corrections thus found were tabulated and applied to all results.

Before weighing, every object was allowed to remain in a desiccator near the balance for at least seven hours. Every weight was determined at least thrice, each time according to a different method of swinging, and all precautions for accuracy were taken which are usual in such work. In the first experiments the weighings were made by substitution, but the conditions were so uniformly constant and the balance so manifestly reliable that this procedure seemed a useless expenditure of time. In fact, the probable error of the ordinary method of weighing under such circumstances is very much less than other possible errors of an investigation like the present. It is certain that the total inaccuracy of any weighing, due to all possible causes combined, could not have exceeded seven or eight one-hundredths of a m.grm., and was without doubt usually very much less than that quantity. All weighings were, of course, reduced to a vacuum standard, allowing for the air displaced by the weights. Since these were standardised with reference to a brass ten-grm. piece, it is evident that the fractions of a grm. must be calculated as brass, and not as platinum.

I. Preliminary Work.

Preparation and Analysis of Hydrobromic Acid.

The next step taken was the preparation of hydrobromic acid pure enough to serve as the basis of research. The acid was made from pure potassic bromide and sulphuric acid, according to the method recommended by Dr. Squibb (*Proceedings of the American Academy of Arts and Sciences*, xvii., 30). It was then purified by repeated fractional distillation, at first in a large platinum retort, and afterward in one of glass, it having been ascertained that the gold used as a solder in the former apparatus was attacked during the process. It was subsequently found that the action of the acid even upon glass was not imperceptible, but as the same retort was used in all later distillations, and as the glass was of good quality, this unavoidable cause of impurity was reduced to a minimum.

The acid was distilled in all ten times,—seven times over potassic bromide, twice over silver bromide, and once alone,—each time the first and last portions of the distillate being rejected. A specimen of the wholly colourless product was preserved for over a year without perceptible change.

The necessity of testing the purity of this hydrobromic acid led at once to the next step of the investigation, the preparation of chemically pure silver. Fused argentic nitrate was first made from pure silver which had been

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* Contributions from the Chemical Laboratory of Harvard College. —From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxv.

reduced from the chloride by milk-sugar and potash. This salt was then dissolved in a large amount of water, and again decomposed by the gradual addition of very dilute hydrochloric acid in slight excess, the precipitate being thoroughly agitated and washed by decantation with dilute hydrochloric acid and hot and cold water. After drying and pulverising, the pure argentic chloride was digested for six hours with aqua regia, and then again washed with the purest hot and cold water until the filtrate gave no test for chlorine.

The final reduction of the cream-coloured product was accomplished as before, by warming it with a dilute solution of the purest caustic potash and milk-sugar, which had previously been filtered through a Gooch crucible. Careful testing showed the completion of the reaction, and the resulting pure silver, having been thoroughly washed with dilute sulphuric acid and a very large amount of pure hot water until perfectly clean, was collected and dried upon a quantitative filter. Small portions of the powder were successively supported upon a carbon dish similar to that described by Professor Cooke (*Proceedings of the American Academy of Arts and Sciences*, xvii., 17), and, after being fused by means of a blowpipe directed downwards, the silver was allowed to cool in a reducing flame. The buttons were hammered upon a clean anvil, scrubbed with sand, rolled out between two plates of pure silver, cut with a hard steel chisel, boiled successively with hydrochloric acid and ammonia, scrubbed once more with sand, and, after heating with melted potassic hydrate in a silver crucible, finally scrubbed, washed, and dried.

In order to prove the absence of any absorbed gases in the resulting metal the following experiments were made:—

I. 1·3412 grms. of silver heated in vacuo to a low red heat weighed after cooling 1·3412 grms.

II. 1·5763 grms. after being subjected to the same treatment weighed 1·5763 grms.

The absolute constancy of these weights is sufficient proof of the point in question. The silver yielded a perfectly clear solution upon treatment with nitric acid and subsequent addition of water, and gave every evidence of being chemically pure.

In order to determine the purity of the hydrobromic acid previously made, the solution of a known weight of the pure silver described above was decomposed by a slight excess of this liquid, and the resulting precipitate was weighed. The metal was dissolved in a very slight excess of warm pure nitric acid diluted with two volumes of water, the whole being contained in the half-litre Erlenmeyer flask, which was afterward to serve for the precipitation. The very small amount of gas formed by the decomposition of the nitric acid was forced to pass through a zigzag tube provided with bulbs, in order that the infinitesimal amount of spray might be retained. The tube apparatus was not ground into the flask, but fitted only with moderate tightness, the joint being sealed by water held in place by capillary attraction. After the complete solution of the silver, the contents of the flask were gently boiled to drive off the lower oxides of nitrogen, and the whole was diluted to about two hundred cubic centimetres. To this hot liquid was added very gradually the least possible excess of a dilute solution of known strength made from the hydrobromic acid above described, and the mixture was constantly and violently shaken, the flask being closed with a smooth rubber stopper. After settling, the precipitate was thoroughly washed with hot water, and collected in a Gooch perforated crucible with all possible care. The crucible with its contents was dried at 130° to constant weight, and showed no loss in any case on additional heating to 180°.

SYNTHESIS OF ARGENTIC BROMIDE.

No. of Experiment.	Silver taken (reduced to vacuum). Grms.	AgBr formed (reduced to vacuum). Grms.	Percentage Ag in AgBr.
1	1·11235	1·93630	57·447
2	1·57620	2·74335	57·455
3	2·16670	3·77170	57·446
		Average	57·449
		According to Stas	57·445

The above variation is not greater than a possible error in the operations concerned, and the testimony which these results give to the purity of the materials is sufficient for the present purpose. Other experimenters in this laboratory have obtained values ranging from 57·442 to 57·450.

Preparation of Cupric Bromide.

The salt used in the preliminary series of experiments upon the atomic weight of copper was formed by the solution of the purest obtainable cupric oxide in the hydrobromic acid which has been described above. For the preparation of the oxide of copper pure electrolytic metal (of the quality used in the experiments published three years ago) was converted into sulphate by means of pure nitric and sulphuric acids, and the resulting salt was purified by six fractional re-crystallisations after the expulsion of the remaining nitric acid by heat. From a dilute solution of the purest cupric sulphate acidified with nitric and sulphuric acids, about half the metal was deposited upon the interior of a large platinum dish. The remaining liquid being decanted, the film was washed, re-dissolved, and partially re-deposited through the agency of two Bunsen cells. It was hoped that this fractionation would rid the copper of that probable impurity which almost invariably manifests itself as minute dark spots upon the surface of the film of a completed electrolysis, but the hope proved to be a vain one, and no method of purification was devised which would wholly remove the difficulty. Some of the copper films obtained in the course of the work were almost free from the minute spots, while others of the same series showed a larger number of them; but the phenomenon did not appear to affect the results. From this it would seem that the supposed impurity might have consisted merely of finely divided copper, but even on the worst supposition the amount was so infinitesimal that it could have had no influence upon the observed atomic weight.

The brilliant metallic film thus prepared was carefully separated from the platinum and thoroughly washed with hot water. The separation of the copper from the dish is greatly facilitated by previously rubbing the surface of this electrode with an exceedingly small quantity of pure semi-liquid paraffin, which seems to fill the microscopic cavities of the platinum without interfering with the continuity of the copper film. The pure washed copper was returned to the clean dish, dissolved in very pure nitric acid, and the product slowly converted into basic nitrate, and finally into oxide, by gradually increasing heat. The last part of the operation was conducted at a low red heat in porcelain, and of the product only the central portions were used in the work. The resulting cupric oxide was a fine black powder, which dissolved completely in acids, and gave every evidence of being chemically pure.

A large quantity of this copper oxide was dissolved in a slight excess of pure hydrobromic acid, and the solution evaporated to dryness over a steam bath. Of course, every possible precaution against dust and other impurity was taken with regard to this as well as to every other operation of the research, neither hydrochloric acid nor ammonia being used in the room devoted to it. During the process of evaporation a very faint odour of bromine was perceptible; and upon the subsequent solution of the brilliant black scales of cupric bromide in water, the clear blue liquid slowly deposited a few microscopic crystals of the basic bromide, which will be described in another place. After standing a few days the crystals ceased to be deposited, and the filtered clear odourless solution remained for about four weeks without further change, serving as the basis of a number of experiments, and furnishing material for the first series of preliminary analysis.

Since it was evidently impossible to obtain the normal salt by the evaporation of the solution at 100° in the air, many attempts were made to prepare it by concentration of the neutral solution over sulphuric acid in air and in nitrogen gas of low tension. The first trials all ended in failure, and it was not until much later that the problem was successfully solved. The purest salt obtained at this stage of the work consisted of brilliant black crystalline scales, which, contrary to all expectation and all literature[*] upon the subject, were not very deliquescent unless moistened with strong hydrobromic acid. Since the normal compound invariably seems to lose a trace of bromine on exposure to the air, the lack of deliquescence may be due to a very thin superficial covering of the basic bromide. The normal salt is soluble in a very small amount of water, forming a brownish black solution; this becomes deep purple after the addition of hydrobromic acid, and upon gradual dilution goes through successive shades of brown and dirty green to a most beautiful "robin's egg" blue.

The basic salt above alluded to was found to be quite insoluble in water, hence it seemed probable that the dilute solution of cupric bromide from which it had separated was perfectly normal, and it became an important problem to settle this point. As the normal salts of copper are wholly without action upon a solution of methyl orange, this indicator formed the most convenient test for the neutrality of the liquid in question. To about 50 cubic centimetres of the clear solution of pure cupric bromide, which had remained standing for three weeks, were added two drops of a dilute solution (1 : 400) of methyl orange, and the greenish liquid was thoroughly shaken. Upon equally dividing the solution between two test-tubes, the most careful observation showed no difference in the colour of the separate portions. To one tube was then added 0·05 c.c. of a twentieth normal solution of hydrobromic acid (= 0·2 m.grm. of bromine) and a change from green to grey was perfectly evident when the portions were again compared. A second equal addition of acid produced a purplish hue. The grey was, of course, due to the simultaneous presence of the red colour of the acidified methyl orange, the yellow of the unchanged compound, and the blue of the copper bromide, and proved that some of the indicator had been acted upon by the acid: hence the solution could not have been basic in the first place. In a few words, the solution, containing about one and a half grms. of cupric bromide, could not possibly have lacked more than 0·0002 grm. of its normal weight of bromine. This being the case, a determination of the relative weights of copper and bromine in such a solution would form a sufficiently accurate basis for the calculation of the atomic weight of copper.

Method of Analysis.

The bromine and copper were determined in separate weighed portions of the solution, according to usual methods. For the estimation of the former, the diluted cupric bromide was slowly added to a slight excess of pure argentic nitrate dissolved in 150 cubic centimetres of hot water. In some of the determinations nitric acid was added to the silver nitrate before the precipitation, and in the other cases the acid was added afterward; but the difference in procedure produced no difference in result. The silver bromide settled readily, and was treated in the manner already described (see *ante*).

The copper was determined in another weighed portion of the solution by electrolysis, after the complete expulsion of the bromine by means of nitric and sulphuric acids. One and a half to three grms. of cupric bromide were used in each determination, and usually one part of nitric acid and two parts of sulphuric acid were taken to decompose one part by weight of the salt; but here again the relative quantities were varied without any perceptible effect upon the result. When the bromine and nitric acid had been expelled over the water bath, the residual copper sulphate and sulphuric acid were dissolved in a small quantity of water, and the whole transferred to the platinum crucible which was to serve as the negative electrode. It was found that within reasonable limits the size of the crucible and the dilution of its contents had no important effect upon the deposition of the copper, provided that the strength of the current was properly regulated. With six gravity cells and eighty ohms external resistance it was possible to deposit perfectly half a grm. of copper in a coherent film from 25 cubic centimetres of solution. The positive electrode consisted in every case of a strong platinum wire fused into the centre of the watch-glass serving as a cover to the crucible. Twice before the completion of each electrolysis the liquid adhering to the lower surface of this lid was washed into the crucible, and the current was always maintained for at least thirty-six hours. Upon breaking the circuit, the sulphuric acid was at once wholly displaced by a stream of distilled water, and after washing by decantation with pure water, alcohol, and ether, the film was finally dried at 95° C. to perfectly constant weight. All the washings were collected in a large porcelain dish, carefully examined in order to be sure that no copper had been carried away, and after evaporation to small bulk tested with uniformly negative result for the presence of traces of metal in solution. It is almost needless to state, that, in every operation involving the quantitative transference of liquid, the original containing vessel was washed out with the most scrupulous care, and finally tested to prove the absence of any trace of its former contents.

Below is the series of four results obtained from the first cupric bromide solution. About two weeks elapsed between the first and last determinations of this series.

PRELIMINARY RESULTS: FIRST SERIES.

Determination of Copper.

No. of experiment.	$CuBr_2$ solution taken. Grms.	Copper found (reduced to vacuum). Grms.	Copper in 25 grms. solution (to vac.). Grms.
1	26·400	0·4397	0·4164
2	26·423	0·4401	0·4164
3	52·824	0·8799	0·4164
4	26·454	0·44075	0·4165
		Average	0·41642

Determination of Bromine.

No. of experiment.	$CuBr_2$ solution taken. Grms.	AgBr found (reduced to vacuum). Grms.	Bromine in 25 grms. solution (to vac.). Grms.
5	26·419	2·5995	1·0468
6	26·436	2·6018	1·0471
7	26·413	2·5996	1·0471
8	26·414	2·5990	1·0468
		Average	1·04695

Atomic Weight of Copper.

From above results, if Ag : Br = 108·00 : 80·007, Cu = 63·644.

From results of previous paper, if Ag : Br = 108·00 : 80·007, Cu = 63·640.

According to Hampe, on same basis, Cu = 63·37±

Since atomic weights are in any case relative, the ratio[*] Ag : Br = 108·00 : 80·007 will be assumed as the present standard of reference, for the sake of convenience and comparison with previous work. Later, all values will be translated into the various generally accepted standards.

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[*] Berthelot, *Ann. de Chim. et de Physique*, 2nd Series, xliv., 386 (1830); Löwig, *Liebig's Handwört. Ch.*, iv., 713; Rammelsberg, *Pogg. Ann.*, lv., 246; and many others.

[*] Although this ratio is not materially different from 108 : 80, we select it as the mean value of all the most accurate determinations.

The second series of analyses was made from the more dilute solution of a new sample of the salt, prepared in the same manner as the first, but perhaps somewhat less pure. The object was to seek further evidence of the constancy of the composition of dissolved cupric bromide, and it will be seen that the result agrees moderately well with the former one.

Preliminary Results: Second Series.

Determination of Copper.

No. of experiment.	$CuBr_2$ solution taken. Grms.	Copper found (reduced to vacuum). Grms.	Copper in 25 grms. solution (to vac.). Grms.
9	77·875	0·8158	0·26190
10	51·891	0·5435	0·26185
Average..			0·26187

Determination of Bromine.

No. of experiment.	$CuBr_2$ solution taken. Grms.	Silver bromide found (reduced to vacuum). Grms.	Bromine in 25 grms. solution (to vac.). Grms.
11	51·871	3·2114	0·65866
12	51·870	3·2113	0·65865
12	40·308	2·4957	0·65871
Average..			0·65867
Atomic weight of copper			63·618

It is certain that the hydrobromic acid used in making this preparation, notwithstanding the care taken in its manufacture, contained a trace of alkali from the glass retort used in distilling; and the presence of this impurity would tend to lower the observed atomic weight of copper. In order to correct this evil, and also in the hope that free hydrobromic acid might prevent the very slight formation of basic salt which invariably took place on the evaporation of water from the neutral salt, the attempt was made to crystallise the cupric bromide from acid solutions. The crystals were still basic, owing to the surface decomposition of exposed scales, but nevertheless two small distinct preparations of such crystals were dissolved, allowed to deposit their basic salt, and each analysed for copper and bromine. Neither of these analyses were wholly satisfactory, but for the sake of completeness their final results are given below.

Preliminary Results: Third Series.

Solution of Crystals.

No. of experiment.	Weight of copper (reduced to vacuum). Grms.	Weight of AgBr (reduced to vacuum). Grms.	Atomic weight copper. AgBr=188·007
14 and 15	0·2500	1·4771	63·64
16 and 17	0·5473	3·2348	63·62

All the results thus far given were regarded merely as preliminary ones; and a complete series in which all possible care should be taken, both in preparation and analysis, remained still to be made. But before proceeding to the final determinations it was thought well to make several experiments with the object of proving the exactness of certain operations of the work. In the first place, two samples of the asbestos used for filtering were tested several times for constancy in weight, after heating to different temperatures; and the greatest loss of any one mat between 130° C. and 700° C. was found to be less than one tenth of a m.grm.

In the next place the copper films of experiments 1 and 2 were heated in their crucibles to 500° C. in a stream of pure hydrogen, which was supplied through a curved tube and a perforated lid after the manner of Rose. The platinum rim left unprotected by the copper film was so small that absorption of hydrogen must have taken place only in unweighable quantities. No change in the weight of the copper was observed.

Finally, 0·3530 grm. of purest electrolytic copper lost 0·00005 grm. on heating to incipient redness in an atmosphere of hydrogen. After dissolving in nitric and sulphuric acids and electrolysing precisely as usual, the recovered copper weighed 0·35305 grm., indicating a gain of only one-tenth of a m.grm. over the lowest weight previously observed. This gain is not greater than a possible error in weighing; hence, as proof of the accuracy of the electrolytic method and the purity of the materials, the experiment leaves little to be desired.

(To be continued).

NOTICES OF BOOKS.

The Patentee's Guide: Information for all Sorts and Conditions of Inventors in all parts of the World. By H. F. Boughton, M.I.Mech.E., Registered Patent Agent. London: Simpkin, Marshall, and Co., Limited.

This work, in addition to the usual information on patent law and patent practice in Britain and in most civilised countries, presents us with the author's views on a variety of subjects not necessarily included in a patentee's guide. Some of these opinions are at least open to criticism. Thus in the initial address the author commits himself to the assertion that the British patent law "is as near perfection as the wit of man can well devise." We must beg to remind him of its two gigantic faults: that it does not, as did the so-called "Old Law," cover all Her Majesty's dominions; and, secondly, that it allows an alien domiciled abroad to obtain and uphold a British patent, refusing all the time to work it upon British soil, though carrying it out at the same time in some foreign country. Thus our patent law is made the means of keeping inventions out of the country and depriving British capital and labour of their legitimate field. An Imperial patent law could be secured, as far as India and the "Crown Colonies" are concerned, by a mere stroke of the pen, giving of course the Calcutta patent office equal scope with that in London. Those Colonies which have obtained *quasi*-independent legislatures would, we think, not hesitate to come on similarly reciprocal conditions. If a Canadian inventor without any additional outlay could obtain at Toronto a patent covering the whole of the British empire he would be immensely the gainer; so would the Australian inventor if he could procure his Imperial patent at Sydney or Melbourne.

In one part of his book the author tells us that "Invention has proved to be the very noblest of sciences or arts, whichever term you wish," and on an earlier page a very similar utterance is ascribed to Mr. Justice Kekewich! We are unable to imagine the process of mental confusion which can lead any man to call invention a "science."

Nor can it be contended that invention has "found work and pleasure for all." It sometimes, as in the case of artificial alizarine, reduces a prosperous district to destitution. If we grant—a very strong concession—that the "high explosives" may discourage war by rendering it too dreadful, they certainly put additional power into the hands of individual criminals and of conspirators. Another unpleasant fact is that the most lucrative inventions are often those of the least benefit to mankind. A new toy, a new piece of folly may bring in to its author hundreds of thousands, whilst a device proved capable of saving the harvest in a wet season is neglected. No law can prescribe to a man what he may invent or try to invent, but invention nevertheless has its ethics, sadly as they are neglected.

The author recommends that all secret nostrums should be compelled to be patented, their composition being of course made known. We can suggest a more excellent way, which would save Britain from being the happy hunting ground of a legion of quacks, both native and alien. We would say let all protection in the form of patents, trade-marks, copyright of labels, and advertisements be refused for all proprietory medicines and foods, or for methods of producing them.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Zeitschrift fur Analytische Chemie.
Vol. xxix., Part 3.

A Contribution to the Valuation of Zinc Powder.—G. Klemp.—(See p. 12).

The Volumetric Determination of Zinc according to E. Donath and G. Hattensaur.—L. Blum.—The above-named chemists have recently published (*Chemiker Zeitung*) a method for the titration of zinc with solution of potassium ferrocyanide in a solution of ammonium tartrate. The present author finds that the results of this method are too high if manganese is present.

The Determination of Iodine in its Compounds.—W. Statenbeker.—This paper requires the accompanying cut.

A New Apparatus for Exsiccating Substances of all Kinds under Reduced Atmospheric Pressure.—D. Sidersky.—This paper also requires the accompanying illustration.

Contributions to the Examination of Spirituous Liquors.—W. Fresenius.—This very extensive memoir does not admit of insertion.

A New Method for Determining the Specific Gravity of Gases.—F. G. C. Müller.—The manometer tube used is 600 m.m. wide, slightly curved below, and fixed horizontally. As a manometric liquid the author employs coloured ether. The atmospheric pressure acts upon one end of the liquid column, and at the other the pressure of the column of gas or steam to be measured, which is placed in a vertical glass tube 2 c.m. in width and 120 c.m. in length, open above and filled from below. If this tube is filled with air the liquid in the manometer stands at zero. For gases which are lighter than air the pressure tube is inverted.—(*Zeit. f. Physik. u. chem. Unternicht*).

The Behaviour of Silicates in a Bead of Phosphatic Salt.—K. Haushofer (*Academie zu München*) and J. Hirschwald (*Journ. f. Prakt. Chemie*).—The former author studies the difference in the effects of "microcosmic salt" upon silicates. Hirschwald gives lists of minerals which, when pulverised, dissolve in the microcosmic salt slowly, easily, or very easily.

Sealing up Very Volatile Liquids in Glass Tubes.—W. H. Greene (Franklin Institute).—The author plunges the tube up a line close below the point to be melted into a mixture of salt and snow. For more volatile liquids he uses liquid carbonic acid, or a mixture of nitrous oxide and ether.

A New Spectrophotometer.—G. Hüfner (*Zeit. Physik. Chemie*).—The arrangement is not described.

A Constant Water-Bath.—B. F. Davenport.—From the *Journal of Anal. Chemistry*.—S. J. Speak (Chemical News) mentions that a water-bath on the same principle was used by G. W. Slatter eight years ago.

A Water-Bath Regulator.—T. H. Easterfield.—From the Chemical News.

A Trough for Hofmann's Apparatus for Determining Vapour Densities.—T. H. Easterfield.—From the Chemical News.

An Electric Blast.—G. Barthel (*Helfenberger Annalen* and *Chemiker Zeitung*).—A current produced by means of four Meidinger batteries is carried round an electromagnet and is continually broken and closed by an arrangement on the principle of Wagner's hammer. The vibrations of the keeper thus produced serve to work small bellows constructed of two plates over which is stretched a membrane of caoutchouc. The current of air thus produced is sufficient for a blast-lamp.

A Sampling-Tool.—Kroupa (*Osterr. Zeit. Berg. und Hutten Wesen*).—The instrument is for obtaining average samples from heaps of finely granular materials. Kroupa inserts a spiral turned by a handle in a cylinder upon which a wider vessel is placed. The spiral is made to revolve whilst the cylinder is forced down into the heap.

On Indicators.—From the *Pharm. Journal and Transactions.*

Vanadium in Caustic Alkali.—Baumgarten, Donath, W. Fresenius, and E. F. Smith (Franklin Institute).—On saturating the lye obtained from common stick-potassa with sulphuretted hydrogen, acidulating with hydrochloric acid, and heating for some hours, there was obtained a chocolate-coloured precipitate. This precipitate was dried, extracted with carbon disulphide, dissolved in yellow ammonium sulphide, re-precipitated with hydrochloric acid, again treated with carbon disulphide, and heated. In this manner was obtained from 1·5 kilo. of ordinary potassium hydrate a crystalline residue of 0·5 grm. in weight, which gave the characteristic reactions of vanadium.

Recovery of Uranium Residues.—Laube (*Zeit. Angewandte Chemie*).—See p. 11.

Production of Pure Hydrochloric Acid for Analytical Purposes.—R. Hamilton.—From the Chemical News.

Preparation of Oxygen from Soda Lye, Bromine, and Copper Sulphate.—G. Denigès.—From the *Journ. de Pharm. et de Chimie.*

Purification of Mercury.—P. Schrödter and A. W. Schrödter.—Instead of bamboo the authors use a piece of Spanish cane 12 c.m. in length, secured to the bottom of the funnel by means of a ring of caoutchouc. Over the upper end of the cane is placed a thin layer of wadding cleansed and freed from grease.

Experiments in Oxidation by Means of the Galvanic Current.—Edgar F. Smith.—From the *Journal of the Franklin Institute.*

Determination of Lithium.—A. Carnot (*Bulletin de la Soc. Chimique de Paris*).

Determination of Chromium by Means of Hydrogen Peroxide.—A. Carnot (*Bulletin de la Soc. Chimique de Paris*).

The Use of Hydrogen Peroxide in the Determination of Chromium, Manganese, and Iron.—A. Carnot.—From the *Bulletin de la Soc. Chimique de Paris.*

Determination of Chrome and Copper in Iron and Steel with the Use of Sodium Hypophosphite as a Reducing Agent.—C. Reinhardt (*Stahl und Eisen*).—This paper will be inserted by opportunity.

Detection of Titanium and Cyanogen.—C. Lüdeking (*St. Louis Acad. of Science*).—The compound—

$$3Ti_3N_2+TiCy_2$$

(which is often found in iron furnaces on smelting titaniferous ores) may be formed in the inner flame of a Bunsen burner, which is made slightly luminous by a proper regulation of the supply of air. On account of the characteristic appearance of this compound very small quantities of titanic acid can be quickly detected. The substance in question is dissolved in a little sodium carbonate in the loop of a thin platinum cone, and all the sodium is volatilised in the inner flame. If titanium is present, the above-named coppery red compound is formed, and may be easily recognised on the platinum wire. Inversely the reaction serves for the detection of cyanogen in flames.

Determination of Zinc in Iron Ores.—Rose Finkener.—Five grms. of the ore are dissolved in strong hydrochloric acid. From 2 to 3 c.c. of strong nitric acid are added to the solution, which is evaporated to dryness and filtered. Into the filtrate, which is heated to 80°—100° and strongly acidified, sulphuretted hydrogen is introduced in order to eliminate any copper, arsenic, or antimony which may be present, to convert ferric into ferrous chloride, and to saturate the solution (200 c.c. at least) with sulphuretted hydrogen. If copper is to be determined, and if a precipitate has appeared, it is filtered off along with the liberated sulphur. In the contrary case the filtration is omitted, acetic acid and ammonium acetate are added, and ammonia is added from a burette the delivery tube of which is immersed in the liquid. It is run in at first in large quantities and then drop by drop, keeping the vessel in motion until the precipitate, consisting of zinc sulphide and a little iron sulphide, has taken a grey colour. If the grey colour no longer disappears after the glass has been briskly shaken dilute hydrochloric acid (1 : 50) is dropped in until it turns white, and dilute ammonia is then again cautiously added until a permanent light grey colour is obtained. On the completion of the precipitation the zinc sulphide coagulates and begins to subside. It is then filtered and washed with water containing acetic acid and sulphuretted hydrogen. The filtrate should be tested as follows:—The filter with its contents is placed in a beaker, a sufficient quantity of dilute hydrochloric acid (1 : 6) is added, the mixture is stirred, filtered, and washed, if copper sulphide is present, with water containing hydrochloric acid and sulphuretted hydrogen. If cobalt or nickel is present the sulphides of these metals remain undissolved. The sulphuretted hydrogen is expelled from the filtrate by heat, the liquid is let cool, mixed with a slight excess of sodium carbonate, heated to a boil, filtered, and the precipitate of basic zinc carbonate so obtained is dried and ignited. If the precipitate of copper sulphide obtained in the acid solution by means of sulphuretted hydrogen is filtered off, and if the zinc sulphide thus obtained is free from cobalt and nickel sulphides (which is generally the case), it is ignited with powdered sulphur in a current of hydrogen and weighed as zinc sulphide.

A Sensitive Reaction for Copper.—M. Denigès.—From the *Comptes Rendus.*

Separation and Determination of Antimony and Tin.—Loriton.—From the *Journal de Pharmacie et de Chimie.*

Separation and Determination of Chlorine, Bromine, Iodine, and Cyanogen.—G. Crieva.—From the *Gazzetta Chimica* and the *Journal of the Chemical Society.*

Determination of Nitric Acid with Ferrous Sulphate.—Pelouze, modified by Bailhache.—From the *Comptes Rendus.*

Reagent for Aldehyd.—L. Crismer (*Chemiker Zeitung*).—The author recommends a solution obtained by mixing a solution of potassium iodide with mercuric chloride and adding potassa or soda-lye or baryta water. Or Nessler's reagent may be used. In this manner aldehyd may be detected in the watery solution of ethers, in chloroform, in ethereal oils, in glycerin, &c.

Fermentability of Galactose.—Em. Bourquelot.—From the *Comptes Rendus.*

MISCELLANEOUS.

Sulphate of Copper.—We have been requested by the Vice-Consul of a foreign government to supply them with statistics relative to the production and consumption of sulphate of copper in the United Kingdom. We shall esteem it a favour if any of our correspondents will indicate how best to procure what is required.

The Douglas Oil Gas Lamp.—We understand that Messrs. J. Griffin and Sons, of Garrick Street, Covent Garden, have now received some of these lamps, which were described in the CHEMICAL NEWS, vol. lxii., p. 84. They have tried them, and find them very satisfactory. They will be glad to show them in operation to any one interested.

Announcement.—Mr. W. H. Stanger and Mr. Bertram Blount, of the Broadway Laboratory and Testing Works, Westminster, desire to correct a rumour which has become prevalent, by stating that the Mr. William Fox who is at present associated with them at the above address is a Member of the Institution of Civil Engineers and not a practising analyst.

Messrs. May and Baker.—We are informed by a circular signed by Messrs. W. G. Baker, R. C. Heath, and W. E. B. Blenkinsop, that the business of this firm will in future be carried on by a limited company at Garden Wharf, Battersea. The conversion of the firm into a company will involve no change in the mode of conducting the business. Mr. Blenkinsop, to whom the manufacturing department has for several years been entrusted, will be the managing director.

Popular Lectures on Chemistry.—In response to a widely expressed demand from the students who attended the former lectures on chemistry, the Battersea Polytechnic Committee have arranged for a course of ten popular lectures (with experiments) by Professor V. B. Lewes, on the Chemistry of Arts and Manufactures, at Crichton Hall, Clapham Junction. The lectures will be delivered on Tuesdays, commencing January 13th, at 8 p.m., and will include the following subjects:—Colour-paint, Iron, Copper, Lead, Zinc, Tin; the Alloys; the Acids; Soap, Soda, and Glass. Tickets for the course of ten lectures (4s.) may be obtained from the Hon. Secs., Messrs. H. Genochio and J. Harwood, on the evenings of the lectures at Crichton Hall.

MEETINGS FOR THE WEEK.

MONDAY, 12th.—Medical, 8.30.
TUESDAY, 13th.—Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Institute of Civil Engineers, 8.
WEDNESDAY, 14th.—Society of Arts, 8. "Steam Lifeboats," by J. F. Green.
THURSDAY, 15th.—Royal, 4.30.
Institute of Electrical Engineers, 8.
FRIDAY, 16th.—Quekett, 8.
Physical, 5. "Photo-electricity," by Prof .G. W. Minchin, M.A. "A Lecture-room Method of Determining "*g*," by Prof. Barrell, B.A. "On the Change in the Absorption Spectrum of Cobalt Glass Produced by Heat," by Sir John Conroy, M.A., Bart.

TO CORRESPONDENTS.

F. J. Chalmers.—We do not know of any book treating on the metallurgy and mining of tin ores. A very complete account is to be found in the first volume of "Kerl's Treatise on Metallurgy," by W. Crookes, published by Longmans and Co.

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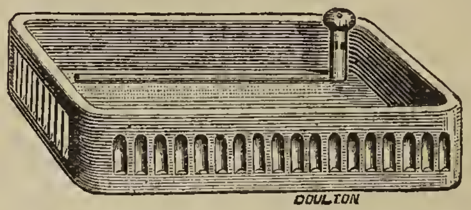

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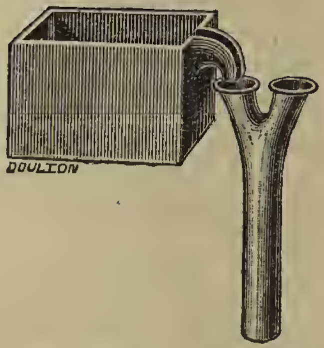

RECEIVER, with Overflow Lip (Fig. D). JUNCTION (Fig. E

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January 9, 1891.

THE CHEMICAL NEWS.

Vol. LXIII. No. 1625.

ON WOLF AND RAYET'S BRIGHT-LINE STARS IN CYGNUS.*

By WILLIAM HUGGINS, D.C.L., LL.D., F.R.S., and Mrs. HUGGINS.

In 1867 MM. Wolf and Rayet discovered at the Paris Observatory three small stars in Cygnus, which in the spectroscope showed several bright lines upon a continuous spectrum.† All three stars have a very bright band in the blue part of the spectrum.

These stars are:—

B.D. + 35°, No. 4001.
B.D. + 35°, No. 4013.
B.D. + 36°, No. 3956.

Their spectra were described in 1873 by Vogel, whose observations agree substantially with the original description given by Wolf and Rayet.‡ A more complete account of their spectra was given by Vogel in 1883, from observations at Vienna with the 27-inch refractor made by Sir Howard Grubb.§

Vogel's measures of the bright blue band place it in the star No. 3956 at from λ 468 to λ 461, with a maximum at λ 464; in the star No. 4013, with a maximum at the same place in the spectrum; while the corresponding blue band in the star No. 4001 has a considerably less refrangible position, commencing at λ 470, reaching a maximum at λ 468, and ending about λ 465.

These latter measures, though they differ from his earlier ones, in so far as they show that the blue band has not an identical position in all three stars, nevertheless support substantially his earlier observations, which Vogel considered to show, contrary to the statements of Secchi, that the bright lines, including the blue band, were not due to carbon.

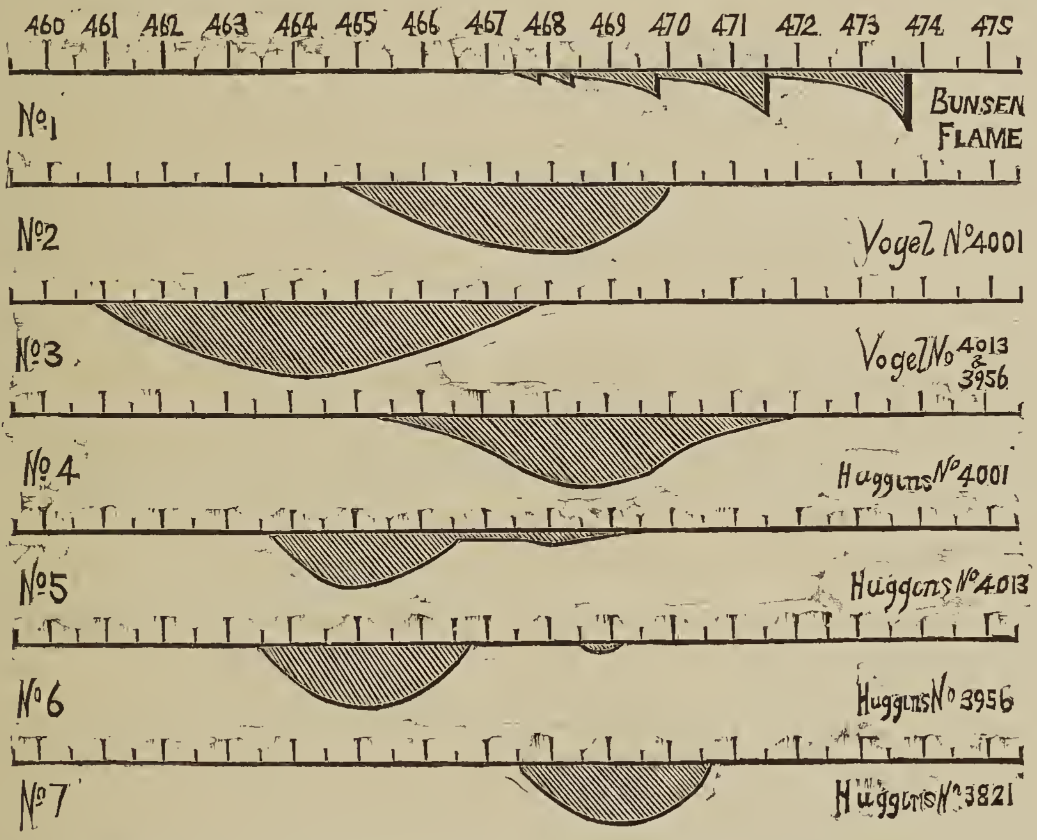
In the diagram, Nos. 1, 2, and 3 show the positions of the bright bands in the three stars, according to Vogel's measures, relatively to the blue band of the hydrocarbon flame.

Vogel's measures are:—

	Beginning of the band.	Brightest part.	End of the band.
Star No. 4001	λ 470	λ 468	λ 465
" 4013	—	λ 464	—
" 3956	λ 468	λ 464	λ 461

His diagram shows the band in No. 4013 to begin and end at about the same positions as in the star 3956.

It has been stated recently that the bright blue band in all three stars is the carbon band in the blue, commencing near λ 474*; and more recently, notwithstanding the difference of position, according to Vogel, of the band in one of the stars from that which it occupies in the other two of as much as λ 0040, that direct comparisons showed an absolute coincidence of the band in all three stars with the blue band of a spirit-lamp flame.†



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* From the Authors. A Paper read before the Royal Society, Dec., 1890.

† *Comptes Rendus*, vol. lxv., 1867, p. 292.

‡ *Berichte K. Sächs. Ges. der Wiss.*, Dec., 1873, p. 556.

§ *Publication Astrophys. Observ. Potsdam*, vol. iv., No. 14, pp. 17 to 21.

* Professor Lockyer, in the Bakerian Lecture for 1888 (*Roy. Soc. Proc.*, vol. xliv., p. 37), says of the star No. 4001:—"The bright band with its maximum at λ 468 is the bright carbon fluting commencing at λ 474 and extending towards the blue, with its maximum at 468, as photographed at Kensington."

Of the star 4013:—"The bright band in the blue at 473 is most probably the carbon band bright upon a faint continuous spectrum, this producing the absorption from 486 to 473" (*loc. cit.*, p. 41).

Of the star No. 3956:—"The bright band at 470 is the carbon band in the blue, commencing at 474, with its maximum at about 468, as observed and photographed at Kensington" (*loc. cit.*, p. 43). See Vogel's measures for the band in this star, which are given in the text.

Diagrams of the spectra of these stars are given at pp. 38, 40, and 41, based on Vogel's observations and his curves, which, on a slightly reduced scale, are placed at the bottom of the diagrams. The maximum of Vogel's curves is placed in all three diagrams at λ 468, and agrees in the diagrams with the carbon band; whereas Vogel's original curves and his measures place the maximum in the case of two of the stars at λ 464, beyond the carbon band.

† Professor Lockyer, in a signed article in *Nature* (August 7, 1890, vol. xlii., p. 344), writes:—

"In the Bakerian Lecture for 1888 I gave a complete discussion of

As the presence or absence of carbon in these stars, as shown by the coincidence or otherwise of the blue band with that of the hydrocarbon flame, was of great importance to us in connection with a wider investigation on which we are at work, we thought it necessary, after these recent statements as to the position of the band, to make direct comparisons of the spectra of these stars with that of the hydrocarbon flame under sufficiently large dispersion to enable us to determine whether Vogel's measures are substantially correct, or whether they are so largely in error as the absolute coincidence of the band with the blue band of a spirit-lamp flame in the case of all three stars would show them to be.

The obvious importance of making the observations with sufficient dispersion is supported by Vogel's own experience. With the small dispersion which he employed in his earlier observations in 1873, he did not detect the large difference of position, about λ 0040, of the band in No. 4001, as compared with its position in the other two stars. On this point Vogel says, in his memoir of 1883:—"Etwas abweichend ist nur died Auffassung der Lage der breiten hellen Bande im Blau, die bei den früheren Messungen bei allen drei Sternen übereinstimmt. . . . Bei den verhältnissmässig geringen optischen Hülfsmitteln, mit denen jene Messungen ausgeführt wurden, ist die Ueberinstimmung aber eine ganz überraschende" (*loc. cit.*, p. 21).

We observed the spectra of the stars successively, first with a direct vision prism of small dispersion, then with a spectroscope (A) containing one prism of 60°, and finally with a spectroscope (B) with two compound prisms, equal to about four prisms of 60°; with the last-named instruthe comparisons with the hydrocarbon flame were made.

A rapid preliminary comparison in the spectroscope (B) of the spectra of the three stars with the blue base of a Bunsen flame showed at once the substantial accuracy of Vogel's measures, and the striking difference of position of the band in the star No. 4001 from that which it holds in the other two stars.

The obvious want of agreement of the star bands with the blue band of the Bunsen flame was seen at once. Their relative positions appeared to agree substantially with the positions represented in No. 2 and No. 3 of the diagram, which are based on Vogel's measures. More careful and repeated observations brought out clearly, as is indeed shown by Vogel's curve, that the star bands differ in character as well as in position from the blue band of the hydrocarbon flame, and also in some respects from each other.

Before giving in more detail the results of our observation on each of the three stars, it should be stated that in all the stars the continuous spectrum is not in our instruments a short one, ending before the position of the bright blue band is reached. On the contrary, an examination with all three spectroscopes showed that the continuous spectrum, though enfeebled by absorption a little before reaching the blue band, can be traced, as is shown in Vogel's curves, quite up to the band, and, indeed, extends for a long distance into the violet beyond the blue band. The blue band does not in our instruments stand out bright beyond the end of a short continuous spectrum, but falls upon a fairly luminous continuous spectrum, which can be traced past the blue band into the violet, apparently as far as the eye could be expected to follow it.

We suspected bright lines or bands in the region more refrangible than the blue band, but in such faint objects this is a point which should be determined by photography.

Professor E. C. Pickering has since kindly informed us that his photographs of the star No. 4001, which extend into the ultra-violet region, show beyond the blue band the bright hydrogen lines at 434, 410, 397, and 389; and also other bright lines at 462, 455, 420, 406, 402, 395, and 388.

In his photographs of the stars 4013 and 3956, however, the only well-marked line is in the blue at 470.

Star 4001.—In this star, as is shown by Vogel's measures and curve, the bright blue band is less refrangible than in the other two stars, and approaches therefore nearer to the position of the blue band of the hydrocarbon flame. The appearance and position of the band in the star as contrasted with that of carbon, when observed in spectroscope B, are represented in spectrum No. 4 of the diagram.

The brightest part of the band, from about λ 468 to λ 469, falls off rather suddenly in brightness at about these wave-lengths, but can be traced towards the red as far as about λ 471·5, and as far in the blue as about λ 465·5.

In our observations of this and the other stars we did not attempt micrometric measures of the blue band, but we estimated their positions by means of the intervals between the five flutings of the band of the Bunsen flame. In the case of objects so faint in our instrument when viewed under the dispersion of spectroscope B, we did not consider there would be any real gain of accuracy by attempting to take measures.

Though the wave lengths assigned to our positions must therefore be regarded as not more than approximately correct, we have no hesitation in considering them fully accurate enough for the purpose of our investigation.

The star band is not split up into well-separated maxima, as is the Bunsen flame band, but we have little doubt that the brightest part of the band, from λ 468 to λ 469, which is much, and rather suddenly, brighter than its beginning and termination, consists of bright lines. Lines appear to flash out at moments, but in our instruments they cannot be seen with sufficient steadiness for us to be sure of their number and position.

Under certain conditions of the electric discharge, the normal relative brightness of the component flutings of the blue hydrocarbon band has been observed to be so far changed that the position of maximum intensity is moved from the less refrangible end of the band towards the blue end; but the five flutings remain without any change of their position in the spectrum.*

Dr. Hasselberg, by means of feeble disruptive discharges from tin-foil terminals placed outside an exhausted tube containing vapour of benzole, obtained a nearly pure spectrum of the order of that in a hydrocarbon flame mixed only with faint lines of hydrogen, He says:—"Es war aber hier die violette Gruppe sehr schwach. Dagegen schien mir die blaue Gruppe relativ heller als im Flammenspectrum, und sie hatte ausserdem entschieden ihre grösste Intensität nicht an der weniger brechbaren Kante, sondern mehr nach dem Violetten hin. Dasselbe schien mir auch mit der gelben Gruppe der Fall zu sein. In Bezug auf die grüne Gruppe konnte ich aber keine Verschiebung des Intensitätsmaximums bemerken."

Dr. Hasselberg gives curves to show the amount of

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the spectra of bright-lined stars, as far as the observations went, and the conclusion arrived at was that they were nothing more than swarms of meteorites a little more condensed than those which we know as nebulæ. The main argument in favour of this conclusion was the presence of the bright fluting of carbon which extends from 468 to 474. This standing out bright beyond their short continuous spectrum gives rise to an apparent absorption band in the blue. . . . Direct comparisons of the spectrum of all the three stars in Cygnus with the flame of a spirit-lamp have been made by Mr. Fowler, and these showed an absolute coincidence of the bright band in the stars with the blue band of carbon seen in the flame. It was found quite easy to get the narrow spectrum of the star superposed upon the broader spectrum of the flame so that both could be observed simultaneously.'

* It is necessary to state that the maximum luminosity of the blue band, under some conditions, is about 468. . . . The conditions under which this band has its maximum luminosity at 468 in Geissler tubes seem to be those of maximum conductivity, If the pressure be high, all the members of the group are sharp, and the luminosity of the band is almost uniform throughout. This always occurs when the pressure is very low. At intermediate stages of pressure, however, the luminosity has a very decided maximum at about 468. (Appendix to the Bakerian Lecture for 1888, *Proc. Roy. Soc.*, vol. xlv. pp. 167, 168).

this change of intensity in the blue group and in the orange group. In the blue group the maximum is moved from the first to the third line, that is, to about λ 4698. His curve gives the brightness of the maximum over that of the first line as about 7 to 6, whereas the normal relative intensity of these two lines is in the inverse direction and as about 2 to 4 (Watts' "Index of Spectra," p. 30).[*]

A similar change from the normal relation of brightness of the flutings within the band, even if removed to λ 468, does not seen to us to bring the star band sufficiently into accordance in character and position with those of the band of the hydrocarbon flame to justify us in attributing the blue band in the star to carbon. Though we traced the band a little further towards the red, than the position of the beginning of the band given by Vogel's measures, yet it is very faint, and without any increase in brightness at the place of the second fluting of the carbon band, beyond which we were unable to see it.

According to Hasselberg's curve, the second bright fluting, where in our instruments the star band ends, still retains a brightness of about 11/12 of that of the maximum, and the first line, at the position of which no brightening of the feeble continuous spectrum of the star could be detected, a brightness of about 6/7 of that of the maximum. That the flutings of the band were not obscured by the absorption band at this part of the spectrum appears clear from the circumstance that we could trace the faint continuous spectrum up to the bright band.

Vogel's and our observations agree in making the band run on some distance beyond the visible termination of the blue band of the Bunsen flame. Piazzi Smyth, under some conditions, observed a large number of faint "linelets" beyond the "5th leader" of the band, where its visibility usually ends; and in the brilliant light of the arc the band can be traced further in the blue. The extension of the band under such circumstances does not seem to us to affect our present argument; for in the very feeble light of the star we may surely take it that the carbon band, if present, could not be seen to extend further than its usual visible limit in a Bunsen flame, namely, about λ 468.

Perhaps it should be stated in connection with the circumstance that we saw the band extend a little further towards the red than Vogel did, that at the time of our observations the hydrogen line at F was not visible in our instruments, whereas it was bright at the time when Vogel observed the star. In the spectrum of a similar star, D.M.+37° 3821, in which the hydrogen line at F at the time was bright, the blue band was seen by us to stop near the place given by Vogel in his measures of the star No. 4001.

Not only is there no coincidence, so far as Vogel and we have observed, of the position of the band in the star with that of the blue band of the Bunsen flame; but, further, the want of accordance of its general characters is so great as to make the view that its origin is carbon very improbable. This improbability is very greatly increased when we find, as will be shown presently, that no traces whatever of the very bright beginnings of the more brilliant green and orange bands could be detected by us in any of the stars. Further, Professor E. C. Pickering has kindly sent to us an account of his photographs of this star, which, though they show the hydrogen line at λ 434, do not exhibit any brightness at the positions of the indigo hydrocarbon bands, beginning near 4312, and λ 4382.

This star, however, can scarcely be taken by itself; in the case of the other two stars, in the spectra of which, according to Vogel's, Copeland's, and our own observations, the brightest part of the blue band is from λ 464 to λ 465, but nearer λ 465, quite outside the ordinary visible limit of the carbon band, the evidence seems very strong indeed that the band does not owe its origin to carbon.

We satisfied ourselves that when the spectrum of the star is examined under the dispersion of spectroscope B, none of the brighter parts of its spectrum fell at, or very near, the green, orange, and indigo flutings of the hydrocarbon flame spectrum; at these positions we were unable to detect any sensible brightening of the star's spectrum. Professor Copeland's measure of the blue band in 1884 was λ 469·5.

No. 4013.—Vogel does not give measures of the beginning and the ending of the band in this star, but only of the brightest part:—"Hellste Stelle, nahezu Mitte, einer breiten verwaschenen Bande, λ 464." He gives, however, a diagram of the spectrum in which the bright blue band is represented as substantially coincident in position and in general character with that in the spectrum of No. 3956.

Our observations agree substantially with those of Vogel, but they make the band to consist of two parts, a very bright part, from about λ 466 to λ 464, but brightest near λ 465; and a very faint band, apparently detached from the bright one from about λ 4685 to about λ 4705. This faint band is brightest near where it ends rather abruptly at the more refrangible end. The very bright band has not the character of a fluting, nor is it broken up into maxima widely separated like those of the Bunsen flame band, but appears to be a group of bright lines. The lines were only glimpsed at moments; it is therefore difficult to make a drawing which truly represents the character of the band as seen in our instruments. The band which is shown at No. 5 of the diagram is left unfinished at the more refrangible end, as we were not certain how far we ought to consider it to extend.

In this star (as we shall show to be the case in No. 3956 also) the great body of bright radiation lies far beyond the ordinary visible limit of the blue carbon band, and no connection whatever with carbon is even suggested to us by the star's spectrum. Dr. Copeland's measure of the band in 1884 was λ 465·4.

The continuous spectrum of the star is unequally bright from the presence of bright groups and also apparently of absorption bands or lines, and therefore with small dispersion it might be easily supposed that the spectrum is brighter at the position of the green carbon band. We examined the continuous spectrum repeatedly with great care, and we were able to satisfy ourselves that, under the considerable dispersion of our instruments, there was no sensible brightening of the spectrum at the positions of the green and of the orange bands of the Bunsen flame.

No. 3956.—Vogel places the brightest part of the band in this star at the same position in the spectrum as in the star last considered, No. 4013, namely, at λ 464, a position beyond the carbon band. The position of the band as it appeared in spectroscope B with the third eye-piece is represented at No. 6 in the diagram. The position of the band relatively to that of the Bunsen flame was determined by estimations made by means of the intervals between the bright flutings of the Bunsen band. The position agrees substantially with that given by Vogel, but places the maximum brightness nearer to 465. This bright part probably consists of a group of bright lines, and falls off rather suddenly at both ends. We were not certain if the light beyond this bright part was due to a continuation of the band or to the continuous spectrum, more or less dimmed by absorption; we have, therefore left the ends of the band incompleted in the diagram Copeland's measure of this band in 1884 was λ 464·9.

The sub-band seen in the star No. 4013 is very much fainter in this star, but we have little doubt that there is a very faint band present at about the same place in the spectrum.

Professor E. C. Pickering has found in the near neigbourhood of these three stars other stars possessing bright lines in their spectra.[*] The brightest of these, indepen-

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[*] *Mém. de l'Acad. Imp. des Sciences de St. Pétersbourg*, vol. xxii., No. 2, 1880, p. 82.

[*] "The following list contains the designations of all eight stars (with bright lines), the first four being those previously known:—

dently discovered by Dr. Copeland in 1884,* namely, D.M. + 37° 3821, in which the spectrum is similar to that of the Wolf-Rayet stars, was examined. Dr. Copeland says of this star:—"It has a spectrum of several bright lines near D, and a very bright band in wave-length 464" (*loc. cit.*). We were therefore surprised to find the blue band, which is very brilliant, not in the position of the band in the stars No. 4013 and No. 3956, but less refrangible, corresponding to the position of the band in the star No. 4001.

The bright line begins about λ 467 and runs on to nearly λ 470·5. It is clearly not made up of flutings similar to those of the Bunsen flame, but is a group of lines nearly uniformly bright throughout the length of the band. The band did not appear to extend in our instruments towards the red quite so far as the band of No. 4001; it stops near the place assigned by Vogel to the beginning of the band of No. 4001.

The band is represented in spectrum No. 7 in the diagram. Direct comparison with hydrogen showed that the line at F is brilliant in this star.

After some scrutiny of this part of the star's spectrum, we became conscious of a very feeble brightening of the spectrum beyond the bright band towards the violet, and as far as we could estimate its position, at about from λ 464 to λ 467, that is to say, about the position assigned to the band by Dr. Copeland in 1884.

We then re-examined the spectrum of No. 4001, and were able to feel pretty sure that a similar faint brightening of the spectrum occurs in this star also at the same place, namely, about the more refrangible position of the blue band in the stars No. 4013 and No. 3956.

(To be continued).

FURTHER CONTRIBUTIONS TO THE METALLURGY OF BISMUTH.†

By EDWARD MATTHEY, F.S.A., F.C.S., A.R.S.M.

In October, 1887, I read a paper before the Royal Society‡ upon a new method which I incidentally discovered while working with a view to separate copper from bismuth, by fusion with bismuth sulphide.

I stated in this paper that bismuth "frequently contains a small proportion of copper, an element most detrimental even in small traces, and hitherto only eliminated by a wet process, costly in practice and tedious in operation. It is necessary by such method to dissolve up the whole of the alloy and precipitate the bismuth in the usual manner—a bulky operation, and one requiring a considerable amount of time. It became therefore advisable, in order to treat cupriferous bismuth rapidly and upon a commercial scale, to effect this separation, if possible, by means of a dry process."

In further researches in the metallurgy of this interesting metal, a case was found in which bismuth contained a very small proportion of copper, under 0·5 per cent, but sufficient to render the metal useless, and, in fact, to destroy those characteristic properties upon which its industrial applications depend.

Instead of treating this cupriferous bismuth by fusion with bismuth sulphide, which necessitates a temperature sufficiently elevated to bring about a complete fusion of the bismuth sulphide, and consequently, unless very great care be taken, great loss by volatilisation of bismuth, it occurred to me to fuse the alloy, and at a temperature a little above its melting-point to add a small proportion of sodium monosulphide. The mass was then stirred well so as to bring every portion of the fused alloy into contact with the fused sulphide.

After about one hour's stirring, a test was made of the molten metal, and it was found that the amount of copper in it was very considerably decreased.

By skimming off the film of scoria which had risen to the surface, adding a further small proportion of the sodium monosulphide, and continuing the operation of stirring, every trace of copper was eliminated and the bismuth so freed from copper rendered in every way suitable for industrial use.

The first experiment was made upon a quantity of 105 kilogrms., which yielded 94 kilogrms. of bismuth free from copper, and about 11 kilogrms. of skimmings containing the whole of the copper, their bismuth contents of course being available for reduction with further and larger quantities of skimmings as they accumulated.

This process has been repeated upon very considerable quantities of cupriferous bismuth, and has proved to be successful.

This question of keeping the temperature low is of much importance, for the lower the temperature the less tendency there is for the bismuth to volatilise, and as it is necessary to obtain the bismuth free from traces of impurity, which entirely change its nature, it will be seen that any improvement in manipulation, or in the process itself, which enables pure metal to be obtained possesses much interest.

ON THE POTASSIUM CYANIDE ASSAY OF LEAD ORES.

By ARTHUR W. WARWICK,
Assayer at the Phœnix Test Works, Battersea.

There being considerable doubt as to the exact value of the cyanide assay of lead ores, some writers on assaying speaking favourably and others disparagingly of it, I thought a few comparative experiments might be of interest to assayers. Mitchell, writing on the potassium carbonate assay, rather unfavourably dismisses the cyanide assay with a couple of lines. Ricketts* states that the cyanide assay gives lower results than the black flux assay, but that it gives cleaner buttons. The ores experimented on were (1) a galena with a siliceous gangue, the lead, however, containing but a small amount of other base metals, (2) a rather poorer galena containing a considerable quantity of copper pyrites, (3) a pure specimen of galena. A few experiments were likewise made with a pure sample of cerussite.

Sampling.

A quantity of the ore experimented upon was crushed and passed through a 60 sieve. When a quantity of the sample was required for an assay, the whole was spread out evenly over a space of about six inches square, and lines ruled down and across, making squares of about one inch; from the centre of each square a small quantity was taken on the end of a spatula, and the required quantity weighed from this smaller quantity. By this means perfectly uniform samples were taken.

The galena (1) first experimented on contained 64·8 per cent of lead. The gangue was quartz. 150 grains of this galena were mixed with 450 grains of potassium cyanide ("gold"). A Battersea crucible, size D, was taken, and a quantity of cyanide well rammed into it. The ore and cyanide was placed above this ramming, and covered with a layer of half an inch of cyanide; the whole was then covered with salt. The amount of cyanide used as ramming came to about 150 grains. The charge was heated at a low red for 15 minutes, and slightly raised for a further period of 5 minutes, when it was withdrawn from

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35° 4001, 35° 4013, 36° 3956, 36° 3987, 37° 3821, 38° 4010, 37° 3871, 35° 3952 or 3953. Of these 37° 3871 is P Cygni, and 37° 3821 is the star in the spectrum of which the bright lines are most distinct" (letter in *Nature*, vol. xxxiv, p. 440.)

[*] *Monthly Notices, R.A.S.*, vol. xlv., p, 91, 1884.

[†] Read before the Royal Society, January 6, 1891.

[‡] *Proc. Roy. Soc.*, vol. xliii., page 172.

[*] "Notes on Assaying," New York.

the furnace, allowed to cool, and the button of lead obtained by breaking the crucible.

Experimt.	Grains of ore.		Grains.	Per cent.
1.	150	gave a button of	87	58
2.	150	,,	86·6	57·73

The buttons were very clean and so soft that they could be scratched with the finger nail. The slag was of a pinkish white colour, but there was a brownish white core just above the button. No traces of undecomposed galena could be seen.

Pure potassium cyanide being expensive, experiments were made using in its stead the commercial cyanide. The "stick" cyanide supplied by Messrs. Becker's, Hatton Wall, was the cyanide employed. In order to allow for the decreased purity of the flux, the amount used was raised to 600 grains, the amount of the covering, &c., however, remaining the same.

The amount of ore used, the temperature, and the time were the same as in experiments 1 and 2.

Experimt.				Per cent.
3.	150 grs. galena gave	86·3 grs. lead	=	57·53
4.	150 ,,	86·4 ,,	=	57·6

The difference between the experiments being so small there can be no objection to using the commercial cyanide. The following experiments, however, show the necessity of using an increased amount of cyanide. 150 grains of galena were mixed with 450 grains of "stick" cyanide, using 50 grains for the ramming, and 100 grains for the covering, salt to cover as usual; this charge was treated as in experiments 1 and 2.

Experimt.				Per cent.
5.	150 grs. galena gave	76 grs. lead	=	50·6
6.	150 ,,	74·5 ,,	=	49·6

The slags yielded by these six assays were very similar, differing only in the degree of pinkishness. This sample became too small to be able to make any comparable assays, so that the pure sample was worked upon next, "stick" cyanide being used instead of the "gold" quality. The quantity of cyanide used was that recommended by Ricketts, viz., three times that of the ore, making allowance, however, for the difference in quality of the cyanides used. 100 grains of pure galena was mixed with 500 grains of "stick" cyanide, using in addition 50 grains for the ramming, the whole covered with salt. This charge was heated for 15 minutes at a low red heat, and the temperature raised to a fair red heat for 5 minutes.

Experimt.	Grains galena.		Grains.	Per cent.
7.	100	gave a button of	76·0	76
8.	100	,,	76·2	76·2

The slag was black and slightly spongy. A quantity of undecomposed galena could be seen floating on the surface of the salt covering on withdrawing the crucible from the furnace, and in order to overcome this the amount of cyanide used to mix with the ore was increased to 600 grains, and a covering of about 80 grains of cyanide used, the whole being covered with salt. The crucible was heated at a low red temperature to commence with, raising the temperature slowly till it was a bright red. The time given was 20 minutes, counting from the time the crucible was red.

Experimt.				Per cent.
9.	100 grs. galena gave	79·1 grs. lead	=	79·1
10.	100 ,,	79·3 ,,	=	79·3

The slag was black and rather earthy in texture.

The above experiments show the reason why Ricketts says that the cyanide assay gives low results, the reason being, no doubt, that the amount of cyanide used was too small.

In order to thoroughly test the method, a few other assays were made upon the pure galena. The black flux substitute assay was first made. 100 grains of galena were mixed with 375 grs. of black flux substitute, made by mixing two parts of carbonate of soda with one each of flour and borax glass. Three nails, heads downward, were placed in a crucible, and the above mixture charged into the crucible. The mixture was covered with borax, and fused at a red heat until the charge was well fused and free from bubbling, kept at this temperature for five minutes, when the nails were withdrawn and the charge poured into a hemispherical mould; the button freed from adhering slag in the usual way and weighed give a mean result of 0·8 per cent *below* the mean cyanide assay.

Experimt.				Per cent.
11.	100 grs. galena gave	78·3 grs. lead	=	78·3
12.	100 ,,	78·5 ,,	=	78·5

Ricketts gives 78·5 as the usual result of this assay. Phillips ("Elements of Metallurgy"), gives 75—78 per cent. Another method was tried. Ore, 200 grains, was mixed with sodium carbonate 300, argol 30 grains, and three nails, salt to cover. This charge was placed in a clay crucible, and heated at a red heat until fusion ensued and all bubbling finished; the charge was kept in the furnace five minutes longer, when the nails were withdrawn and the charge poured, giving results about 6·5 per cent lower than the cyanide assay. Phillips remarks that the alkaline flux assay yields about 70 per cent of lead from pure galena. Ricketts finds that by using the bicarbonate of soda that from 73·0—73·4 per cent of lead can be obtained.

Experimt.				Per cent.
13.	200 grains gave	145·3 grains lead	=	72·65
14.	200 ,,	145·6 ,,	=	72·80

The foregoing experiments are quite sufficient to show that with pure galena the cyanide assay is as perfectly reliable as most dry assays. The galena containing the pyrites had a few comparative assays made upon it. The cyanide assay was performed exactly as in experiments 9 and 10, and the black flux assay as in experiments 11 and 12.

Experiment.		Per cent lead.	
15.	Cyanide assay gave	56	Mean 55·85.
16.	,, ,, ,,	55·7	

Exp.		Per cent lead.	
17.	Black flux substitute assay gave	54·0	Mean 54·3.
18.	,, ,, ,,	54·6	

These experiments show that with poor and impure lead ores the potassium cyanide assay has an advantage of 1·5 per cent over the black flux substitute assay.

Cerussite was the next sample experimented upon. The sampling was performed as before. The cerussite used was a very pure specimen from the Broken Hill district, but was not very argentiferous. 100 grains of the cerussite were mixed with 600 grains of cyanide and placed in a crucible prepared as in experiments 9 and 10, and fused at a low temperature for 15 minutes, during which time a rather violent bubbling took place, but was fairly tranquil at the end of that time. The temperature was slightly raised for five minutes, the charge withdrawn, and the crucible allowed to cool and broken.

Experimt.				Per cent.
19.	100 grs. cerussite gave	74·6 grs. lead	=	74·6

The slag was pinkish white on the top and next to the crucible, but contained a white crystalline core. The button, however, had a rather vesicular appearance, as if all the CO_2 had not been expelled. In the next experiment the temperature was rather higher, and the time (20 minutes) counted from the time the fusion of the charge commenced.

Experimt.		Per cent.
20.	100 grs. cerussite gave 75 grs. lead =	75·0

The foregoing experiments show that the potassium cyanide assay when carefully performed is capable of giving with rich ores results as trustworthy as the best of the other methods, and is to be preferred when the ore is poor. The precautions to be observed are that the temperature be not allowed to rise too high, the time not to exceed 20 minutes, and that the amount of cyanide used be not too small. When these precautions are observed the method gives perfectly trustworthy results. The furnace in which the fusions were performed was Fletcher's gas furnace. For convenience in working and control of the temperature it is to be preferred, when moderate temperatures are required, to the coke furnace.

The proprieters of the works, Messrs. Bowes, Scott, and Western, allowing me to continue the experiments to other ores of lead, I hope to be able to publish further results shortly.

ON GASEOUS ILLUMINANTS.*

By Professor VIVIAN B. LEWES.

III.

Ordinary coal gas of an illuminating power of 14 to 16 candles can be produced at a fairly low rate, but if a higher quality is required considerable additional expense has to be incurred in order to enrich it. Up to now, the material almost universally employed for this purpose had been cannel; but as this article is rapidly rising in price, and the best qualities are not easily obtainable, attention is being seriously directed to other means of bringing up the illuminating power of gas. This question of enrichment has been the study of inventors from the earliest days of the gas industry; and the methods employed for this purpose may be classified as:—(1) The carburetting of low-power gas by impregnating it with the vapour of volatile hydrocarbons. (2) Enriching the gas by vapours and permanent gases obtained by the decomposition of the tar formed at the same time as the gas. (3) Mixing with the coal gas, oil gas obtained by decomposing crude oils by heat. (4) Mixing with the coal gas, water gas which has been highly carburetted by passing it, with the vapours of various hydrocarbons, through superheaters, in order to give permanency to the hydrocarbon gases.

In the first method, many points have to be taken into consideration, as the hydrocarbons which have from time to time been used for this purpose vary so greatly in composition. A very volatile naphtha, although it evaporates quickly and larger quantities of its vapour are taken up by the gas, often giving a less increase of luminosity than a heavier hydrocarbon, of which but little is vapourised.

The great trouble which presented itself in the older carburetting systems was that all the commercial samples of naphtha are mixtures of various hydrocarbons, each having its own boiling-point, and that, therefore, when used in any of the old forms of carburetters, they gave up their more volatile constituents very freely at the beginning of the experiment, while the amount rapidly diminished as the boiling-point of the residue became higher; so that when 2113 cubic feet of poor coal gas were passed through a naphtha having a specific gravity of 0·869 and a boiling-point of 103° C., the temperature during the experiment being 22° C., the first 80 cubic feet of gas took up 23·2 grains of the naphtha, whilst the last 450 cubic feet only took up 7·3 grains. Another difficulty found was the increase of evaporation with the rise in the temperature of the gas, as with an ordinary form of carburetter exposed to atmospheric changes, the enrichment of the gas, which reached 54·4 per cent in summer with an average temperature of 22° C., fell in winter to only 22 per cent with an average temperature of 3° C. Of course, in these carburetters a good deal depended upon the form of apparatus; and it was found, on trying different shapes with the same naphtha, that when the gas merely flowed through a box containing a layer of it, only about 3·2 grains were taken up; while with a carburetter in which the naphtha was sucked up by cotton fibre, so as to expose a large surface to the gas, as much as 22 to 23 grains were absorbed. One of the most important points noticed during these experiments was, that it was only a poor gas which could be enriched in this manner, and that if a rich cannel gas was passed through the naphtha, it became robbed of some of its illuminating power.

It must be clearly borne in mind, in approaching this subject, that the evaporation of a hydrocarbon into a permanent gas—*i.e.*, a gas which does not liquefy within the ordinary range of temperature—is a question neither of specific gravity nor of boiling point, although the latter has more to do with it than the former. It is purely a question of vapour tension. Most liquids, when left to themselves in contact with the atmosphere of other gases, gradually pass into the state of vapour, and disappear; and those which evaporate the quickest are said to be most volatile. If ether, for example, is dropped upon an exposed surface, it at once disappears, and causes, by its evaporation, considerable cold; and the lightest forms of naphtha do the very same thing. But although this evaporation takes place with rapidity with liquids of low boiling-point, it must not be forgotten that even many solids have the same property—naphthalene, camphor, and iodine being cases in point. It must also be remembered that evaporation occurs over a very wide range of temperature; but that for each substance there is a limit below which evaporation does not seem to take place. So that, when considering the suitability of a liquid for carburetting in this way, it is far more important to determine its vapour tension than its specific gravity or its boiling-point.

So far, all systems for carburetting gas with liquid hydrocarbons at the burner have proved failures, but in the Albo-Carbon light the vapour of naphthalene is caused to mingle with the gas just before combustion, the volatilisation being effected by a spur of metal heated by the flame itself, which conducts the heat back into a chamber containing solid naphthalene, through which the gas passes, and this process has proved very successful.

Any system to be generally adopted must be applied to the gas in bulk before distribution. In doing this there are two factors to be considered—the vapour added must be in such proportion to the gases which have to carry them that no fear need exist of their being deposited by any sudden cooling of the gas; and care must be taken that the vapour added is not in sufficient quantity to throw out of suspension the volatile hydrocarbons in the gas. The carrying power of a gas depends upon its constituents; for in the same way that liquids vary in their power of dissolving and carrying—*i.e.*, keeping in solution—solids, so do gases vary in their power of bearing away the more volatile hydrocarbons. If the carrying power of air is taken as unity, then the power of ordinary coal gas is about 1·5, while hydrogen would be nearly 3·5; and it is manifest that attention must be paid to the ratio of the constituents present, if gases of varying composition are to be carburetted to the same degree.

During the past few months the idea of the possibility of carburetting coal gas in bulk has again been revived by the construction of an extremely ingenious apparatus, the outcome of the combined engineering skill and practical experience of Messrs. Maxim and Clark, which obviates, to a very great extent, the difficulties which arose with the older forms of carburetter. It has been shown that, when carburetting a gas with a gasolene or light naphtha spirit, the more volatile portions enrich the gas to an

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* Abstract of the Cantor Lectures delivered at the Society of Arts. Communicated by the Author.

undue extent at first, and that as the process continues, the amount taken up becomes gradually less. This would not so much matter in carburetting the gas in bulk before it went into the holder, as it would become to a great extent mixed by diffusion, and a gas of fairly even illuminating power would result; but the Maxim-Clark apparatus is intended not only to do this, but also to carburet the gas used in large establishments and works.

This apparatus is of such a form that in small installations the whole of the gas to be used can be passed through and each portion supplied with its own share of hydrocarbon; whilst, when carburetting gas in bulk, a certain portion can be withdrawn from the main, carburetted, and again returned to the main, where mingling with the steady flow of gas, the whole becomes of uniform composition.

In the earlier days of the gas industry, attempts were made to utilise tar for the production and enrichment of gas; and the patent literature of the century contains many hundred such schemes, most of them being stillborn, while a few spent a short and sickly existence, but none achieved success. The reason of this is not difficult to understand. In order to make gas from tar, two methods may be adopted—either to condense the tar in the ordinary way, and afterwards use the whole or portions of it for cracking into a permanent gas; or to crack the tar vapours before condensation by passing the gas and vapours through superheaters. If the first method is adopted, the trouble which at once presents itself, and in a few hours brings the apparatus to grief, is that tar contains 60 per cent of pitch, which rapidly chokes and clogs up all the pipes; while if an attempt is made to use a temperature at which the pitch itself is decomposed, it is found that a non-luminous or very poorly luminous gas is the result, and that a heavy deposit of carbon remains in the superheater and retort, and even at high temperatures easily condensable vapours escape, to afterwards create trouble in the pipes.

The most successful attempt to utilise certain portions of the liquid products of the distillation of coal is undoubtedly the Dinsmore process, in which the coal gas and the vapours which, if allowed to cool, would form tar are made to pass through a heated chamber, and a certain proportion of otherwise condensable hydrocarbons are thus converted into permanent gases. Using a poor class of coal, it is claimed that 9800 cubic feet of 20 to 21 candle gas can be made by this process; while by the ordinary system, 9000 cubic feet of 15-candle gas would have been produced.

In distilling the coal in the ordinary way, the yield of tar is 11 gallons per ton; but by the Dinsmore process, only seven gallons. On examining the analysis of the ordinary and Dinsmore tar, it is at once evident that the 4 gallons which have disappeared are the chief portions of the light oils and creosote oil; and these are the factors which have given the increase of illuminating power to the gas.

In enriching a poor coal gas by injecting paraffin oil into the retort during distillation, it must be borne in mind that, as the coal is undergoing distillation, in the earlier stages a rich gas is given off, while towards the end of the operation the gas is very poor in illuminants and rich in hydrogen; the methane disappearing with the other hydrocarbons, and the increase in hydrogen being very marked. Mr. Lewis T. Wright employed a coal requiring six hours for its distillation, and took samples of the gas at different periods of the time. On analysis, these yielded the results given in Table.

This may be regarded as a fair example of the changes which take place in the quality of the gas during the distillation of the coal. In carburetting such a gas by injecting paraffin into the retort, it would be great waste to do so for the first two hours, as a rich gas is being given off which has not the power of carrying a very much larger quantity of hydrocarbons—being practically saturated with them. Consequently, to make it take along with it, in a condition not easily deposited, any further quantity, the paraffin would have to be broken down to a great extent; and the temperature necessary to do this would seriously affect the quality of the gas being given off by the coal. When, however, the distillation had gone on for three hours, the rich portions of the coal gas would all have distilled off, and the temperature of the retort would have reached its highest point; and this would be the time to feed in the oil, as its cracking being an exothermic action, the temperature in the retort would be increased, and the gas rich in hydrogen which was being evolved would carry with it the oil gas, and prevent any re-deposition.

	Time after commencement of distillation.			
	10 m.	1 h. 30 m.	3 h. 25 m.	5 h. 35 m.
Sulphuretted hydrogen	1·30	1·42	0·49	0·11
Carbon dioxide	2·21	2·09	1·49	1·50
Hydrogen	20·10	38·33	52·68	67·12
Carbon monoxide ..	6·19	5·68	6·21	6·12
Marsh gas	57·38	44·03	33·54	22·58
Illuminants..	10·62	5·98	3·04	1·79
Nitrogen	2·20	2·47	2·55	0·78

ON DETERMINING THE SENSITIVENESS OF PHOTOGRAPHIC PLATES BY MEANS OF THE SPECTROGRAPH.*

By Professor VICTOR SCHUMANN.

As long as photographers employ exclusively collodion or gelatin plates, sensitive only for blue and indigo and, to a limited degree, to ultra-violet rays, their relative sensitiveness can only be found by a series of objective exposures, or by means of any of the sensitometers proposed for practical use during the last decade. None of these instruments has become so popular as that constructed by Warnerke, and many plate manufacturers state with its aid the numerical sensitiveness of their wares. Notwithstanding the limited efficacy of the instrument, and the want of reliability of its luminous plate, practice has proved it to be not deceptive enough to lead to entirely useless results. This refers, of course, to the ordinary plate only.

Of late, however, when the relations of absolute sensitiveness have been entirely changed by the introduction of orthochromatic methods, the advantages offered by the Warnerke sensitometer have become seriously sceptical, not only in abstract scientific examination but also to a very great extent in practical working. The reason of that is simply an insufficiency of light rays radiating from its phosphorescent plate. It is of a light blue colour and homogeneous to all appearances; any other rays I have not yet been able to detect. To be fully convinced of this fact I have adopted a method of investigation, much safer unquestionably than any other heretofore proposed. After making the plate luminous in the ordinary manner it is covered with a card, in the centre of which is cut a slit of 2×30 m.m. dimensions. The rays passing through it, when examined by means of a prism, show the whole spectrum to consist of a single band only, equal in colour as well as width to the luminous slit, as far at least as ocular observation goes, but neither yellow nor red is perceptible. No other light but blue is radiated from the luminous plate; not perfect blue, however, it is of distinct tone. Supposing, then, a photographic plate, not at all sensitive for this particular ray, were examined with the Warnerke sensitometer, the test for sensitiveness can result only in total failure, because the plate might possibly be highly sensitive for rays other than those radiated from the luminous substance.

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* Communicated by the Author.

Similar facts will be found to exist with all orthochromatic plates. They are all sensitive for blue, but likewise so for yellow and red, according to the sensitive they contain. As far as the least refrangible light rays are concerned, the Warnerke sensitometer cannot be depended upon, and the results obtained when orthochromatic plates are obtained with it are totally unreliable. If those highly sensitive plates should be generally adopted for practical work, of which not the least doubt can exist, the days of Warnerke's instrument are numbered.

To describe here other sensitometers may be well omitted; they all have been superseded by the reliable spectrograph, by the aid of which more distinct information on the sensitiveness of photographic plates is obtained. Whoever desires to learn of their relations to the action of light rays of different colours should resort to the spectrograph. Heavy flint glass, like that of the Amici prisms, should, however, be entirely excluded from the instrument; these glasses are impenetrable to ultra-violet. Violet even, and not less so indigo and blue, are held back with much energy, while the luminous rays, yellow and red, are allowed to pass through flame without any hindrance almost. Such prisms must naturally lead to erroneous sensitometer numbers. On account of partial absorption, yellow is reproduced with excessive force, and plates found to be highly sensitive for yellow and red in the spectroscope will fail to show the same properties with objective exposures.*

Lenses and prisms made of crown glass or of light flint with less dispersive power are preferable for ordinary purposes. With any camera and without much trouble a suitable spectrograph may be easily constructed. To obtain faultless spectrum photographs a scrupulously correct instrument is not necessary. I have made sharpest pictures with precision instruments as well as with apparatus but roughly built, and even professional spectroscopists have made the most astounding discoveries with improvised instruments.

To find the behaviour of plates towards any light source a series of spectra, with regularly increasing time of exposure, should be photographed, the plates dried, and be examined in regard to the time required to produce a developable impression by different colours. The different sensitiveness will then be found to be reversely proportioned to the time of exposure. Were we, for example, to inquire how the sensitiveness of a Vogel eoside of silver plate (manufactured by Prentz, of Munich), is proportioned to our own instrument the *first spectrum of the series to be photographed should be exposed for such a short time as not to produce a developable impression.* Subsequent and longer exposure will then generally produce an image of extremely feeble character —a mere breath upon the plate. The thinner the picture of the spectrum, and the clearer ground of the plates, the more reliable is the sensitometer number derived from the series of spectrograms made by increasing time of exposure. As long as sensitiveness alone is the object of inquiry, the intensity of the plate is of no importance whatever. *It is totally wrong to determine numerical value of light-sensitive films by the density of the negative.*

Sensitiveness and intensity are two entirely different things, as every photographer knows who understands the use of the sensitometer. How little hold is offered by the intensity of the plate, when inquiring into its sensitiveness, is proved by the fact that the two never go hand in hand. Some plates resist strenuously the action of certain rays before decomposition of the light-sensitive components takes place; but when their stability has yielded at all to the force of the developer the intensity of the negative increases with much rapidity. Density builds up easily when the exposure has been longer than required for the production of the breath-like picture; not proportionately, however, but progressively. This phenomenon occurs with Vogel's eosine plates to an unusual extent. A hundred times have I had opportunity to observe these properties when associated with Dr. Zettnow, of Berlin, and to whom we are indebted for the most important researches of erythrosine plates, to examine extensive series of orthochromatic plates. Other phenomena occurring and observed by studious investigators may be well explained by this progressive increase of density, pre-eminently among them two peculiarities—the very changeable intensity of the maximum in yellow, and different yellow action even under strictly normal conditions.

Whoever wishes, with the foregoing explanation on hand, to determine the yellow and blue sensitiveness of erythrosine plates, will find that the former never reaches the height, numerically, stated by Dr. Vogel when the exposure is made by high altitude of the sun. Far from mid-day, or in winter-time, the proportions of brightness in the sun spectrum are entirely changed. The general sensitiveness of the plate advances them more and more towards the red end of spectrum. When the sun stands low, at its rise and set, the erythrosine silver plate may triumph to a still greater extent, for then it is nearly exclusively sensitive for yellow and red, but for no other rays.

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* To understand clearly the great influence of partial absorption produced by Amici prisms compare my spectrograms of erythrosine silver (David and C. Scolik; Die orthoskiegraphishe Photographie. Knapp; Halle a/S. 1890) with those of Vogel's soda-eosine silver plates (his Handbuch der Photographie, 4th Ed., 1890.) Both photogravures illustrate the sensitising action of one and the same dye, for erythrosine is identical with sodo-eosine. Vogel made his spectrum photographs with a spectrograph furnished with an Amici prism; mine was made with the large Quartz spectrograph. Vogel's prism has swallowed up the ultra-violet so completely that not a trace of it is discernible; and how much the action of indigo and blue has been suppressed may be judged of by the high intensity of the maximum in yellow, according to Vogel's own calculation of six and even ten times force, and as impenetrable as the blue maximum. No erythrosine plate has this enormous sensitiveness for yellow, unless it be exposed under abnormal conditions. But when colour-sensitive plates are exposed in the gloom of an Amici prism, and the sombre light filtered through the terrestrial atmosphere, and when the sun is at its lowest altitude (the first days of January), it is quite easy to demonstrate ocularly a high sensitiveness for yellow, that under no other conditions is possible to attain. Furthermore are the ideas of intensity and sensitiveness sadly confused, ostensibly with a purpose—that of shedding lustre upon the eosine-silver plate for a long time to come. Of quite a different character are my erythrosine silver spectrograms. They are distinguished by powerful action in ultra-violet, an intense violet and a vigorous blue. Astonishing is the much lower yellow sensitiveness of my plates when compared with the action of blue on the one side and with the Vogel spectra on the other. Had I placed before the slit of my instrument a heavy flint, like an Amici prism, and had I exposed my plates when the sun stands low, when the refrangible rays of the spectrum half act with little energy, my spectrograms would have been equal to Dr. Vogel's. But I preferred to show how erythrosine silver behaves under normal conditions. Errors in the photographing of my spectra, and upon which the difference of time and Dr. Vogel's might be based, are improbable. Researches made at other times and occasions have invariably led to the same results.

THE ANALYSIS OF CUPRIC BROMIDE, AND THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 23).

II. Final Determination.

Preparation of Cupric Bromide.

In preparing cupric bromide for the final series of experiments it was decided to adopt a wholly new method, namely, the action of excess of bromine upon copper in the presence of water. Pure copper was prepared from a new source, the chemically pure sulphate from a noted German house, by the method which has so often been described.† The salt was freed from a possible trace of bismuth and iron by potassic hydrate in very dilute solution, precipitated from the concentrated filtrate by sul-

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* Contributions from the Chemical Laboratory of Harvard College. —From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxv.

† *Proceedings of the American Academy of Arts and Sciences*, xxii., 346; xxiii., 178; see *ante*.

phuric acid, and after many re-crystallisations was finally twice successively decomposed by fractional electrolysis. The resulting copper was a very brilliant and beautiful substance; after being thoroughly washed and dried at 90°, it showed no trace of oxidation on standing three months.

The problem of the preparation of pure bromine has been admirably solved by Stas,[*] and the method adopted in the present case was largely based upon his, although differing from it in several important particulars. Sixty grms. of potassic bromide in dilute solution were completely freed from a trace of iodine by two additions of a small quantity of bromine water, shaking out each time with successive portions of pure carbon disulphide until the two liquids in the separating funnel were alike colourless. After evaporation the aqueous solution of potassic bromide was mixed with pure dilute sulphuric acid and pure powdered manganese dioxide, and the mixture was subjected to distillation from a glass retort over a water-bath into a glass condenser packed in ice. The manganese dioxide had previously been washed with an aqueous solution of bromine, pure water, hot dilute sulphuric acid, and finally with pure water again until neutral to litmus.

Thirty-seven grms. of bromine thus prepared were washed twice with water and distilled four times in two very small flasks with long side tubes, the bulbs being alternately packed in ice and immersed in hot water as they alternately served for condenser and retort. The neck of the one serving as the latter was stopped with a glass rod wrapped in fine asbestos, and this bulb was always cleaned and dried before being in its turn used as condenser. In this way bromine may be indefinitely re-distilled with very little escape of vapour and without the least inconvenience.

The resulting bromine, although free from iodine, of course still contained an impurity of chlorine, which it is possible to remove by the solution of the whole mass in concentrated aqueous calcic bromide. The required salt was made by the addition of bromine to a mixture of milk of lime with sufficient ammonia water to prevent the formation of oxygen salts of calcium. The clear filtrate from this operation was evaporated to dryness, and the slight excess of lime was neutralised by means of pure hydrobromic acid. The calcic bromide thus formed was freed from iodine in the manner described in the case of the potassium salt, and a very small amount of the pure product served to dissolve all the bromine previously made. The intensely coloured heavy solution parted with some of its bromine on dilution, and with nearly all the remainder on gentle distillation.

Bromine thus prepared is absolutely free from chlorine as well as from iodine. After being twice more distilled, it was taken at once for the preparation of the bromide of copper used in the final determinations of the atomic weight. The combination of the halogen and the metal took place in a cooled flask containing water, and after its completion the slight excess of bromine—added to insure absence of cuprous bromide—was expelled by gentle evaporation to dryness in a glass dish. The nearly normal cupric bromide was then dissolved in a small amount of water, and the strong solution filtered through asbestos in a perforated crucible.

All experiments hitherto tried upon the salt had led to the conclusion that the solid alone loses bromine in the air, the solution being perfectly stable. If, therefore, it were possible suddenly to crystallise the salt and immediately to wash and dissolve it, we might hope to obtain a normal solution by a method which would insure perfect purity. This result was at last attained by the concentration of the dissolved cupric bromide, barely acidified with pure hydrobromic acid, to the consistency of syrup—the containing vessel being left wholly undisturbed in vacuo for thirty-six hours. Upon agitation and cooling with ice, the resulting odourless, black supersaturated solution at once crystallised into a mass of brownish green needles, which were collected on a perforated crucible and washed three times with a very little water. These needles were wholly different in form and appearance from the black scales previously prepared: they were undoubtedly identical with those described by Berthemot and Lowig.[*] The dilute solution of these crystals deposited only a wholly insignificant amount of the basic bromide upon standing, and this small amount was undoubtedly formed by the rapid current of air drawn through the Gooch crucible. After remaining for more than a week longer there was no sign of further deposition, and the pure liquid was subjected to analysis, with the results given below.

Method of Analysis.

The copper was determined in the same manner as before, except that in experiment 18 the crucible serving as the negative electrode was previously coated inside with a thin film of copper, so that the external conditions before and after the analysis might be the same. The data of this experiment may perhaps make the understanding of the method more clear.

Experiment 18.

	Grms.
Weight of glass-stoppered flask with $CuBr_2$ solution	=93·872
Weight of glass-stoppered flask alone ..	32·289
,, solution taken	61·583
	Corrected wts Grms.
Crucible with copper before analysis ..	=36·5516
1st drying crucible with additional Cu after analysis	37·2260
2nd drying crucible with additional Cu after analysis	37·22605
Gain of copper film	0·6744
Correction to vacuum	0·0000
Weight of copper found	0·6744

Result.

Weight of copper in 50 grms. solution = $= \frac{50 \times 0·6744}{61·583}$	0·54755

In precipitating the bromine from new portions of the solution, not only was the resulting silver bromide weighed, but also the silver required to form it; and this last value was determined according to two distinct methods. In the first place, the weight of silver required for a given weight of the copper bromide was calculated, and somewhat less than this amount was weighed out and dissolved in nitric acid in the manner before described. The cupric bromide was then cautiously added to the warm dilute solution, and the deficiency of silver made up by very careful titration with a solution containing one grm. of silver to the litre.[†] After noting carefully this first value for the amount of silver required, a slight known excess of the standard solution was added, and the silver bromide was washed, collected, and weighed upon a perforated crucible as before. The excess of silver in the filtrate was now carefully determined by means of a standard solution of ammonic sulphocyanide, using as a standard of colorimetric comparison solutions containing an equivalent amount of pure copper nitrate and small known amounts of silver nitrate. This second method of determining the amount of silver required to precipitate the bromine is not so accurate as the first, but is of value

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[*] Stas's "Untersuchungen," p. 158; Uebergesetzt von L. Aronstein, Leipzig.

[*] Berthemot and Löwig, *loc. cit.*

[†] For a further description of the method by Prof. J. P. Cooke, see *Proceedings of the American Academy of Arts and Sciences*, xvii., 18

as a check upon the other. The most complete experiment tried is given in detail, as an example of the method.

Experiments 22 and 25.

	Grms.
Glass-stoppered flask with $CuBr_2$ solution	=47·711
,, ,, alone	21·776
Cupric bromide solution taken	25·935
	Corrected wts. Grms.
Amount of silver dissolved (cor. to vac.)..	=0·9639
,, ,, added in titration	0·0001
First value found for required silver . ..	0·9640
0·50 c.c. excess of $AgNO_3$ solution added to filtrate. Silver present	0·0005
Total weight of silver used..	0·9645
Excess of silver was precipitated by 0·07 c.c. NH_4SCN solution. Corresponding silver	0·0007
Second value for required silver	0·9638
Weight of crucible + AgBr dried at 130°..	18·2516
,, ,, ,, ,, 220°..	18·2516
,, Gooch crucible alone	16·5738
,, AgBr in air..	1·6778
,, ,, vacuo	1·6779

Results.

Weight of silver bromide from 50 grms. of solution	3·2348
Weight of silver (average) for	1·8583
,, bromine in 50 grms. solution ..	1·3765
,, Br calculated from AgBr $\left(\frac{80·007}{188·007}\right)$	1·3766

(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. cxi., No. 25, December 22, 1890.

On the Ultra-violet Limit of the Solar Spectrum according to Proofs obtained by Dr. O. Simony on the Summit of the Peak of Teneriffe.—A. Cornu.—The results of Dr. Simony's observations are given in the form of a diagram. The author proposes the establishment of a permanent station for astro-photography on the summit of Mont Blanc.

A New Series of Ammoniacal Combinations of Ruthenium derived from the Nitroso-chloride.—A. Joly.—The author has obtained a number of compounds, but defers giving the description of their properties.

On the Combinations of Gaseous Ammonia with Phosphorus Chlorides and Bromides.—A. Besson.—The author has verified the composition assigned by Rose to the compound of phosphorus trichloride and dry ammonia; viz., $PCl_2,5NH_3$. He has also obtained a definite combination of PCl_5 and NH_3. With phosphorus pentabromide and ammonia there is obtained an analogous compound, $PBr_5,9NH_3$. The action of gaseous hydrogen phosphide, PH_3, upon phosphorus chlorides and bromides has also been studied.

A Method for Obtaining Pure Phosphoric Acid either in the Vitreous State or in Solution.—M. Nicolas.—The author acts upon phosphates with hydrofluoric acid instead of sulphuric acid. The reaction is so energetic that the hydrofluoric acid must be diluted with water and the powdered phosphate added in successive portions. The mixture must be frequently stirred.

Coloured Reactions of the Aromatic Amines.—Ch. Lauth.—This paper will be inserted in full.

New Process for Detecting the Sophistication of Olive Oils.—R. Brulé.—The process is founded upon the use of silver nitrate dissolved in the proportion of 25 per cent in ethylic alcohol at 90°. 10 c.c. of the oil in question are poured into a test-tube with 5 c.c. of the silver solution and left for about half an hour in the water-bath. The colour of the oil is then observed: 1. Pure olive oil remains transparent and takes a fine grass-green. 2. Pure earth-nut oil takes a reddish brown colour. 3. Sesame takes the colour of very dark rum. 4. Colza becomes black and then a dirty green. 5. Linseed takes a dark reddish tint. 6. Cotton seed oil turns black. 7. Camelina becomes black; by daylight, on inclining the tube, it presents a brick-red colour.

Vol. cxi., No. 26, December 29, 1890.

This issue is merely an account of the annual public meeting, with the lists of the prizes awarded and proposed.

Zeitschrift fur Analytische Chemie.
Vol. xxix., Part 3.

The Determination of Zinc in Ores.—Delfo Coda.—The author dissolves 2·5 grms. zinc ore in 15 to 20 c.c. of aqua regia, evaporates to dryness, adds 15 to 20 c.c. sulphuric acid, and heats again until the white vapours of sulphuric acid show that all nitric and hydrochloric acid have been expelled. If copper, cadmium, &c., are present the liquid is diluted, and these metals are precipitated by means of sulphuretted hydrogen and filtered off. The filtrate is boiled until the sulphuretted hydrogen is expelled; if only lead is present it is sufficient to dilute the solution with water and to filter. To the filtrate which contains only iron, zinc (manganese and alkalies) ammonia is added to neutrality, and 40 c.c. ammonia in addition, containing $\frac{1}{4}$ ammonium carbonate. The iron falls at once without carrying zinc oxide along with it. After the flask has become cool it is filled with water up to 500 c.c., and filtered through a dry, folded filter. Three portions of 100 c.c. each are taken from the filtrate, and each is diluted to 250 c.c. Each portion consequently contains the zinc of 0·5 grm. ore, and the solution thus obtained is ready for titration. The standard liquid is prepared by dissolving a known quantity of pure zinc in 4 c.c. hydrochloric acid; the quantity of zinc should be approximately equal to that which is supposed to be present in 0·5 grm. of ore. The solution is diluted, rendered alkaline with 20 c.c. ammonia, and again diluted to 250 c.c. For precipitating the zinc from the standard liquid and from the solution the author uses a graduated Mohr's burette, containing a 2 per cent solution of sodium sulphide. As indicator there is used an 8 per cent solution of sodium nitro-prusside, which is placed upon a perfectly dry porcelain slab in drops of about 5 m.m. each. When the zinc has been almost perfectly precipitated in the two solutions by sodium sulphide, the zinc sulphide is let settle until a transparent layer appears above the precipitate. A little of this clear liquid is taken up with a pipette and some of it is let fall upon one of the drops of nitro-prusside until the drop is 30 m.m. in diameter. If the well-known red colour does not appear (which would indicate the presence of free alkaline sulphide) $\frac{1}{2}$ c.c. of solution of sodium sulphide is added to each solution, which is then shaken, let settle, and the operation repeated until the red colour appears upon the tile. If one of the liquids has a fainter colour than the other an attempt is made to get the same shade by adding quantities of one-tenth c.c. sodium sulphide. If the known weight of zinc in the standard liquid is called a, the c.c. of solution of sodium sulphide required to throw down the pure zinc, b, and those used for the solution of the ore c, then the percentage of zinc in the ore is—

$$\frac{200 \ . \ a \ . \ c}{b} \text{ per cent.}$$

In order to determine the accuracy of this process the iron precipitate was analysed after being carefully washed with ammoniacal water. It contains not a trace of zinc, but 3·5 per cent of its weight of ammonium sulphate. But if no ammonium carbonate is added to the ammonia 0·10 per cent of zinc is lost.

Nitrogenous Bases in the Products of Alcoholic Fermentation.—E. C. Morin.—From the *Comptes Rendus.*

Action of Air and Heat upon the Tannin of Willow Bark.—W. Sonne and F. Kutscher.—This form of tannin is partially decomposed if its aqueous solution is heated or concentrated.

Notes on Kjeldahl's Determination of Nitrogen.—Schönherr (*Chemiker Zeitung*) and Saugerod (*Arch. de Pharmacie*) recommend the determination of the ammonia formed by means of the azotometer. A. Devarda recommends Jodlbauer's modification of the original process. Lindot (*Comptes Rendus*) obtains good results with the Kjeldahl process in determining nitrogenous bases in alcoholic liquids. Poporici prefers the Kjeldahl method to that of Varrentrap and Will in determining nitrogen in tobacco.

Determination of the Neutralising Power of Acids.—F. Fuchs (*Akademie in Wien*).—The author employs the action of the acids upon the alkaline sulphohydrates.

On the Oxybenzoic Acids and on Benzoic Acid.—Oechsner de Coninck (*Chemiker Zeitung*).—Meta- and para-oxybenzoic acids can be determined by the cautious evaporation of their solutions in ethyl and methyl alcohols. Salicylic acid can be determined in their solutions in ethyl and methyl alcohol, acetone, &c., by a gradual evaporation with the aid of the water air-pump. Meta- and para-oxybenzoic acids can be determined by the slow evaporation of their aqueous solutions. Salicylic acid begins to sublime between 80° and 85°; both its isomers require higher temperatures. Benzoic acid begins to sublime between 45° and 50°.

Determination of the Hydroxyl Group.—C. Loring, Jackson, and G. W. Rolfe.—From the *American Chemical Journal.*

Determination of Methoxyl in Organic Compounds. — S. Zeisel — The author utilises the well-known property of the methoxyl group (OCH_3) to form iodmethyl with hydriodic acid. As iodmethyl is decomposed by an alcoholic solution of silver nitrate with elimination of silver iodide, we have the means for a quantitative determination of methoxyl. Rudolf Benedikt and Anton Grüssar recommend the application of Zeisel's process for testing fats, resins, ethereal oils, &c. They have examined an entire series of ethereal oils by this method, and calculated the values obtained as methyl originally present. They call the percentage thus obtained the "methyl-number," remarking that ethyl and the higher alkyls appear also expressed as methyl.

A New Method for the Quantitative Examination of Saccharine.—J. Remsen and W. M. Burton.—From the *American Chemical Journal.*

Detection and Determination of Yolk of Egg.—S. Bein (*Berichte der Deutsch. Chem. Gesellschaft*).—See page 11.

Detection of Copper in Wine.—T. Gigli (*Orosi* and *Chemical Centralblatt*).—The author steeps a galvanic element (zinc and platinum) in the wine, which is first acidified with hydrochloric acid. The plates are 8 c.m. long, 0·8 c.m. wide, and connected with each other at one end by means of a platinum wire, which also serves to suspend the element to a glass rod. In carrying out the test, 1 litre of wine is mixed with 20 c.c. hydrochloric acid at specific gravity 1·15, the liquid is divided into 5 parts, and an element is suspended for 24 hours in each portion. The copper present is deposited upon the platinum.

Examination of Whiskey.—Clifford Richardson.—From the *American Chemical Journal.*

A Chemical Reaction for the Bacteria of Cholera.—It is known that cultures of the bacillus in question are coloured red by hydrochloric acid. R. Pfeiffer (*Zeit. f. Hygiene*) states that this reaction is also produced by cultures of another comma-bacillus, *Vibrio metschnikoff.*

Examination of Beet Sugar for Inverted Sugar, Dextrine, &c.—Ihl (*Chemiker Zeitung*). — The author adds a solution of methylene blue, which is decolourised by the impurities in question.

A Process for Detecting Colouring Matters.—Gaston Dommergue. —From the *Moniteur Scientifique.*

The Use of the Kjeldahl-Wilfarth Nitrogen Process for Investigations on the Transformations of Matter.—Argutinsky (*Pflüger's Archiv.*).—The author is satisfied with the results.

New Process for Determining Uric Acid. — Arthand and Butte (*Comptes Rendus Soc. de Biologie*).—The process is founded on the insolubility of cuprous urate, the phosphates present being first removed by means of sodium carbonate.

Detection and Determination of Sugar in Animal Fluids.—Fr. Schenck (*Pflüger's Archiv.*).—The author comes to the conclusion that glucose is capable of combining with the albumen of blood.

Detection of Albumen in Urine.—Const. Zouchlos (*Vienna Med. Zeit.*).—A solution of mercuric chloride produces in albuminous urines a distinct turbidity, which does not disappear on adding acetic acid. A mixture of 1 part acetic acid with 6 parts of a 1 per cent solution of mercuric chloride precipitates albumen, but not peptone, uric acid, or phosphates.

Journal de Pharmacie et de Chimie.
Vol. xxii., No. 1.

On the Influence of Different Fruit-Ferments upon the Aroma of Fermented Liquors, and on the Production of Cider from Barley.—Georges Jacquemin.—Already noticed.

Improvement in the Manufacture of Soda, Potassa, and Chlorine.—W. P. Thompson.—An English patent, No. 13306, 1888.

Preparation of Metallic Manganese by Means of Manganese Chloride and Magnesium.—E. Glatzel.

Improvements in the Manufacture of Alkalies, Alkaline Salts, and Chlorine from Sodium and Potassium Chlorides.—T. Parker and E. Robinson.—An English patent, No. 14199, October 3rd, 1888.

Process for Detecting Wood-Paper.—M. Wurster.—The following reagents serve to distinguish wood-paper from pure cellulose:—

Reagent.	Wood-paper.	Cellulose.
Orcine	Dark red	Nothing.
Resorcine	Deep green	Violet.
Pyrogallic acid .	Blue-green	,,
Phenol	Yellow-green . ..	,,
Phloroglucine ..	Blue violet	Nothing.

The presence of wood in paper can be detected and the quantity even estimated by means of dimethyl paraphenylendiamine.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Vol. v., No. 58.

Report Presented by M. le Chatelier on M. Candlot's Memoir concerning the Properties of Cement.—M. Candlot, discussing the action of sea-water on cements, proves that of the three principal salts present, sodium chloride exerts no influence. Calcium chloride in dilute solutions (20 grms. per litre), retards the setting of cement just as does sea-water, whilst solutions at 300 grms. per litre cause a considerable acceleration. He further shows that the reason why weak solutions of calcium chloride retard setting is because they prevent the solution of the alumina of the calcium aluminates. Concentrated solutions of calcium chloride, on the contrary, increase the solubility of the aluminates and even of the ferrites. This increase of the solubility of alumina, the direct cause of the acceleration of the setting, results from the formation of the calcium chloro-aluminate.

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

This issue does not contain any chemical matter.

MEETINGS FOR THE WEEK.

Monday, 19th.—Medical, 8.30.
— Society of Chemical Industry, 8. "On the Constitution of Butter" (Illustrated by Specimens), by J. Alfred Wanklyn. "Some Experiments on the Cyanide Process for the Extraction of Gold from Low Grade Gold Ores," by T. Graham Young and Watson Smith.
Tuesday, 20th.—Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F R.S., B.S.. F.R.C.S., Fullerian Professor of Physiology, R.I.
Wednesday, 21st.—Society of Arts, 8. "Photography in Aniline Colours," by A. G. Green, C. F. Cross, and E. J. Bevan.
— Meteorological, 7. (Anniversary).
— Geological, 8.
— Microscopical, 8. (Anniversary).
Thursday, 22nd.—Royal, 4.30.
— Royal Society Club, 6.30.
— Institute of Electrical Engineers, 8.
— Society of Arts, 4.30. (Indian Section). "Hall-Marking of Silver Plate, with Special Reference to India," by Edward J. Watherston.
— Royal Institution, 3. "The Little Manx Nation," by Hall Caine.
Friday, 23rd.—Royal Institution, 9. "Some Applications of Photography," by The Right Hon. Lord Rayleigh, M.A., D.C L., LL.D., F.R S.
Saturday, 24th.—Royal Institution, 3. "Pre-Greek Schools of Art," by W. Martin Conway, M.A., F.S.A.

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THE CHEMICAL NEWS.
Vol. LXIII. No. 1626.

ON WOLF AND RAYET'S BRIGHT-LINE STARS IN CYGNUS.*

By WILLIAM HUGGINS, D.C.L., LL.D., F.R.S., and Mrs. HUGGINS.

(Concluded from p. 30).

Dr. Copeland, during his travels in the Andes in 1883, observed γ Argûs, and five small stars with bright lines in their spectra. He says:—"As far as my measures and estimates go, all of them belong to the same class as the three Wolf-Rayet stars in the Swan, to which Professor Pickering has since added a fourth outlying member."†

Dr. Copeland gives the position of the bright blue band in γ Argûs as λ 464·6.

Among the stars in the great cluster G.C. 4245, near ζ Scorpii, Dr. Copeland found a star, P. XVI. 204=Stone 9168, which has a similar spectrum, namely, with a bright band in the blue and two in the yellow. He found the position of the blue band to be λ 465·1.

In the case of two other small stars with similar spectra, he found respectively for the blue band the approximate measures λ 463·3 and λ 463·6.

These four stars were similar, therefore, at the time of the observations to No. 4013 and No. 3956, in which the maximum of the blue band is not far from λ 464, and therefore outside and beyond the ordinary visible limit of the blue carbon band.

Professor Vogel observed two other stars with similar spectra, of which the main feature is the very bright band in the blue region, namely, Arg. Oeltzen 17681 and Lal. 13412. These stars are too low in southern declination to be reached from our observatory.

Vogel places the blue band in Lal. 13412 at λ 469, which shows that it has a position similar to that of No. 4001 and of Dr. Copeland's star. In the case of Arg. Oeltzen 17681, Vogel makes the band to extend through about the entire range of refrangibility occupied by the two positions of the blue band in the Wolf-Rayet stars according to his measures of them, namely, from λ 461 to λ 470, with a maximum at the place where they would overlap, namely, λ 466.

Let us consider the four stars with an intensely brilliant blue band which we have examined; in two of them the band extends from about λ 464 to λ 467, and in the other pair the band has a less refrangible position, from about λ 466 to λ 471, but there is also in the case of each pair a very faint band visible, or suspected, at the position of the blue band in the other pair. Further, in Arg. Oeltzen 17681, Vogel found the bright band sufficiently long to include both positions of the band.

One suggestion which presents itself is whether these bands, or, more correctly, these groups of bright lines, may be variable, so that, under certain conditions, one or other of them becomes brilliant. Such a state of things would reconcile our observations of +37° 3821 with the earlier measures of Dr. Copeland, and, indeed, might possibly explain, if this variability should be established, the circumstance that so accurate an observer as Professor Vogel did not detect, even with his smaller instrument in 1873, the very large difference of position of the band in 4001 from that of the corresponding band in the stars 4013 and 3956, which was so conspicuous in 1883, and is so still at the present time. In the broad characters of their spectra, and in their magnitudes, the Wolf-Rayet stars have remained unchanged since the discovery of their remarkable spectra in 1867.

As the only direct evidence of such a variability rests upon the change of position of the band in Dr. Copeland's star since his observation of it in 1884, I wrote to Dr. Copeland to ask if his position rested upon sufficiently accurate measures or was arrived at by estimation only. In reply, he says:—"The place of the blue line (rather, band) in D.M. +37° 3821, given in the *Monthly Notices*, is a mere estimate to show the character of the star."

Whether any change of position of the band has taken place must therefore remain at present uncertain; but, independently of any such direct evidence of variability, the two positions of the very bright blue band, with the suspicion of faint bands at the alternate positions, appear to us suggestive of possible variation, especially when we consider that the spectra of these stars consist of numerous absorption bands and groups of bright lines upon a feeble continuous spectrum, a character of spectrum which seems to point to a probably unstable condition of the atmospheres of these stars.

The large difference of position of the bands in the two groups of stars is much too great to admit of an explanation founded upon a possible orbital motion of the stars. Besides, the near coincidence of Dr. Copeland's measures of two bright lines common to the stars 4001 and 4013 shows that the difference of position of the blue band is not due to motion in the line of sight.*

If future observations should show that the bright blue groups are variable, we must look, it would seem, to causes of a physical or a chemical nature.

If the two bright groups, differing in position by about λ 0040, belong to different substances, or, less probably, perhaps, to different molecular conditions of the same substance, it is conceivable that one or other substance, or molecular state, may predominate and appear brilliant, according to certain unknown conditions which may prevail in the star's atmospheres.

It might be suggested that both bands are due to a long group of bright lines extending from about λ 461 to λ 471, and that this long group is cut down by absorption bands; in one pair of stars an absorption from the green cuts off the less refrangible part of the long group down to about λ 467, while in the other two stars the more refrangible part is eclipsed, and the bright group appears as in 4001.

The appearance of the spectra in our instruments scarcely seems to us to be in accordance with such a view, because, though we did suspect brightenings in the alternate places, the appearance of the spectrum was not such as to suggest a bright group dimmed by absorption, for in that case the amount of absorption needed to all but obliterate a group, as bright as it appears in the other pair of stars, would have blotted out completely the relatively feeble continuous spectrum. This continuous spectrum, though faint, was still distinctly seen.

More observations are needed, but it appeared to us desirable by these suggestions to invite the attention of observers to the points in question.

As the main object of our examination of these stars was to determine whether the bright band in the blue was to be regarded as showing the presence of carbon by its coincidence with the blue band of the hydrocarbon flame, we were not able, from the pressing claims of other work, to extend our examination to many other

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* From the Authors. A Paper read before the Royal Society, Dec., 1890.

† "An Account of some recent Astronomical Experiments at High Elevations in the Andes," *Copernicus*, vol. iii., 1883.

* Dr. Copeland permits me to give the following measures of the bright lines in the Wolf-Rayet stars, which were made by him and Mr. Lohse on January 28, 1884;—

Star.	1st yellow line.	2nd yellow line.	Bright line.	Faint line.	Large blue band.
+35° 4001..	—	—	541·2(3)	522·0(1)	469·5(3)
+35° 4013..	582·4(2)	568·9(2)	541·0(2)	—	465·4(2)
+36° 3956..	581·0(2)	570·4(2)	—	523·3(1)	464·9(2)

points in connection with the spectrum of these faint stars, for an exhaustive examination of which, indeed, our instruments are not sufficiently powerful.

We have stated already that the fairly luminous continuous spectrum reaches up to the bright band in all three stars, and extends beyond into the violet, as far as the eye could be expected to follow it.

The spectra are weakened at many points by what appear to be absorption bands, and are crossed by several brilliant lines, the positions of some of which have been given by Vogel and by Copeland.

An examination with spectroscope B of some of these bright lines, as they appear under small dispersion, showed them to be really not single lines, but short groups of closely adjacent bright lines.

One of the brightest of these lines is found in the star No. 4013, at the position, according to Vogel, of λ 570.

Dr. Copeland's measure for this line is λ 568·9 in star 4013, and λ 570·4 in the star 3956.

As this position is not very far from that of the green pair of sodium lines at λ 5687 and λ 5681, it has been suggested that the line in the star is due to sodium, though there is no line of comparable brightness in the star's spectrum at the position of the dominant pair of the sodium spectrum at D.*

On confronting in spectroscope B the star line with the green sodium lines, the bright space in the star's spectrum was seen to consist of a short group of several bright lines close together, and nearly equally bright. This group appeared to extend through about four times the interval of the sodium pair, which would make the length of the group about λ 0024. The green sodium lines cross the group at about one-fourth to one-third of the length of the group from its more refrangible end. The group in the star is rather less bright at the two ends, but there is no gradual shading off in either direction, as in the case of a fluting.

When we examined this part of the spectrum with the small dispersion of a prism of 45°, we were pretty sure of a feeble bright line, less refrangible than the pair of bright groups in the yellow, and not far from the position of D. We were not able to see this line in spectroscope B with sufficient clearness to enable us to fix its position. It may be D, or, perhaps more probably D_3.

In No. 4001, Vogel saw a line at the position of the F line of hydrogen. It is probable that this line, as is the case in so many stars in which it appears bright, is variable, as we were not able to see it when the $H\beta$ line from a vacuum tube was thrown in. In the similar star D.M. +37° 3821, as we have stated already, the F line of hydrogen was very bright.

We were unable to detect in any of the stars a brightening of the spectrum at the position of the chief line of the bright-line nebulæ. For this examination, the lead line at λ 5004·5 was thrown in, and the continuous spectrum of the star near to this position carefully scrutinised.

In their original paper, Wolf and Rayet state that they were not able to detect any nebulosity about the stars. They say:—"Elles ne présentent non plus aucune trace de nébulosité" (*loc. cit.*, p. 292).

In a recent paper, Mr. Keeler, the Lick Observatory, confirms this view. He says:—"At my request, Mr. Burnham and Mr. Barnard examined the Wolf-Rayet stars in Cygnus for traces of surrounding nebulosity, but with only negative results."

Notwithstanding these negative results, it appeared to us of great interest to ascertain further if any nebulosity would come out in a photograph of the stars taken with a long exposure.

Mr. Roberts responded at once to our wish when we asked his invaluable assistance, and on November 1st, 1890, he took a photograph of this region of Cygnus, with an exposure of two hours.

The three stars come out strongly upon the plate, but there is no nebulosity to be seen near any of them. There are faint stars in close proximity to the three stars, and apparently surrounding them, and, in the case of No. 3956, six of these faint stars are seen close to it, in an apparent spiral arrangement.

Though this surrounding of faint stars should be pointed out, it should, at the same time, be stated that the whole neighbouring region is so densely studded with similar faint stars that it would be rash, perhaps, at present to suggest that this apparent connection of the bright-line stars with faint ones near them may be other than accidental.*

Professor E. C. Pickering informs me "that photographs have been obtained at the Harvard College Observatory of all the stars hitherto discovered whose spectra consist mainly of bright lines and are of the class discovered by Rayet. Part of these have been photographed at Cambridge, and the remainder in Peru." He states that they may be divided into three sub-classes, according to the characters of the bright lines. He says, further:—"Photographs of the spectrum of fifteen planetary nebulæ have also been obtained. They resemble closely the spectra described above, except that the line 500 is strongly marked; 470 is seen in most of them, while the lines due to hydrogen are also bright."

It would seem that Professor Pickering's photographs do not permit him to distinguish the different positions of the bright blue band in some of these stars, for he gives for all the stars the same position, namely, λ 470.

We regret that the insufficiency of our instrumental means has left our examination of the spectra of these stars less complete than we could wish. Our observations appear to us, however, to be conclusive on the main object of our enquiry, namely, that the bright blue band in the three Wolf-Rayet stars in Cygnus, and in D.M. +37° 3821, is not coincident with the blue band of the Bunsen flame.

ON GASEOUS ILLUMINANTS.†

By Professor VIVIAN B. LEWES.

IV.

When carbon is acted upon at high temperatures by steam, the first action that takes place is the decomposition of the water vapour; the hydrogen being liberated, while the oxygen unites with the carbon to form carbon dioxide, thus:—

$$\begin{array}{ccccccc} \text{Carbon.} & & \text{Water.} & & \text{Carbon dioxide.} & & \text{Hydrogen.} \\ C & + & 2(H_2O) & = & CO_2 & + & 2H_2 \end{array}$$

The carbon dioxide so produced interacts with more red-

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* The 570 line is most probably the green sodium line 569, the absence of the yellow sodium being explained by the half-and-half absorption and radiation mentioned in the discussion of the causes which mask and prevent the appearance of a line in a spectrum (Bakerian Lecture for 1888, *Roy. Soc. Proc.*, vol. xliv., p. 41).

* [Mr. Roberts has furnished us with the following description of the stars as they appear on his photograph:—

"*No.* 4001 appears as a multiple star made up of one bright, two fainter, and one very faint star partly behind the others; there is also a fourth bright star close to the multiple star. The group is surrounded by at least eight faint stars within a radial distance of ±86″ of arc from centre to centre.

"*No.* 4013.—The photo-image of this star is made up of three stellar images touching each other in a line slightly curved. Two are bright and one faint; and there are indications of two other faint stars behind the two bright ones. This multiple image of four or five stars is surrounded by five bright and seven faint stars; all within a radial distance of 82″ of arc measured from centre to centre of the multiple star. The multiple image measures ±55″ in length and ±19″ in breadth.

"*No.* 3956.—Its photo-image is ±27″ in diameter. It is encircled by three stars of lesser brightness, and six faint ones within a radial distance of 59″, *i.e.*, there are nine stars within a radial distance of 59″."—Dec. 5.]

† Abstract of the Cantor Lectures delivered at the Society of Arts Communicated by the Author.

hot carbon, forming the lower oxide, carbon monoxide, thus:—

$$CO_2 + C = 2CO.$$

So that the completed reaction may be looked upon as yielding a mixture of equal volumes of hydrogen and carbon monoxide—both of them imflammable, but with non-luminous flames. This decomposition, however, is rarely completed, and a certain proportion of carbon dioxide is invariably to be found in the water-gas, which, in practice, generally consists of a mixture of about the following composition:—

Hydrogen	48·31
Carbon monoxide	35·93
Carbon dioxide	4·25
Nitrogen	8·75
Methane	1·05
Sulphuretted hydrogen	1·20
Oxygen	0·51
	100·00

The above is an analysis of water-gas made from gas coke in a Van Steenbergh apparatus. The ratio of carbon monoxide and carbon dioxide present depends entirely upon the temperature of the generator and the kind of carbonaceous matter employed. With a hard, dense, anthracite coal, for instance, it is quite possible to attain a temperature at which there is practically no carbon dioxide produced; while with an ordinary form of generator, and a loose fuel like coke, a large proportion is generally to be found. The sulphuretted hydrogen in the analysis quoted is, of course, due to the high amount of sulphur to be found in the gas coke, and is practically absent from water-gas made with anthracite. The nitrogen is due to the method of manufacture, the coke being, in the first instance, raised to incandescence by an air-blast, which leaves the generator and pipes full of a mixture of nitrogen and carbon monoxide (producer gas), which is carried over by the first portions of water-gas into the holder. The gas so made has no photometric value—its constituents being perfectly non-luminous; and attempts to use it as an illuminant have all taken the form of incandescent burners, in which thin "mantles" or "combs" of highly refractory metallic oxides are heated up to incandescence. In the case of carburetted water-gas the gas is only used as a carrier of illuminating hydrocarbon gases made by decomposing various grades of hydrocarbon oils into permanent gases by heat.

Water-gas generators can be divided into two classes: (1) Continuous processes, in which the heat necessary to bring about the interaction of the carbon and the steam is obtained by performing the operation in retorts externally heated in a furnace. (2) Intermittent processes, in which the carbon is first heated to incandescence by an air-blast, and then, the air-blast being cut off, superheated steam is blown in until the temperature is reduced to a point at which the carbon begins to fail in its action, when the air is again admitted to bring the fuel up to the required temperature; the process consisting of the alternate formation of producer gas with rise of temperature, and of water-gas with lowering of temperature.

Of the first class of generator, none, so far, have as yet been practically successful in England.

Of the intermittent processes, the one most in use in America is the Lowe, in which the coke or anthracite is heated to incandescence, by an air-blast in a generator lined with fire-brick; the heated products of combustion, as they leave the generator and enter the superheaters, being supplied with more air, which causes the combustion of the carbon monoxide present in the producer gas, and heats up the fire-brick baffles with which the superheaters are filled. When the necessary temperature of fuel and superheater has been reached, the air-blasts are cut off and steam is blown through the generator, forming water-gas, which meets the enriching oil at the top of the first superheater, called the "carburetter," and carries the vapours with it through the main superheater, where the firing of the hydrocarbons takes place. The chief advantage of this apparatus is that the enormous superheating space enables a lower temperature to be used for the fixing, which does away, to a certain extent, with the too great breaking down of the hydrocarbon, and consequent deposition of carbon.

The Springer apparatus differs from the Lowe only in construction. In the former the superheater is directly above the generator, and there is only one superheating chamber instead of two. The air-blast is admitted at the bottom, and the producer gases heat the superheater in the usual way; and when the required temperature is reached, the steam is blown in at the top of the generator, and is made to pass down through the incandescent fuel. The water-gas is led from the bottom of the apparatus to the top, where it enters at the summit of the superheater, meets the oil, and passes down with it through the chamber, the finished gas escaping at the middle of the apparatus. This idea of making the air-blast pass up through the fuel, while in the subsequent operation the steam passes down through it, is also to be found in the Loomis plant, and is a distinct advantage—the fuel being at its hottest where the blast has entered; and, in order to keep down the percentage of carbon dioxide, it is important that the fuel through which the water-gas last passes should be as hot as possible to ensure its reduction to carbon monoxide.

The Flannery apparatus is also only a slight modification of the Lowe plant; the chief difference being that, as the water-gas leaves the generator the oil is fed into it, and with the gas passes through a ∩-shaped retort tube, arranged round three sides of the top of the generator. In this tube the oil is volatilised, and passes with the gas to the bottom of the superheater, in which the vapours are converted into permanent gases.

The Van-Steenbergh plant stands apart from all other forms of carburetted water-gas, in that the upper layer of the fuel itself forms the superheater, and that no second part of any kind is needed for the fixation of the hydrocarbons. This arrangement reduces the apparatus to the simplest form, and leaves no part of it which can choke or get out of order—an advantage which will not be underrated by anyone who has had experience of these plants. While, however, an enormous advantage is gained there is also the drawback that the apparatus is not at all fitted for use with crude oils of heavy specific gravity, such as can be dealt with in the big external superheaters of the Lowe class of water-gas plant, but requires to have the lighter oils used in it for carburetting purposes. This, which appears at first sight to be a disadvantage, is not altogether one, as, in the first place, the lighter grade of oils, if judged by the amount of carburetting property they possess, are cheaper per candle power added to the gas than the crude oils; while their use entirely does away with the formation of pitch and carbon in the pipes and purifying apparatus—a factor of the greatest importance to the gas manufacturers. The fact that light oils give a higher carburation per gallon than heavy crude oils is due to the fact that the crude oils have to be heated to a higher temperature to convert them into permanent gases, and this causes an over-cracking of the most valuable illuminating constituents. This trouble cannot be avoided; as, if a lower temperature is employed, the result is the formation of non-permanent vapours, which, by their condensation in the pipes, give rise to endless trouble. The simplicity of the apparatus is a factor which is a considerable saving of time and expense, as it reduces to a minimum the risk of stoppages for repairs; while the initial cost of the apparatus is necessarily low, and the expense of keeping it in order practically nil.

In such an apparatus, 1000 cubic feet of carburetted water-gas having an illuminating value of 22 candles can be made with the consumption of about 30 lbs. of coke or anthracite, and 2·5 gallons of light naphtha.

The great objection to the use of carburetted water-gas is undoubtedly the poisonous nature of the carbon monoxide, which acts by diffusing itself through the air-cells of the lungs, and forming with the colouring of the blood corpuscles a definite compound, which prevents them carrying on their normal function of taking up oxygen and distributing it throughout the body and at once stops life. All researches on this subject point to the fact that something less than 1 per cent only of carbon monoxide in air renders it fatal to animal life; and this, at first sight, seems to be an insuperable objection to the use of water-gas. It has, indeed, influenced the authorities in several towns—notably Paris—to forbid the introduction of water gas for domestic consumption. It would be well, however, to carefully examine the subject and see, by the aid of actual figures, what the risk amounts to compared with the risks of ordinary coal gas. Many experiments have been made with the view of determining the percentage of carbon monoxide in air which is fatal to human, or, rather, to animal life; the most reliable, as well as the latest, results being those obtained by Dr. Stevenson of Guy's Hospital, after an investigation instituted in consequence of two deaths which took place at the Leeds Forge, from inhaling uncarburetted water-gas containing 40 per cent of carbon monoxide. Dr. Stevenson found that 1 per cent visibly affected a mouse in 1½ minutes, and killed it in an hour and three quarters; while 0·1 per cent was highly injurious. Taking, for the sake of argument, the last figure as being a fatal quantity, so as to be well within the mark, it is found that in ordinary carburetted water-gas, as suplied by the superheater processes such as the Lowe, Springer, and others, the usual amount of carbon monoxide is 26 per cent; but in the Van Steenbergh gas, for certain chemical reasons to be discussed later on, it is generally about 18 per cent, and rarely rises to 20 per cent. An ordinary bedroom is 12 ft. by 15 ft., and 10 ft. high; and therefore it will contain 1800 cubic feet of air. Such a room would be lighted by a single ordinary batswing burner, consuming not more than 4 cubic feet of gas per hour, and if this were left full on, in one hour the 1800 cubic feet of air would be mixed with four-fifths of a cubic foot of carbon monoxide (the carburetted water-gas being supposed to contain 20 per cent), or 0·04 per cent. In such a room, however, if the doors and windows were absolutely air-tight and there were no fire-place, diffusion through the walls would change the entire air once in an hour. Therefore the percentage would not rise above 0·04, while in any ordinary room imperfect workmanship and an open chimney would change it four times in the hour, and reduce the percentage to 0·01—a quantity which the most inveterate enemy of water-gas could not claim would do more than produce a bad headache. The point under consideration, however, was the use of carburetted water-gas as an enricher of coal-gas, and not as an illuminant to be consumed *per se;* and it might be calculated that it would be probably used to enrich a 16-candle coal gas up to 17·5-candle power. To do this, 25 per cent of 22-candle power carburetted water gas would have to be mixed with it. Taking the quantity of carbon monoxide in London gas at 5 per cent (a very fair average figure), and 18 per cent as the amount present in the Van Steenbergh gas, we have 8·25 per cent of carbon monoxide in the gas as sent out—a percentage hardly exceeding that which is found in the rich cannel gas supplied to such places as Glasgow, where it is not found that an unusual number of deaths occur from carbon monoxide poisoning. Moreover, carburetted water gas has quite as strong a smell as coal gas, and can be quite as easily detected by the nose.

The cost of most of these methods of enriching coal gas can be calculated, and give the following figures as the cost of enriching a 16-candle gas up to 17·5-candle power per 1000 cubic feet:—

By cannel coal	4d.
By the Maxim-Clark process	2$\frac{6}{10}$d.
By the Lowe or Springer water gas ..	1½d.
By the Van Steenbergh water gas ..	¾d.

In adopting any new method, the mind of the gas manager must, to a great extent, be influenced by the circumstances of the times; and the enormous importance of the labour question is a main factor at the present moment. With masters and men living in a strained condition, which may at any moment break into open warfare, the adoption of such water-gas processes would relieve the manager of a burden which is growing almost too heavy to be borne. Combining, as such processes do, the maximum rate of production with the minimum amount of labour, they practically solve the labour question. The cost of paraffin oil of lighter grades, and the fear that the supply might be hampered by the formation of a huge monopoly, has been a great drawback; but we have materials which can be equally well used in this country, and of which an almost unlimited supply can be obtained.

At three or four of the Scotch iron-works, the Furnace Gases Company are paying a yearly rental for the right of collecting the smoke and gases from the blast-furnaces. These are passed through several miles of wrought-iron tubing, gradually diminishing in size from 6 feet to about 18 inches; and as the gases cool, there is deposited a considerable yield of oil. At Messrs. Dixon's, in Glasgow, which is the smallest of these installations, they pump and collect about 60 million feet of furnace gas per day, and recover, on an average, 25,000 gallons of furnace oils per week; using the residual gases, consisting chiefly of carbon monoxide, as fuel for distilling and other purposes, while a considerable yield of sulphate of ammonia is also obtained. In the same way a small percentage of the coke-ovens are fitted with condensing gear, and produce a considerable yield of oil, for which, however, there is but a very limited market; the chief use being for the Lucigen light and other lamps of the same description, and also for pickling timber for railway sleepers, &c. The result is that four years ago the oil could be obtained in any quantity at ½d. per gallon, though it has since been as high as 2½d. a gallon. It is now about 2d. per gallon, and shows a falling tendency. Make a market for this product, and the supply will be practically unlimited, as every blast-furnace and coke-oven in the kingdom will put up plant for the recovery of the oil. As, with the limited plant now at work, it would be perfectly easy to obtain 4 or 5 million gallons per annum, an extension of the recovery process would mean a supply sufficiently large to meet all demands.

Many gas managers have from time to time tried if they could not use some of their creosote oil for producing gas; but on heating it in retorts, &c., they have found that the result has generally been a copious deposit of carbon, and a gas which has possessed little or no illuminating value. Now the furnace and coke-oven oils are in composition somewhat akin to the creosote oil; so that, at first sight, it does not seem a hopeful field for search after a good carburetter. But the furnace oils have several points in which they differ from the coal-tar products. In the first place, they contain a certain percentage of paraffin oil; and, in the next, do not contain much naphthalene, in which the coal-tar oil is especially rich, and which would be a distinct drawback to their use. The furnace oil, as condensed, contains about 30 to 50 per cent of water; and, in any case, this has to be removed by distilling. Mr. Staveley has patented a process by which the distillation is continued after the water has gone off; and, by condensing in a fractionating column of special construction, he is able to remove all the paraffin oil, a considerable quantity of cresol, a small quantity of phenol, and about 10 per cent. of pyridine bases—leaving the remainder of the oil in a better condition, and more valuable for pickling timber, its chief use.

If the mixed oil so obtained, which we may call "phenoloid oil," is cracked by itself, no very striking result is obtained; the 40 per cent of paraffin present cracking in the usual way, and yielding a certain amount of illuminants. But if the oil is cracked in the presence of carbon, and is made to pass over and through a body of carbon heated to a dull red heat, it is converted largely into benzene. As this is the most valuable of the illuminants in coal gas, and also the one to which it owes the largest proportion of its light-giving power, it is manifestly the right one to use in order to enrich it. On cracking the phenoloid oil, the paraffin yields ethane, propane, and marsh gas, &c., in the usual way; while the phenol interacts with the carbon to form benzene:—

Phenol. Benzene.

$$C_6H_5HO + C = C_6H_6 + CO.$$

And in the same way the cresol first breaks down to toluene in the presence of the carbon; and this in turn is broken down by the heat to benzene. A great advantage this oil has is that the flashing-point is 110, and so is well above the limit; this doing away with the dangers and troubles inseparable from the storage of light naphthas in bulk.

In using this oil as an enricher, it must be cracked in the presence of carbon, and it is of the greatest importance that the temperature should not be too high, as the benzene is easily broken down to simpler hydrocarbon of far lower illuminating value.

THE ANALYSIS OF CUPRIC BROMIDE, AND THE ATOMIC WEIGHT OF COPPER.[*]

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 36).

Following are the essential data of all the experiments made with the pure solution of crystallised cupric bromide. The results are expressed in the same terms as those given above, and from the combination of these figures a final average value for the atomic weight of copper may be readily deduced.

Final Analyses.

Determination of Copper.

No. of experiment.	$CuBr_2$ solution taken. Grms.	Copper found (reduced to vacuum). Grms.	Copper (red. to vac.) in 50 grms. solution. Grms.
18.	61·583	0·6744	0·54755
19.	51·955	0·5689	0·54750
		Average	0·54753

Determination of Bromine.

No. of experiment.	$CuBr_2$ solution taken. Grms.	Silver bromide found (reduced to vacuum). Grms.	Bromine (red. to vac.) in 50 grms. solution. Grms.
20.	25·998	1·68205	1·3767
21.	25·957	1·6789	1·3762
22.	25·935	1·6779	1·3766
		Average	1·3765

Determination of Silver.

No. of expt.	$CuBr_2$ solution taken.	Silver required (red. to vac.).		Silver (red. to vac.) for 50 grms. solution.
	Grms.	Direct titration. Grms.	Sulpho-cyanide. Grms.	Grms.
23.	25·998	—	0·9664	1·8586
24.	25·957	0·9645	—	1·8579
25.	25·935	0·9640	0·9638	1·8583
		Average ..	..	1·8583

Atomic Weight of Copper.

Calculated from the data given above, on the assumption that Ag : Br = 108·00 : 80·007.

		Atomic weight of copper. [Br=80·007.]
I.	From experiments 18 and 20	= 63·643
II.	,, ,, 18 ,, 21	= 63·664
III.	,, ,, 18 ,, 22	= 63·648
IV.	,, ,, 19 ,, 20	= 63·636
V.	,, ,, 19 ,, 21	= 63·657
VI.	,, ,, 19 ,, 22	= 63·641
	Average	63·648
		[Ag=108·00.]
VII.	From experiments 18 and 23	= 63·634
VIII.	,, ,, 18 ,, 24	= 65·659
IX.	,, ,, 18 ,, 25	= 63·645
X.	,, ,, 19 ,, 23	= 93·628
XI.	,, ,, 19 ,, 24	= 63·653
XII.	,, ,, 19 ,, 25	= 63·638
	Average . ..	63·643
	Total average	= 63·645

Highest value = 63·664
Lowest ,, = 63·628
Greatest variation from mean = ±0·018
If Ag = 108, result previously published = 63·640
,, ,, accepted value (Hampe) = 63·37±

Each analytical result is combined with every other result above, in order that a better idea may be obtained of the variations of the figures. The combination of the averages of the three series of analyses would of course have given the same final average in a much more simple manner. Of the tabulated experiments, No. 23 is the least reliable, for the reasons before given; and rejecting values VII. and X. upon this gound, the total average would become 63·648, with a "probable error" of about ±0·002.

The importance and value of the method of analysis, involving as it does the weighing of the silver used as well as of the argentic bromide formed, must be at once evident. Not only does the method give two wholly distinct classes of results for the atomic weight of copper, but besides this the relative weights of silver and bromine afford the sharpest possible test of the purity of the materials and the accuracy of the work. This method was first used by Professor Cooke in verifying the atomic weight of antimony, and he strongly insisted on the strength of the evidence thus furnished;[*] although the point has been strangely overlooked by commentators.

Percentage of Silver in Argentic Bromide.

From experiments 20 and 23	= 57·454
,, ,, 21 ,, 24	= 57·448
,, ,, 22 ,, 25	= 57·447
Average	= 57·450 –
Average rejecting expt. 23 as before	= 57·448 –
According to Stas	= 57·445

Previous determinations made in this Laboratory by various experimenters have given values ranging from 57·442 to 57·450

The agreement of the present value of the atomic weight of copper with the result which I previously published in the *Proceedings of the American Academy of Arts and Sciences*, vol. xxiii., p. 180, is a rather remarkable one, especially since the methods of work were wholly different in the two cases. The very slight difference between the preliminary and final results of this

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[*] Contributions from the Chemical Laboratory of Harvard College. —From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxv.

[*] *Proceedings of the American Academy of Arts and Sciences*, xvii., 19; also Huntington on "Atomic Weight of Cadmium," *Ibid.* xvii., 28.

paper has already been explained, so that all the experiments which have been tried in this laboratory point to precisely the same figure.

In this connection it is worthy of notice that H. Baubigny,* a recent experimenter upon the atomic weight of copper, dried cupric sulphate at 440° without evidence of the formation of basic salt, and from the weight of copper oxide produced by the ignition of this salt obtained the value 63·47 for the constant under discussion. Baubigny's experiments are too briefly described to be fairly discussed, but their evidence agrees with that of the results of Shaw† in pointing toward a higher value of the atomic weight of copper than that usually accepted.

In the critical review of the present investigation it must be remembered that three distinct methods have been used, the last two being united for the sake of convenience. The chief probable constant error in the first series, given in the two preceding papers, is the chance of a secondary reaction between the copper and the argentic nitrate; but the purity of the silver produced, the absence of the slightest gas evolution during the progress of the chemical action, and the total lack of effect of dilution upon the final result, alike point to the conclusion that no such secondary action took place. In the research upon cupric bromide the chief probable constant error which could raise the observed atomic weight of copper is the presence of basic salt in the solution, but the final crystallisation of a neutral salt from an acid solution makes this chance very unlikely. Moreover, the basic salt was shown to be perfectly insoluble in water, and a direct experiment with methyl-orange proved the solution to be normal.

While no experimental knowledge can be said to be even relatively certain, and these with all other results are submitted only to be revised, and perhaps changed, by later experimentation, careful thought seems to show that the presumption is now upon the side of the later determinations of the atomic weight of copper.

During the last few years the atomic weights of antimony‡ and of cadmium§ have also been determined in this Laboratory, and have been referred to the same elements as those used in the present work. A statement of the final comparison might not be uninteresting.

Ag : Br : Sb : Cd : Cu = 108·00 : 80·00 +
+ : 120·00 : 112·31 : 63·64.

The collective results of the research must now be referred to the various different units of atomic weight usually adopted. Recently, an investigation‖ has been conducted here upon the atomic weight of oxygen, and since then many other investigators¶ have taken up the same subject, all but one** confirming the result of that work. In view of this fact, and also in the light of the recent re-calculation of Stas's results,†† it seems not out of place to state the value of the atomic weight of copper upon the basis O = 15·87, as well as according to the usual standards.

Atomic Weight of Copper.

If Ag = 108·00	From [Cu : 2Ag]	Cu = 63·640
	From [$CuBr_2$: 2AgBr]	Cu = 63·648
	From [$CuBr_2$: 2Ag]	Cu = 63·643
	Average	= 63·644
If Ag = 107·93	(O = 16·000)	Cu = 63·60
If Ag = 107·675	(Clarke)	Cu = 63·45
If Ag = 107·66	(Meyer and Seubert)	Cu = 63·44
If Ag = 107·06	(O = 15·87)	Cu = 63·09

In conclusion, the writer would express his deep sense of obligation to the kind friends whose interest and advice have so materially assisted the progress of the investigation.

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* *Compt. Rend.*, xcvii., 854, 906.
† *Phil. Mag.*, 5th Series, xxiii., 138.
‡ J. P. Cooke, *loc. cit.*
§ O. W. Huntington, *Proceedings American Academy*, xvii., 28.
‖ Cooke and Richards, *Proceedings American Academy*, xxiii., 149 and 182. Result, O = 15·87
¶ Lord Rayleigh, *Roy. Soc. Proc.*, xliii., 356 (1888); W. A. Noyes, *Am. Chem. Journal*, xi., 155, xii., 441; E. W. Morley, results as yet unpublished. Also discussions by Crafts, *Compt. Rend.*, cvi., 1662, and many others.
** Keiser, *Am. Chem. Journal*, x., 249. Result, O = 15·95.
†† J. D. Van der Plaats, CHEM. NEWS, liv., 186. These results point to a value of oxygen between 15·87 and 15·89.

SEPARATION OF BARYTA, STRONTIA, AND LIME.

By A. RUSSMANN.

(Concluded from p. 14.)

Method of E. Fleischer.

FOR the separation of barium, strontium, and calcium this method directs that the precipitated carbonates, after weighing, should be dissolved in a measured quantity of hydrochloric acid of known strength, the excess of acid titrated back, the barium precipitated with potassium chromate from the neutralised solution, the barium chromate being determined volumetrically with ferrous sulphate. The poportion of calcium and strontium is calculated from the amount of baryta found, and the quantity of hydrochloric acid consumed in dissolving the weighed carbonates after deducting the proportion belonging to the baryta.

Russmann has shown, in speaking of the method of Frerichs, under what conditions the determination of barium and its separation from strontium can best be effected. As for the volumetric determination of barium chromate with ferrous sulphate, it does not, according to Russmann, lead to satisfactory results. The washed precipitate was dissolved in hydrochloric acid, the barium thrown down with sulphuric acid, the filtrate titrated with ferrous sulphate, and the excess of the latter determined with permanganate. The results were always too low.

If only barium and calcium have to be determined in the absence of magnesia, Fleischer converts the barium into sulphate and the calcium into carbonate by digesting the solution of both with a mixture of 3 parts potassium sulphate and 1 part potassium carbonate. The precipitate is dried and ignited, and the calcium carbonate present is determined volumetrically.

According to the experiments of Russmann this method may be used successfully.

Method of W. G. Leison.

W. Gibbs has already shown that some metals may be determined by precipitating their sulphates, nitrates, or chlorides in a concentrated solution with oxalic acid and strong alcohol, and determining the oxalic acid in the precipitate by titration with permanganate. Alkaline salts must, of course, not be present.

Leison has applied this method to the determination of calcium, strontium, and barium. For the decomposition of the oxalates he uses either hot hydrochloric acid or ordinary dilute sulphuric acid. In the latter case the solution must be filtered through sand, as sulphuric acid dissolves matter out of paper filters, which is capable of acting upon permanganate. Barium oxalate cannot be completely decomposed by sulphuric acid, as the barium sulphate formed occludes undecomposed barium oxalate.

For the determination of calcium Russmann obtained good results with this method. He finds the use of paper filters admissible, even if the calcium oxalate is decomposed with sulphuric acid; but the titration must be effected in a very dilute solution to prevent a separation of calcium sulphate possibly accompanied by calcium oxalate.

Similarly satisfactory results were obtained on determining strontium oxalate. The sulphuric solution becomes, indeed, at once turbid, and a strong precipitate is formed on heating, but the strontium sulphate does not carry down any oxalate.

In determining barium, Russmann, like Leison, could not effect the complete decomposition of barium oxalate with sulphuric acid. If the precipitate was dissolved in hydrochloric acid, carefully avoiding excess, good results were obtained on titrating the highly diluted solution. In the majority of cases an ignition of the precipitates of the earthy oxalates is found more expeditious.—*Zeit. fur Anal. Chemie.*

ON THE

QUESTION OF CONCORDANCE IN ATOMIC WEIGHT DETERMINATIONS.

By F. W. CLARKE.

IN the determination of atomic weights the subject of constant errors has of late years received much attention. On the experimental side, that is with reference to individual series of data, the possibility of constant error is always carefully considered; but another phase of the question, involving antecedent values, is too apt to be ignored. Under the latter heading one special case is familiar to all chemists, namely, the uncertainty in the ratio between oxygen and hydrogen, in consequence of which we have two distinct standards for atomic weights, the one H = 1, the other O = 16. The difference between these standards is small in itself, but among the higher atomic weights it becomes multiplied to serious proportions. In other words, if the atomic weight of hydrogen be taken as unity, the uncertainty in the atomic weight of oxygen becomes a large constant error in the calculation of other values. This particular error is merely a type of its class; for whenever an atomic weight is computed from other atomic weights which are assumed to be known, their errors, together with the experimental errors of the determinations themselves, are accumulated in the final result. Thus it sometimes happens, when an atomic weight has been determined by different methods, involving the use of different compounds, that the concordance or discordance between the several series of data obtained may depend upon the factors assumed in the final calculation. These factors are themselves subject to errors, great or small, which become constant errors in calculation, and which, although cumulative in their effects, are commonly neglected altogether. Only those determinations of atomic weight which depend upon direct comparison of an element with the standard of value are free from errors of this class.

In a recent paper upon the atomic weight of cadmium, by E. A. Partridge,* the foregoing suggestions are well exemplified. Experimentally Mr. Partridge's work appears to be excellent, and on their face his results are concordant in the highest degree. Three methods were adopted for the determinations as follows:—First, the ignition of CdC_2O_4 to CdO; second, the conversion of $CdSO_4$ into CdS by heating in a stream of H_2S; third, a similar conversion of CdC_2O_4 into CdS. In each series ten experiments were made, and from each experiment individually the atomic weight of cadmium was computed. In brief, the results obtained were as follows, omitting details and taking O = 16 as the standard of comparison:—

	CdC_2O_4 : CdO.	$CdSO_4$: CdS.	CdC_2O_4 : CdS.
Cd = maximum,	111·834	111·818	111·833
minimum,	111·759	111·778	111·771
mean,	111·8027	111·7969	111·805

The mean of all is Cd = 111·8015, with an extreme range from lowest to highest of only 0·075.

Curiously, however, Mr. Partridge does not state what values he assumed for the atomic weights of carbon and sulphur in making his computations. Working back from some of his figures, I find that he must have taken the round numbers 12 and 32; and just here the question of concordance may be raised. In a re-calculation of the data I have reduced all the experiments to percentage form, getting the averages of the three series into the subjoined proportions:—

1st series, $CdC_2O_4 : CdO :: 100 : 63{\cdot}964;\ \pm 0{\cdot}0011.$
2nd series, $CdSO_4 : CdS :: 100 : 69{\cdot}199;\ \pm 0{\cdot}0012.$
3rd series, $CdC_2O_4 : CdS :: 100 : 71{\cdot}973;\ \pm 0{\cdot}0007.$

Now, when O = 16, these ratios give equations containing each an absolute term. If we compute with C = 12 and S = 32, we get one set of values for Cd; if we take Stas' figures, C = 12·005 and S = 32·074, we get another set; and if we assume the factors given in my own "Re-calculation of the Atomic Weights," viz., C = 12·001 and S = 32·058, we have still a third series. The results are as follows, in mean:—

	C, 12. S, 32.	C, 12·001. S, 32·058.	C, 12·005. S, 32·074.
1st series, Cd =	111·801	111·8036	111·8178
2nd series, Cd =	111·785	111·7271	111·7111
3rd series, Cd =	111·808	111·6054	111·5788
Range,	·023	·1982	·2390

Hence we see clearly that the concordance between the three series of determinations is conditioned, under the ordinary modes of calculation, by the uncertainties in the factors used. If the concordance shown by Partridge is real, Stas' values for C, or S, or both, are in error. If Stas' values are correct, then the three series of Mr. Partridge are discordant by nearly one-fourth of a unit in the atomic weight of cadmium. The small variations in the low atomic weights are multiplied in the higher figures.

In a discussion of this sort it is perhaps not possible to establish any distinct criterion of accuracy by means of which constant errors can be detected and placed. It is possible, however, at least in certain cases, to so handle data that the results of calculation shall involve no extraneous uncertainties. In the present instance the ratios measured by Partridge are capable of quite independent discussion, and by the simplest of means.

If we continue to put O = 16 as our standard of comparison, and use the symbols of the elements algebraically to represent atomic weights, the three proportions given above may be transformed into the following linear equations:—

1st series, $36{\cdot}036\,Cd = 127{\cdot}928\,C + 2493{\cdot}696.$
2nd series, $30{\cdot}801\,Cd = -\,30{\cdot}801\,S + 4428{\cdot}736.$
3rd series, $28{\cdot}027\,Cd = 143{\cdot}946\,C - 100\,S + 4606{\cdot}272.$

Here we have three equations with three unknown quantities, Cd, C, and S, and no assumption need be made in advance as to the value of either. Solving directly, these equations give us the following results:—

$$\begin{aligned} Cd &= 111{\cdot}7850 \\ C &= 11{\cdot}9958 \\ S &= 32{\cdot}0002. \end{aligned}$$

These values are independent of all other determinations, and contain only the errors of Partridge's own work, divided into three portions, instead of being accumulated upon the atomic weight of cadmium alone. They involve, however, the assumption that the three sets of observations are of equal weight, which may or may not be true. If different weights are assigned we must then form normal equations by the method of least squares, and their solution might modify our final figures. For present purposes, however, the more laborious method of computation, with its discussion of weights and probable errors, is quite unnecessary. Such a discussion may be found in Strecker's re-calculation of Liebig and Redtenbacher's

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* *Am. Jour. Sci.* Nov., 1890, p. 377.

data relative to the atomic weight of carbon.[*] So far as I know, that paper stands alone in chemical literature, the only one of its kind.

Recurring now to the three atomic weights deduced from the three equations, we find that the values for carbon and sulphur vary slightly from the best recognised determinations. The extent of that variation may perhaps serve as an index of the accuracy of the work done, and the question of concordance of data assumes a new form. The more nearly the figures for C and S agree with established values, the better the determinations probably are; and in the present case the agreement is close enough to establish a reasonable presumption in favour of Partridge's methods. The constant errors in his work cannot be large, and they are probably all in one direction.

But between Partridge's determinations, however discussed, and the atomic weight of cadmium as measured by either Dumas or Huntington, there is a discordance of nearly half a unit. The latter chemists, both working with haloid salts of cadmium, are in close agreement; and their data, with Stas' values for Ag, Cl, and Br, and with $O = 16$, make Cd about 112·23, very nearly. This discordance is probably real, and due mainly to differences in experimental methods. Its cause can only be found by further experiments, and certain lines of investigation are easily suggested. Apart from the obvious plan of scrutinising each method by itself, and seeking for the constant errors which must exist on one side or the other, it is clear that new modes of determination should be attempted, lying between and connecting the existing data. For example, the ratios $CdO : CdSO_4$, $Cd : O$, $Cd : S$, $Cd : Ag$, $Cd : Cl$, and $Cd : Br$ are all apparently capable of direct measurement; and they would, if determined, serve to check each other and to control the older determinations. A system of such interlacing ratios can be discussed collectively, by least squares, so as to distribute errors of observation, the constant error of any one series of data being equivalent to an accidental error in its relations to the other series. In a large system of ratios the constant errors can hardly be all in one direction, and they must tend to neutralise each other to a very considerable degree. Each ratio should contribute to our knowledge of every atomic weight involved in it, and not be considered solely with reference to a single component. The current methods of computation are fallacious in so far as they tend to magnify and accumulate errors which could be partially eliminated.—*American Chemical Journal*, vol. xiii., No. 1.

A CURIOUS FORMATION OF THE ELEMENT SILICON.

By H. N. WARREN, Research Analyst.

During the preparation of specimens of crystalline and other forms of silicon, I obtained a most curious formation of that substance, which would appear, when tested analytically, to be composed of graphitoidal silicon, constituted so as to form most perfect and well-developed crystals consisting of oblique octahedrons. This peculiar form of silicon first made its appearance upon subjecting potassium silicofluoride to a most intense heat in contact with impure aluminium. Upon separating the graphitoidal silicon thus formed by the aid of dilute acids, small quantities of the other substance was observed. Direct steps were at once taken to procure it, if possible, in larger quantities, after numerous experiments had failed to reproduce it; the following method was used with success, although still very uncertain. Graphitoidal silicon was first obtained by introducing pieces of metallic aluminium about the size of a walnut into a clay crucible of convenient dimension, and subjected to a heat sufficient to maintain in a fused state a mixture of four parts potassium silicoflouride, one of potassium carbonate, and two of potassium chloride. After the violent reaction attending the introduction of the aluminium had subsided, the crucible was urged to whiteness for about five minutes; after cooling and breaking the same a perfect round button containing about 80 per cent of silicon was obtained. This, after carefully detaching any adhering slag, was placed in a plumbago crucible containing about twelve times as much aluminium as the button obtained, together with an addition of two parts of metallic tin, and covered with a layer of sodium silicate. The crucible and its contents were then subjected to the most powerful heat that could be obtained for about two hours; after cooling the same and breaking the piece of aluminium contained therein, the new modification was obtained in large perfect crystals possessing a full metallic lustre and true models of oblique octahedrons. After dissolving the small quantity of aluminium mechanically entangled, the analysis of the residue showed pure silicon, insoluble in all acids except hydrofluoric and infusible. In appearance the crystals resemble crystals of cast-iron which are sometimes met with upon breaking a pig of that substance, the largest assuming a size of over half an inch across the faces, and as perfect as a crystal of alum.

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THE FILTRATION OF NATURAL WATERS.[*]

By THOMAS M. DROWN,
Member Boston Society Civil Engineers.

In the study of the subject of filtration of water for drinking purposes, we shall arrive at no clear and valuable ideas unless we distinguish sharply between mechanical filtration, which deals only with the interception and retention in the filter of the solid particles suspended in the water, and filtration combined with the oxidation of organic matter, — that in solution, as well as that in suspension in the water. This latter process —the purification of the water by the oxidation of its organic contents—can be accomplished only by *intermittent* filtration; the former—the mere removal of the solid particles in the water—may be accomplished by *continuous* filtration, as practised in many large cities in Europe.

When we speak of the purification of water by filtration, we mean in a general way, that a water is thereby rendered fit to drink which was unfit or unattractive before it was filtered. The change effected by filtration may be simply the removal of vegetable or earthy matters, whereby the water is made more palatable and more attractive in appearance, or it may be more radical, in converting water which was positively harmful into a good drinking water. Widely different in action as are the two systems of filtration, the intermittent and the continuous, yet it is possible by both systems to improve the quality of a bad water.

In the system of continuous filtration, in which there is little or no change made in the dissolved organic matter, it might at first thought seem as if there could be only imperfect purification; but it must be borne in mind that it is possible in this system to remove in great part even those very minute organisms, the bacteria.

The germ theory of disease furnishes us with the simplest explanation of the way in which water does harm, and if we can, by simple mechanical filtration, remove the harmful germs from the water, we have effected a true and efficient purification of that water, whatever

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[*] *Ann. Chem.* (Liebig) lix., 280 (1846).

[*] From a Paper read January 15, 1890. Reprinted in part from the *Journal of the Association of Engineering Societies.*

may be its chemical composition. Let us push this idea a little further. If we take as the basis of our theory of harmfulness of water that disease is caused by it only when micro-organisms are present in it, then, if we could by the continuous filtration of sewage remove absolutely all the germs which it contained, leaving unchanged its other characters — appearance, taste, odour, &c.—this sewage would be perfectly safe to drink. To put the matter in another form, a sterilised water or sewage has no possibilities of producing disease except so far as it may contain saline or other substances which may produce derangements of the system, in the same way as would a drug—a dose of salts or of senna. It is foreign to my present purpose to consider whether our knowledge at present justifies this position, but it is important to bear it in mind in judging of the efficiency of filtration.

When water is said to be well, or moderately well, or completely purified by filtration, we cannot know what is meant unless we know what is the standard of purity implied. Is it simply the removal of colour, odour, and suspended matter; is it chemical purity, meaning thereby the absence of unoxidised organic matter, or is it bacterial purity, or freedom from germs? Again, what shall we say of water of high chemical purity, with high bacterial contents; or what of a water with few or no bacteria which contains considerable organic matter capable of undergoing change?

Intermittent filtration is capable of giving water free from organic matter and free from germs; continuous filtration, if conducted very slowly, is capable of giving water free from bacteria, without odour and colour, but which may contain much dissolved organic matter. Intermittent filtration effects the oxidation of the organic matter in solution as well as that in suspension; continuous filtration has little or no effect on the organic matter in solution.

After laying such stress on the removal from water of bacteria, it sounds like a paradox to say that purification both by intermittent and continuous filtration depends on the presence in the filter of bacteria in enormous numbers, and that without them the purification would, in both cases, be impossible.

The idea is not a new one that the bacteria of decomposition are benign and useful organisms which break up organic matter, rearrange its atoms, and convert it into mineral matter, so that it may again serve as food for plants. If we keep away the bacteria from a mass of dead organic matter it undergoes no change whatever. All processes of decay of organic matter are absolutely dependent on the presence of these micro-organisms, which, so far as we know, have no other than a beneficent *role* to play in nature. I say this is now a matter of common knowledge, and one is therefore not unprepared to hear, that in the purification of water by intermittent filtration the ground or sand upon which the water is poured is full of bacteria; in fact, that it is the design of the process to cultivate them and have as many of the micro-organisms in a cubic inch of ground as possible.

If one pours over a column of clean, bright sand, free from bacteria, impure water, as sewage, it will flow out about as bad as it entered the sand. But if it is poured over a column of sand in which septic bacteria have been cultivated, so that the sand may be said to be fairly reeking with bacteria by the million, the water may flow out as pure (organically) as spring water. But even in continuous filtration, where there is little or no oxidation going on, the bacteria are, according to Piefke (the engineer of the Berlin water-works), the efficient agents in removing the suspended matters, including the micro-organisms in the water. To this subject we will return later; let us first briefly study the nature of oxidising or intermittent filtration on the typical polluted water, namely sewage.

Sewage is a substance which contains all of its nitrogen in the unoxidised form. Its principal ingredient is free ammonia; it also contains considerable (but a much less amount usually) organic nitrogen, or albumenoid ammonia, but of nitrous or nitric acid it contains none. When sewage is exposed to the air in mass, oxidation goes on very slowly, because it can only get air from its surface; when it flows out into streams, the oxygen dissolved in the water of the streams quickly oxidises the ammonia, and we find in the water a short distance below the entrance of the sewage nitrites and nitrates abundantly. When the sewage is exposed to the air in very thin layers, as when a porous material like sand is moistened with it, oxidation goes on with great rapidity. It was until recently considered that this oxidation was a direct chemical combination of the elements of the organic matter with the oxygen of the air, or the oxygen dissolved in the water, but we now know that nitrogen is not oxidised by the direct contact of decomposing nitrogenous matters with air unless bacteria are present, and the inference seems a fair one that the greater the number of bacteria the more rapid the process of oxidation. Sewage itself usually contains hundreds of thousands of bacteria to the c.c., which are dormant until air gets access to it. If sewage is preserved out of contact of air, the bacteria of decomposition will in time all die.

The experiments of the Massachusetts State Board of Health on the purification of sewage by intermittent filtration which have been carried on at Lawrence for the past two years, under the direction of Mr. Hiram F. Mills, the engineer member of the Board, have added largely to our knowledge of the conditions governing the purification of nitrogenous organic matter. Here are large tanks, one two-hundredth of an acre in surface, filled with different materials—coarse sand, fine sand, river silt, muck, garden soil, clay, &c., to the depth of five feet, on which is poured, from day to day, sewage in known amount and of known composition. The effluent water from this sewage filtration is collected, measured, and analysed, and the precise amount of purification determined. The result of two years' work at this station will shortly be published in the Report of the Board now in the press. I will at present give one or two of the facts that have been there developed. The purification of the sewage means the complete oxidation of all its organic ingredients both in solution and in suspension, the carbon to carbonic acid, the hydrogen to water, and the nitrogen to nitric acid. The filtering materials best adapted to the purpose are those which are fine enough to retain considerable sewage in their pores, and also plenty of air at the same time.

The body of porous material is, when in good working order, a very delicate machine. It must be coaxed up to its high efficiency by gradually increasing the amount of sewage. This means, in all probability, that we must develop in the pores of the sand an immense number of bacteria to be constantly on hand in the different layers to attend to the sewage as it reaches them. During the first winter there was no nitrification in these tanks, and consequently no perfect purification, but on the advent of spring, when the temperature of the effluent water reached 39° F. nitrification began and has continued ever since, the cold weather of the second winter failing to stop it.

The tank which has given the best results, that is, a good purification of the largest quantity of sewage for a long period, is filled with course mortar sand, most of the grains of which average about 0·06 in diameter. This has given an effluent day after day organically as pure as many drinking waters, when receiving sewage at the rate of nearly 60,000 gallons per acre per day.

One would naturally ask why is not this the ideal system of purification of all surface waters, even those that are not polluted by drainage of any kind, but which contain much vegetable suspended matter, and have, in consequence, sometimes a bad odour; or waters which are unattractive in appearance by reason of dissolved colouring matter?

One of the tanks of the Lawrence Experiment Station has filtered Merrimack water intermittently for more than two years at the rate of 300,000 gallons per acre per day. The filtering material consists of 3′ 8″ of coarse and fine sand and fine gravel; 10″ of yellow sandy loam, and 6″ of brown soil in the same position as found on the river bank. During the day the surface of the sand is generally covered with a few inches of water, but at night and on Sunday air gets access to the sand. The following figures give the composition of the filtered water during last December, compared with the Merrimack water applied:—

	Merrimack River Water. Parts per 100,000.	Filtered Water. Parts per 100,000.
Turbidity	Very slight	None.
Sediment	,,	,,
Colour	0·35	0·0
Odour	Faintly vegetable	,,
Total solids	4·2	3·5
Loss on ignition	1·6	0·9
Free ammonia	0·0015	0·0005
Albumenoid ammonia	0·0127	0·0059
Chlorine	0·18	0·18
Nitrogen as nitrates	0·0124	0·0191
,, ,, nitrites	None.	None.

The water is free from microscopic organisms, and the bacteria rarely exceed 10 or 20 per c.c., while the water applied has generally a few hundred. During the two years that this tank has been in operation the surface has not been cleaned or disturbed in any way. The slow rate of filtration (being only about one-half an inch an hour per square foot of surface), is due to the considerable amount of very fine material contained in the soil and loam.

But one must bear in mind, in connection with the rate of filtration, that the thoroughness of the purification, meaning thereby the oxidation of the organic matter, is much greater in intermittent than in continuous filtration.

This system of intermittent filtration for natural waters has never, I believe, been carried out on the large scale, although the possibility of its being practicable in some localities has been discussed. It is the system that nature suggests, for it is intermittent filtration which supplies the springs, which furnish the ideally pure and perfect drinking water. In the report of the Massachusetts State Board of Health to the Springfield Water Board with regard to the purification of the water of its Ludlow reservoir, which contains an immense growth of blue-green algæ, Mr. Stearns, the chief engineer of the Board, suggested that surveys be made to discover, if possible, suitable ground conveniently situated, on which to pour intermittently the water of the reservoir, and to collect it again at lower levels in wells and springs. It is probable that continuous filtration would be inapplicable to water of this kind, for the jelly-like masses which are secreted by these algæ would probably close the pores of the filter in a very short time. With intermittent filtration the deposit of organic matters in the pores of the sand would dry out or become oxidised when the ground was more or less dry.

It has been to many a difficult matter to explain how filters working continuously, and constantly covered with water, could intercept objects so much smaller than the spaces between the particles of sand, It was easy to imagine that some of the minute suspended particles might be caught between the particles of sand, but that practically all the suspended matter, even the minute bacteria, could be removed in a good-working filter, seemed to indicate that the efficient working of a filter depended on the fact that it became nearly clogged on the surface by the algæ and other matter which held back even the smallest objects. But if this were the case it would save time to use a finer sand at the outset which experiment shows will not accomplish the purpose.

Piefke* has given us the clearest conception of the action of sand filters in removing the suspended matters, including bacteria, from surface waters. The chemical effect is very slight, as might be supposed when one reflects that the duration of the passage of the water through the sand seldom, if ever, exceeds five and a half hours, and since the filter is kept constantly covered, there is no oxygen present but that dissolved in the water. But the mechanical effect in removing suspended matter, mineral and organic, is very great. The Spree water, which forms part of the supply of Berlin, contains as high as 100,000 bacteria per c.c. at times, and the number in the filtered water rarely exceeds 100, that it, the reduction of bacteria may reach 99·9 per cent. The thickness of the sand layer is generally from 2′ to 3′, and this rests on a layer of coarser gravel which is without any effect on the filtration. The size of the sand is seldom finer than one-fiftieth of an inch, which leaves channels between the grains that 500 micro-organisms could pass abreast. Smaller still are the particles of clay which give a milkiness to water; and yet when one of these sand filters is working well, both clay and bacteria are held back in the sand.

It takes a new filter about two weeks to get to its maximum efficiency, and if the sand be first carefully cleaned and sterilised by heat, then it takes much longer, many weeks, before the filter works well.

On examining with the microscope the surfaces of the particles of sand when the filter is in perfect working order, they are found to be coated with a greasy, slimy substance which is a mass of bacteria jelly. Piefke found in a kilogrm. of sand taken from the surface of a filter 5,600,000,000 bacteria; just below the surface 734,000,000, and at the depth of a foot 92,000,000. These numbers, he says, are far below the truth, because of the difficulty of cleaning the particles of sand thoroughly. It is to this coating of bacteria jelly that Piefke attributes the efficiency of these filters, and until the jelly forms in sufficient amount to completely envelope each particle of sand, the filters work imperfectly. This, then, is his explanation of the fact that minute micro-organisms and particles of clay of infinitely smaller size than the channels in the sand are stopped in their passage through it—they are simply caught in this slimy coating and cannot get further.

A filter of this kind is, like that used in intermittent filtration, a very delicate instrument, and it is very easy to disarrange it. Disturbance of the sand or suddenly increasing the pressure of the water may have, as a consequence, a rush of bacteria into the filtered water. Quite regular working is an essential condition of success. The rate of filtration is on an average only four inches vertically an hour, so that in the passage of the water through the sand, one-third of which is interstitial space, its rate is three times as great, or twelve inches an hour, and the sand layer, being two feet thick, the water is in contact with the sand only two hours. In very turbid waters, or waters very high in bacteria, the filtration is often decreased to one-half this rate, or even less, and in comparatively clear water, with low bacteria, the rate may be doubled. The working of the filters in Berlin is governed entirely by the number of the bacteria in the filtered water, this being the simplest way of judging of the efficiency of their working. One hundred bacteria per cubic centimetre in the filtered water is considered a good result on the Spree water, which contains always many thousands. To give practically sterile water would require a diminished rate say to one vertical inch an hour, which would be impracticable without enlarging the filtering plant.

(To be continued).

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* "Mittheilungen über natürliche und künstliche Sandfiltration," pp. 75, Berlin, 1881.

"Die Boden Filtration," p. 51, Berlin, 1883.

"Die Principien der Reinwasser Gewinnung vermittelest Filtration," p. 50, Berlin, 1887.

"Aphorismen über Wasserversorgung von higienisch—technischen Standpunkte aus bearbeitet."—*Zeitschrift fur Hygiene*, 1889, Vol. 7, p. 115.

With C. Frankel.—Ueber die Wirksamkeit der Sandfiltration zur Befreiung des Trinkwassers von etwaigen Infectionskeimen.—*Zeitschrift fur Hygiene*, 1890, I.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

January 16, 1891.

Prof. W. E. Ayrton, F.R.S., President, in the chair.

The thanks of the meeting were unanimously accorded to the Maxwell Memorial Committee for presenting to the Society a copy of Maxwell's Scientific Papers.

Prof. G. M. Minchin, M. A., read a paper on "*Photo-Electricity.*"

His experiments on the subject were commenced in 1877, in attempting to produce a photographic image of a distant object. The result sought for has not hitherto been obtained, but the experiments have led to the discovery of many interesting phenomena. Some of these were shown to the meeting.

Electric currents are produced by the action of light on silver plates coated with collodion or gelatin emulsions of bromide, chloride, iodide, and other silver salts, or with eosine, fluorescine, and other aniline dyes, when the plates are immersed in a suitable liquid, and one plate is illuminated whilst the other is screened. The direction of the currents depend on the materials employed, and the blue end of the spectrum is most effective. Currents have a photographic effect on the plates, and this action is strictly confined to the parts through which the current has passed.

Comparatively strong currents are obtained from plates coated with eosine and gelatin. A curious reversal was observed with some cells, the exposed plate first being positive to the screened one, and almost immediately afterwards became negative. On shutting off the light, a transient increase of current resulted, and afterwards disappeared gradually.

M. Becquerel, who has studied the action of silver plates coated with bromide, &c., concludes that the nature of the exposed plate (whether positive or negative) depends on the thickness of the surface layer. The electromotive force of such cells rarely exceeds one-twentieth of a volt.

Uncleaned tin-foil plates in common tap water give a current when one is exposed to light and the other screened. Cleaning the plates destroys the effect. In nearly every case the exposed plate was first positive and after a time became negative; and by exposing various parts of a plate (some portions of which had been previously exposed) the currents could be varied in direction at will. These peculiarities may explain the known divergence of tin from Volta's law. The phenomena have also been studied by aid of the electrometer. Tin foil obtained from tobacco packages was found to be very sensitive to light. One side of such foil is dull and the other bright. By pasting slips of it on opposite sides of a glass plate so that dissimilar sides are outermost, and immersing them in alcohol, a cell giving an E.M.F. of $\frac{1}{16}$th volt when the dull side was exposed to light was obtained. The addition of any salt to the liquid, with a view to diminishing the resistance, invariably reduced the E.M.F. Experiment showed that the alcohols were by far the best liquids to use with tin plates.

A process for producing very sensitive tin plates was described, which apparently results in the formation of white oxide of tin on the surface of the foil. With one such plate and another sensitised plate the best results have been obtained by immersing them in methyl alcohol prepared from oil of wintergreen. From experiments on the variation of E.M.F. with intensity of light, it was found that the square of the E.M.F. is proportional to the intensity.

Some tin cells behave in a very peculiar manner, for it often happens that a good cell will exhibit no E.M.F. after being kept a few days. A slight impulse or tap given to the cell or its support restores the sensitiveness; another impulse makes the cell insensitive; and these effects can be repeated indefinitely. Such cells the author calls "impulsion cells," and some were exhibited at the meeting. The sensitised plate of one of these cells had different properties at its two ends, for impulses had no effect on the nature of the lower end, but changed the upper end from positive to negative and *vice versâ*. Electro-magnetic impulses, such as produced by sparks, are capable of altering cells from the insensitive to the sensitive state, but fail to produce the reverse effect. A Hertz oscillator restored the sensitive state in a cell placed at a distance of 81 feet away. The "impulsion effects" can be got rid of by renewing the alcohol on several successive days.

During last year, the author made some selenium cells by spreading the melted substance on metal plates and immersing them in liquids together with an uncoated plate. Of the various metals and liquids tried, aluminium and acetone gave the best effects. The process of forming these "seleno-aluminium cells" was described. One of their peculiarities is that they are nearly equally sensitive to rays of all colours, and when exposed to strong light may give an E.M.F. of $\frac{1}{2}$ to $\frac{2}{3}$ of a volt, the sensitised plate being negative. An arrangement of 50 cells in series, with an electrometer, was exhibited, whereby the E.M.F. generated by light falling on the cells could be caused to ring a bell, light or extinguish electric lamps, &c.

In conclusion, the author pointed out the possible application of photo-electricity to photometry, telephotography, and the utilisation of solar energy.

At the request of the President, Prof. Minchin promised to show the experiments on February 13th, on which date the discussion on the paper is to take place.

Prof. F. R. Barrell, B.A., exhibited and described "*A Lecture Room Apparatus for Determining the Acceleration due to Gravity.*"

A number of iron balls are allowed to fall through a certain height in such a way that one starts off when its predecessor has arrived at its destination. From the time occupied by all the balls, the time for one can be found, and, knowing the distance traversed, "*g*," can be determined.

The apparatus consists of two electro-magnets, joined in series with a battery and key, together with a ball-feeding device. One of the magnets is vertically over the key, and serves to catch the balls as they emerge from the feeding tube, whilst the other magnet actuates a kind of slide for supplying successive balls.

When one ball falls on the key it breaks circuit, and thus causes the first mentioned magnet to let go its ball. The key then springs up again, thus making circuit, and the feeding magnet then supplies another ball, which is caught by the holding magnet until the falling ball reaches the key, and the operations are repeated. Fairly accurate results can be obtained by the apparatus.

Sir John Conroy's paper, "On the Change in the Absorption Spectrum of Cobalt Glass by Heat," was postponed.

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. cxii., No. 1, January 5, 1890.

On the Explosive Wave, on the Characteristic Data of Detonation and its Speed of Propagation in Solids and Liquids, and especially in Methyl Nitrate.—M. Berthelot.—The explosive wave with its simple characters and its definite laws exist only in the detonation of gases. These laws and characters exist only in part in the detonation of liquids and solids.

On the Absorption-Spectra of Solutions of Iodine.—H. Rigollot.—Among homologous bodies or compounds of one and the same radicle used as solvents for iodine, it is found that as the molecular weight increases, the absorption band advances very slightly towards the violet end of the spectrum, whilst the minimum of light transmitted diminishes.

Influence of the Co-Volume of Gases upon the Speed of Propagation of Explosive Phenomena.—M. Vieille.—The speed of propagation of a very small shock, like the speed of sound in a very hot liquid, increases very rapidly with the gaseous condensation.

On the Conductivities of Isomeric Organic Acids and of their Salts.—D. Berthelot.—This paper is not adapted for useful abstraction.

On Triethenyl. — Adolphe Rénard. — Triethenyl forms yellow needles, which melt at 147° to a yellow liquid. It boils at 357°. It is very soluble in benzene, ether, chloroform, less soluble in alcohol, acetic acid, and petroleum essence. Its vapour density is 8·6, or theoretically 8·68.

Action of Sodium Benzylate upon Camphor Cyanide.—J. Minguin.—The author obtains a solid body which crystallises in fine transparent laminæ, melting at 70—71°. It dissolves readily in benzene, toluene, and xylene, even in the cold. It is less soluble in ether and in the methylic ethylic and propylic alcohols. Its rotatory power is $a_D = +428°$; its composition is—

$$C_{18}H_{23}O_2N.$$

A General Method of Analysis of the Spirits and Alcohols of Commerce.—Ed. Mohler.—This paper will be inserted in full.

Revue Générale des Sciences Pures et Appliquées.
Vol. i., No. 23.

Recent Researches on Starch and the Diastases.—B. Petit.—The author recognises on the one hand the intervention of a diastase in the migration of starch from the leaves of plants to their seeds, and on the other hand the mode of action of the diastase and the composition of the extract of malt. But the constitution of starch is still unknown, and both the composition and the origin of the diastases have not been ascertained.

Journal de Pharmacie et de Chimie.
Vol. xxii., No. 2.

On the Densimetric Determination of Alcohol in Wines on the Principle of Tabarié.—Léon Perier.—The author deduces the alcoholic strength of wines from the difference between the specific gravity of the wine in its natural state, and when the alcohol has been expelled. His results are given in a table.

Colorimetric Method for Determining Tannin in Barks.—S. J. Hinsdale (*Amer. Jour. of Pharmacy*).—The author first prepares a ferric liquor by dissolving 0·04 grm. potassium ferricyanide in ½ litre of water, and adding 1½ c.c. solution of ferric chloride. A tannic solution is then made by dissolving the same weight of pure tannin in an equal vol. of water. The substance in which it is intended to determine the tannin (oak-bark, galls, sumacs, catechu, &c.), is brought in contact with a little boiling water, and the solution is then diluted with cold water. For substances containing less than 10 per cent of tannin he operates upon 0·8 grm., and makes ½ litre of solution; if from 10 to 20 per cent it is diluted 1 litre. On the contrary, if there is less than 1·5 per cent he operates with 8 grms. instead of 0·8 grm. Six flat-bottomed glasses are set upon white paper, and in the first there are put 5 drops of the solution to be titrated; into the others there are put, respectively, 4, 5, 6, 7, and 8 drops of the solution of tannin. To each there are then added 5 c.c. of the ferric liquor, and after the lapse of three minutes he observes the tint of the tannin solution which corresponds the most closely with the solution under examination.

Vol. xxii., No. 3.

On Tetrachlorophenol.—Louis Hugounenq.—This compound has been obtained by saponifying anisol tetrachloride by hydriodic acid of specific gravity 1·7. The The tetrachloro-anisol is heated for twenty hours in a closed vessel to 145°—148°, with four times its weight of acid. The composition of the product obtained is $C_6HCl_4.OH$. It is produced in white needles, which when pure melt at 152°. The new compound is insoluble in water, but soluble in all organic solvents, and boils at 278°. The alcoholic solution behaves like an acid with indicators, and it decomposes carbonates. It is not poisonous.

The Odoriferous Principle of the Seeds of Rosa Canina.—This odour is found to be actually due to the presence of vanillin in the seeds to the extent of 0·1 part per 1000. Vanillin has also been recognised in the seeds of the white lupin.—*Journal de Pharm. von Elsass Lothringen.*

MEETINGS FOR THE WEEK.

Monday, 26th.—Medical, 8.30.
—— Society of Arts, 8. "The Construction and Capabilities of Musical Instruments," by A. J. Hipkins, F.S.A.
Tuesday, 27th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S., B.S., F.R.C.S., Fullerian Professor of Physiology, R.I.
—— Royal Medical and Chirurgical, 8.30.
—— Society of Arts, 8. "Lithography: A Finished Chapter of Illustrative Art," by William Simpson.
Wednesday, 28th.—Society of Arts, 8. "Illustrated Journalism," by Carmichael Thomas.
Thursday, 29th.—Royal, 4.30.
—— Royal Institution, 3. "The Little Manx Nation," by Hall Caine.
Friday, 30th.—Royal Institution, 9. "British Mosses," by The Right Hon. Sir Edward Fry, Lord Justice, F.R.S., F.S.A., F.L.S.
Saturday, 31st.—Royal Institution, 3. "Pre-Greek Schools of Art," by W. Martin Conway, M.A., F.S.A.

THE CHEMICAL NEWS.

Vol. LXIII. No. 1627.

THE TELLURIC SCREW.

Many of our readers will have felt surprised by the recent announcement that MM. Lecoq de Boisbaudran and A. de Lapparent have discovered a new claimant for priority in the recognition of the Periodic Law. Their surprise will not be lessened when they see the memoir which was read on the 12th instant, and which we reproduce textually. The chemist who is said to have anticipated Mr. J. Newlands, and *a fortiori* Professor Mendeleeff and Professor Lothar Meyer, in announcing the periodic arrangement of the simple bodies is M. Béguyer de Chancourtois. His researches, made known in 1862, have not been disinterred from some forgotten "*pli cacheté*," or found in the back numbers of some obscure journal. They are to be seen in the *Comptes Rendus!* Hence, MM. de Boisbaudran and Lapparent seek to know how these documents can have escaped the attention of Mr. Newlands? To answer one question by another we must ask how they can have escaped the notice of M. de Boisbaudran and his friend for a term of nearly twenty-nine years to be at last suddenly sprung upon the world?

The Periodic Law, it must be remembered, when first announced was not immediately accepted. When Mr. Newlands read his memoir before the Chemical Society (March, 1886), it by no means met with a very enthusiastic reception. One gentleman present even inquired, sarcastically, whether the author "had ever arranged the elements according to the order of their initial letters?" but no one suggested any anticipation.

Then came the announcement by Professors Mendeleeff and L. Meyer of their independent and simultaneous discovery of the same truth. The details were quickly circulated and discussed in the scientific press, and the respective merit of the two savants was for a time a bone of contention. Professor Mendeleeff said (Chemical News, vol. xliii., page 15):—"It is possible that Newlands has, prior to me, enunciated something similar to the Periodic Law, but even this cannot be said of L. Meyer." Yet none of all the authorities who criticised or applauded the new discovery suggests that Newlands, Mendeleeff, and Meyer might all have been anticipated. When M. Lecoq de Boisbaudran made his discovery of gallium he seemed not gratified at the assertion that its existence and its properties had been foreseen in accordance with the Periodic Law. But he made no reference to the "Telluric Screw."

When the successful attempt was made to vindicate the claims of Newlands as the first discoverer, the question was thoroughly re-discussed. But none of the savants who entered into the question ever breathed the name of De Chancourtois. His memoirs were at all times accessible in the *Comptes Rendus.* But no one found in them that meaning which MM. de Boisbaudran and de Lapparent now assert. They certainly contain a proposal to classify the elements with reference to their atomic weights. But we may be permitted to doubt whether they can be fairly considered as the germ of the Periodic Law.

In going over old researches we often find in them matter which we may now regard as a forecast of subsequent discoveries; but there is no sufficient evidence that the author disentangled such matter from accompanying speculations. In the third paragraph from the end of the memoir which we have translated, we find an admission that such has been the case with the writings of M. de Chancourtois. Were his writings placed textually before us in lieu of the paraphrase of MM. de Boisbaudran and de Lapparent, we should, doubtless, see the reason why they have had no influence on the development of chemical science.

A RECLAMATION OF PRIORITY ON BEHALF OF M. DE CHANCOURTOIS REFERRING TO THE NUMERICAL RELATIONS OF THE ATOMIC WEIGHTS.

By MM. LECOQ DE BOISBAUDRAN and A. DE LAPPARENT

In 1884 Mr. John Newlands collected under the following title, "On the Discovery of the Law of Periodicity, and on Relations among the Atomic Weights," a number of memoirs which he had previously published in the Chemical News during the years 1864, 1865, and 1866.

The object of the publication was to claim on behalf of Mr. Newlands the priority of the announcement of certain numerical relations which exist among the atomic weights, and which enable us to group the simple bodies in natural families. The author took care to establish that his researches had preceded those of Professor Mendeleeff, and he affirms that he was the first to publish (on July 30th, 1864), a list of all the elements known arranged in the order of their atomic weights.

It is not our intention to contest the merit of the well-known works of Mr. Newlands. Our object is merely to establish that the priority in this matter does not belong to him, as several of the ideas which he believes he was the first to announce in 1864 had been formulated two years previously by a French savant before the Academy of Sciences.

On April 7th, 1862, Béguyer de Chancourtois, at that time Chief Engineer and Assistant Professor of Geology at the School of Mines, presented to the Academy a work entitled: "On a Natural Classification of the Simple or Radicle Bodies entitled 'The Telluric Screw.'" In two subsequent communications (April 21st and May 5th, 1862), the author furnished supplementary details. On October 13th of the same year, he presented to the Academy a lithographic table which summed up all his ideas. Finally, on March 16th, 1863, he concluded with certain general considerations on the numerical character of the simple bodies, as well as on the verifications which spectral analysis might furnish. In this paper is found the very explicit assertion that "the properties of bodies are properties of numbers."

The fundamental idea of the "telluric screw" consists in writing the values of the atomic weights along the generatrix of a vertical cylinder, the circular base of which was divided into 16 equal parts, 16 being the atomic weight of oxygen. If we then trace upon this cylinder a helix with an angle of 45 to its axis, each point of the helix may be considered as the characteristic point of a simple body, the atomic weight of which to the proportional corresponding length of the spiral will be read upon the generatrix which passes by this point.

At each turn the helix returns on one and the same perpendicular at distances from the summit of the cylinder, which are entire multiples of 16, and mark the bodies whose atomic weights conform to this condition. In the same manner the various points of intersection of the helix with any of the 16 principal generatrices, correspond to elements whose atomic weights differ among themselves by 16 or a multiple of 16. Lastly, if after having developed the cylinder upon a plane which transforms the helix into a series of straight parallel segments, we join by a straight line any two points taken upon two segments, after coiling up this right line will produce a secondary helix, and the intersections of this latter with the various turns of the principal helix will mark bodies for which the differences of the atomic weights will be multiples of a constant quantity. In this manner, the development of the "telluric screw" by simply drawing right lines enables us to show simple numerical relations which it would have been less easy to detect by a mere inspection of the figures.

The relations thus established among the atomic weights correspond for the most part to real analogies in the properties of the corresponding elements. This Chancourtois affirmed in his first memoir, asserting that the "relations of the properties of bodies are manifested by simple relations of position of their characteristic points; and then that each of the helices carried through two characteristic points, and passing by several other points, or merely in their proximity, shows relations of properties of a certain kind, the analogies or the contrasts being manifested by certain numerical orders of succession like the immediate sequence or the alternations at diverse periods.

The "telluric screw" shows at once a classification of the elements according to the order of their atomic weights and the indication of a true periodicity. This is exactly what Mr. Newlands has claimed as especially belonging to him. It is not up to the comparison of atomic periodicity with the musical gamut, of which we cannot deny that it has been, if not proclaimed, at least "interviewed" by Chancourtois. For in his paper of May 5th, 1862, he says expressly: "We cannot refrain from remarking the predominance of the number 7 in the types of the groups occupying the spirals which are most occupied. . . . . We arrive easily at the idea of transforming the cylinder upon which the screw is realised into a sonorous tube pierced at the characteristic points." But especially when he published in 1863 a pamphlet containing, along with his memoirs to the Academy some additions which the plan of the *Comptes Rendus* had not allowed him to give *in extenso*. Chancourtois spoke of "direct developments of the system which enable us to perceive at the same time approximations of the series of numerical characteristics to the series of musical sounds, and to that of the bands and rays of the spectrum."

We are far from pretending that the theory of the screw is free from faults, and that the author has not grafted upon his work many considerations which he had better had left in the shade. Several approximations were inaccurate or were strained, and some of them evince a too great part allowed to the imagination. Confiding too much in the virtue of whole numbers (and even of primary numbers), Chancourtois set out with the idea that in the natural series the differences between the atomic weights ought to be constant (an error which, indeed, is also to be met with in the earliest researches of Newlands). If he, indeed, recognised certain gaps in the series of the elements, he endeavoured to fill them up by imagining new varieties of the known simple bodies (which he called *secondary characters*), and which often led him to arrangements little conformable to natural analogies.

Nevertheless, the "telluric screw" was, for its time, an original and even a fruitful conception, for it sufficed to let the author conjecture that the formula of zirconia should probably be written ZrO_2, that of beryllia BeO, and that of yttria Yt_2O_3. Further, nothing but the consideration of his helix could have suggested to Chancourtois the slight correction which it was proper to make in the atomic weight of cadmium.

How then does it happen that this publication, inserted in the most widely-circulated scientific journal in the world, the *Comptes Rendus*, has escaped the attention of Mr. Newlands, whose good faith cannot be doubted? It is, we believe, because the text of M. de Chancourtois, somewhat obscure in its conciseness, was not accompanied by any diagram, and that the original memoir circulated by the author had not a sufficiently wide distribution. We have therefore thought proper to join to this memoir (arranging it for simplicity in two parallel columns which should be joined end to end), a reduction of that part of the graphic table which extends from hydrogen to tellurium. The secondary helix has been traced which passes by sulphur, iron, selenium, tellurium, and which, if produced, would extend to gold.—*Comptes Rendus*, vol. cxiii., p. 77.

A NATIONAL CHEMICAL SOCIETY IN AMERICA.

The second general meeting of the American Chemical Society was held in the University of Pennsylvania, at Philadelphia, December 30th and 31st, 1890. Professor George F. Barker, M.D., President. The attendance was large, the arrangements for both business and for entertainment were excellent, and many valuable papers were read which will be published in the *Journal*.

Under the auspices of the American Chemical Society a conference of chemists, representing seven different bodies, assembled to consider the formation of a National Organisation of American Chemists. The societies or bodies represented by delegates were the following:—(1) Chemical Section of the American Association for the Advancement of Science. (2) American Chemical Society. (3) Chemical Section of the Franklin Institute, Philadelphia. (4) Chemical Section of the Brooklyn Institute. (5) Association of Official Agricultural Chemists. (6) Chemical Society of Washington, D.C. (7) Manufacturing Chemists' Association of the United States. The newly-formed Chemical Society of Cincinnati was not represented.

Professor Albert B. Prescott, of Ann Arbor, Michigan, President-Elect of the American Association for the Advancement of Science, was called to the chair, and Dr. H. Carrington Bolton, of New York, was appointed Secretary.

After a prolonged and interesting discussion the following resolutions were adopted.

Resolution 1.—It is desirable that an American Association of Chemists be formed to embrace all existing American Chemical organisations.

Resolution 2.—Resolved, That this conference recommend to all existing American Chemical organisations that they call a meeting of their bodies to be held in Washington, D.C., in connection with the meeting of the American Association for the Advancement of Science for 1891, and that each of these organisations be requested to appoint a committee, or to continue their present committee for the further discussion of the subject submitted to the conference now in session.

Resolution 3.—Resolved, That this general conference committee, composed of the present sub-committees, or such others as may be appointed by the several organisations, be called together at as early a time as practicable before the joint meeting recommended in Resolution 2.

Resolution 4.—Resolved, That meanwhile, each sub-committee through its chairman, by correspondence or otherwise, shall formulate such modifications of the Constitution of the American Chemical Society as it shall deem necessary to adapt it to the requirements of the Association proposed.

Resolution 5.—Resolved, That the chairmen of these sub-committees shall then, so far as possible, harmonise the views embodied in these reports of their several organisations, and shall have printed, for presentation at the joint meeting, a report, or minority and majority reports, on a constitution for the proposed Association of American Chemists.

The secretary of the conference was desired to communicate the above resolutions to Scientific Journals with a view to obtain a wide publication of the same.—Adjourned to meet at the call of the chairman.—H. Carrington Bolton, *Secretary of the Conference*.

ELECTRICITY *IN TRANSITU*: FROM PLENUM TO VACUUM.*

By WILLIAM CROOKES, F.R.S.,
President of the Institution of Electrical Engineers.

Introduction.

Whilst steadily bearing in mind that I have the honour to address a Society, not only of physicists, but of Electrical Engineers, I shall not, I hope, be out of order in venturing to call your attention to a purely abstract phase of Electrical Science. Numberless instances show that pure research is the abundant source from which spring endless streams of practical applications. We all know how speculative inquiry into the influence of electricity on the nervous system of animals led to knowledge of current electricity, and ultimately to the priceless possession of the telegraph and the telephone. The abstract study of certain microscopic forms of parasitic vegetable life has enabled us to give to fermented solutions of sugar the exact flavour and aroma of the most highly prized wines, and probably, ere long, will put us in a position to increase at will the fertility of the soil. In a different direction the same class of abstract researches applied to medical science has brought us within measurable distance of the final conquest over a large class of diseases hitherto incurable; and without egotism I may, perhaps, be allowed to say that my own researches into high vacua to some extent have contributed to the present degree of perfection of the incandescence lamp. Surely, therefore, whilst eagerly reaping and storing the harvest of practical benefits, we must not neglect to scatter more seed for future results, perchance not less wonderful and valuable.

In another respect I deviate to some extent from the course taken by many of my predecessors. I am about to treat electricity, not so much as an end in itself, but rather as a tool, by whose judicious use we may gain some addition to our scanty knowledge of the atoms and molecules of matter and of the forms of energy which by their mutual reactions constitute the universe as it is manifest to our five senses.

I will endeavour to explain what I mean by characterising electricity as a tool. When working as a chemist in the laboratory, I find the induction spark often of great service in discriminating one element from another, also in indicating the presence of hitherto unknown elements in other bodies in quantity far too minute to be recognisable by any other means. In this way, chemists have discovered thallium, gallium, germanium, and numerous other elements. On the other hand, when examining electrical reactions in high vacua, various rare chemical elements become in turn tests for recognising the intensity and character of electric energy. Electricity, positive and negative, effect respectively different movements and luminosities. Hence the behaviour of the substances upon which electricity acts may indicate with which of these two kinds we have to deal. In other physical researches both electricity and chemistry come into play simply as means of exploration.

In submitting to you certain researches in which electricity is used as a tool, or as a means of bringing within scope of our senses phenomena that otherwise would be unrevealed, I must for a moment recal to your minds the now generally accepted theory of the constitution of matter.

Kinetic Theory of Gases.

Matter, at its ultimate degree of extension, is conjectured to be not continuous, but granular. Maxwell illustrates this view as follows:— To a railway contractor driving a tunnel through a gravel-hill the gravel may be viewed as a continuous substance. To a worm wriggling through gravel, it makes all the difference whether the creature pushes against a piece of gravel or directs its course between the interstices. To the worm, therefore, gravel seems by no means homogeneous and continuous.

With speculations as to the constitution of liquid and solid matter I need not trouble you, but will proceed at once to the third or gaseous state of matter.

The kinetic theory of gases teaches that the constituent molecules dart in every possible direction with great but continually varying velocities, coming almost ceaselessly in mutual collision with each other. The distance each molecule traverses without hitting another molecule is known as its *free path*; the average distance traversed without collision by the whole number of molecules of a gas at any given pressure and temperature is called the *mean free path*. The molecules exert pressure in all directions, and are only restrained by gravitation from dissipating themselves into space. In ordinary gases, the length of the mean free path of the molecules is exceedingly small compared with the dimensions of the vessel, and the properties we then observe are such as constitute the ordinary gaseous state of matter, which depend upon constant collisions. But if we greatly reduce the number of molecules in a given extent of space the free path of the molecules under electric impulse is so long that the number of their mutual collisions in any given time in comparsion with the number of times they fail to collide may be disregarded. Hence, the average molecule can carry out its own motions without interference. When the mean free path becomes comparable to the dimensions of the containing vessel, the attributes which constitute gaseity shrink to a minimum, the matter attains the ultra-gaseous or "radiant" state, and we arrive at a condition where molecular motions under electrical impulse can easily be studied.

The mean free path of the molecules of a gas increases so rapidly with progressive exhaustion, that whilst that of the molecules of air at the ordinary pressure is only 1-10,000th of a millimetre, at an exhaustion of a hundred-millionth of an atmosphere—a point (which, with present appliances, is easy to attain) corresponding to the rarefaction of the air 90 miles above the earth's surface—the mean free path will be about 30 feet; whilst at 200 miles above the earth it will be 10,000,000 miles, and millions of miles out in the depth of space it will become practically infinite. I could go on speculating in spite of Aristotle, who said:—"Beyond the universe there are neither space, nor vacuum, nor time."

In discussing the motions of molecules we have to distinguish the *free path* from the *mean free path*. Nothing is yet known of the *absolute* length of the free path nor of the *absolute* velocity of a molecule. For anything we can prove to the contrary, these values may vary almost from zero to infinity. We can deal only with the *mean* free path and the *mean* velocity.

The Vacuum Pump.

As most of the experiments I put before you to-night are connected with high vacua, it is not out of place to refer to the pump by means of which these tubes are exhausted. Much has been said lately in recommendation of the Geissler pump and its many improvements, but I am still strongly in favour of the Sprengel, as with it I have obtained greater exhaustion than with any other. I should like to point out that the action does not stop when we cease to see air specks passing down the tubes but continues long after this point has been passed. Neither is the non-conducting vacuum, so easily obtained by the Sprengel pump, due in any way to the presence of mercury vapour, since non-conduction can be obtained just as rapidly when special precautions have been taken to keep mercury vapour out of the tubes.

One of the great advantages of the Sprengel pump over all others lies in the fact that its internal capacity need not exceed a few cubic centimetres, and there is, therefore much less wall surface for gases to condense upon. I have brought the very latest modification of this form

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* Inaugural Address delivered January 15th, 1891.

of pump here to-night, and you will have an opportunity of seeing it in action and of measuring with the McLeod gauge the rarefaction it produces.[*]

The Passage of Electricity Through Rarefied Gas.

The various phenomena presented when an induction spark is made to pass through a gas at different degrees of exhaustion point to a modified condition of the matter at the highest exhaustions. Here are three exactly similar bulbs, the electrodes being aluminium balls, and the internal pressures being respectively 75 m.m., 2 m.m., and 0·1 m.m. If I pass the induction current in succession through the bulbs, you will perceive in each case a very different luminous phenomena. Here is a slightly exhausted tube (Fig. 1), like the first in the series just exhibited (75 m.m.), the induction spark passes from one end to the other, A, B, and the luminous discharge is seen as a line of light, acting as a flexible conductor. Under the tube I have an electro-magnet, C, and on making con-

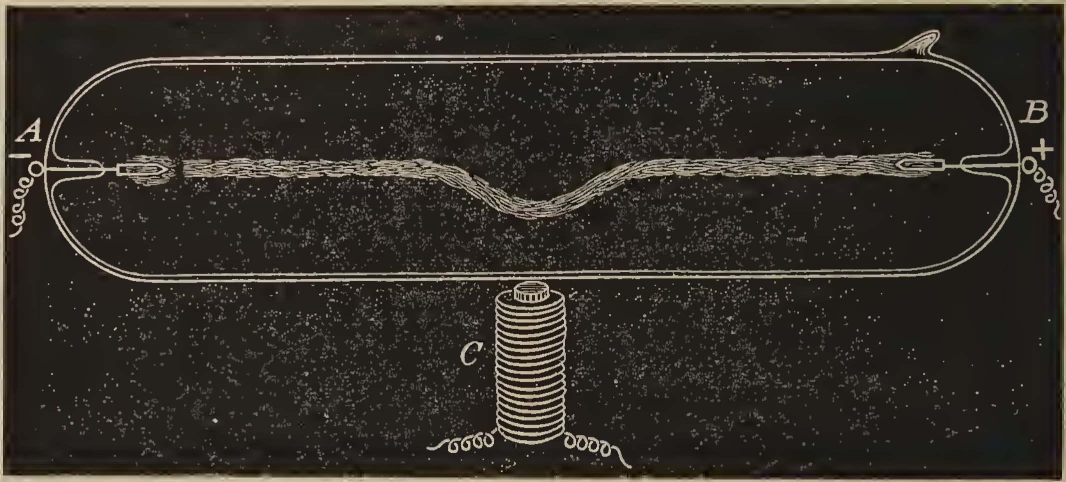

Fig. 1.—P. = 75 m.m.

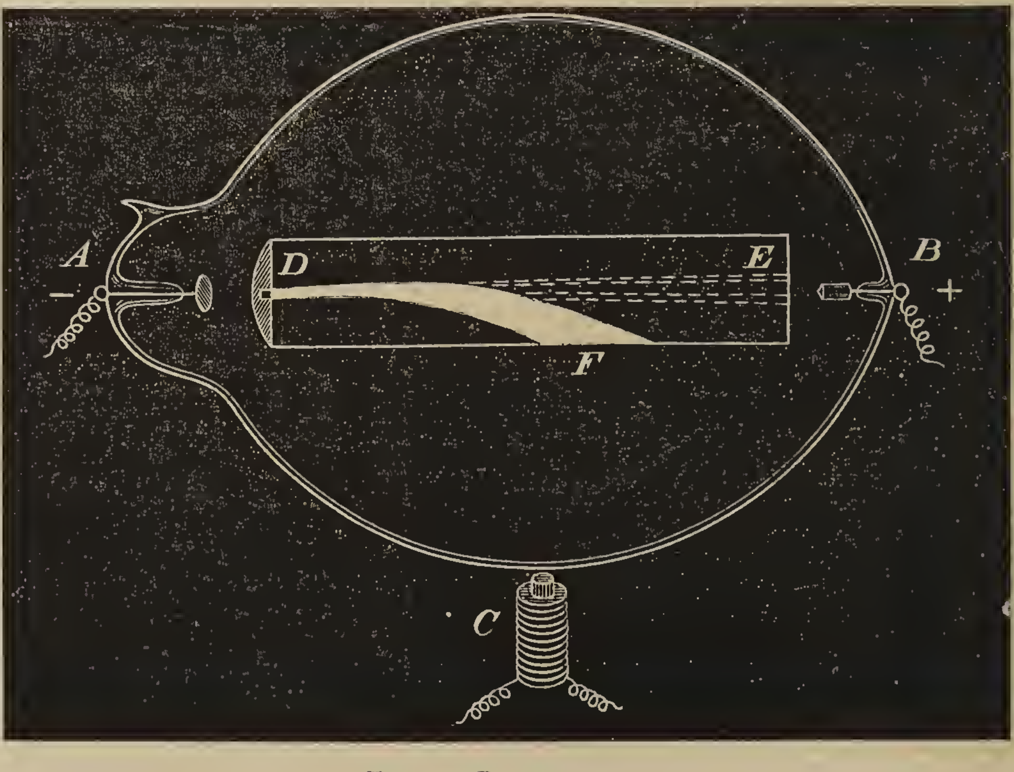

Fig. 2.—P. = 0·1 m.m.

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[*] My measurements of high vacua have all been taken with the beautiful little gauge devised by Professor McLeod. Unmerited discredit has recently been cast on this gauge, the principal fault alleged being its inability to distinguish between the tension of the permanent gas and that of the mercury vapour present. Now it is evident that, under ordinary circumstances, the tension of mercury vapour may be disregarded, as it will be the same on both sides of the gauge; and it will be only in cases where no mercury is present on one side of the gauge that a slight error is introduced. It is, however, very difficult to devise and successfully experiment with apparatus in which a trace of mercury vapour shall not enter, and it is not likely that an experimentalist who would be working with such mercury-free apparatus would attempt to use the gauge without remembering that in this special case the indications would be incorrect. To use the McLeod gauge requires much patience and some amount of experience, but I have always found it trustworthy to register exhaustions far beyond the millionth of an atmosphere. I can adduce circumstantial evidence of the accuracy of its readings at these high vacua. In the year 1881 I read a paper before the Royal Society on "The Viscosity of Gases at High Exhaustions" (*Phil. Trans.*, 1881, p. 387), and illustrated my results in three large diagrams, on which I plotted the experimental results obtained at rarefactions up to 0·02 millionth of an atmosphere, giving curves comparing the decrease in viscosity with that of the repulsion resulting from radiation, at the different pressures. Now these curves, in the case of air for instance, are perfectly regular and uniform in their falling off, and it is evident that this could not have been the case unless the ordinates representing viscosity and the abscissæ representing pressure were equally accurate. I am satisfied that, within narrow limits, the ordinates of viscosity are correct to the highest point, and the conformity of experiment to theory in the shape of these curves is a conclusive proof that, at as high an exhaustion as 0·02 M., the McLeod gauge is to be trusted to give accurate results within 2 per cent of the truth. To give some idea what these high exhaustions mean I may mention that the highest measured exhaustion—0·02 M.—bears the same proportion to the ordinary pressure of the atmosphere that a millimetre does to 30 miles, or in point of time, that one second bears to 20 months.

tact the line of light dips in the centre down to the poles of the magnet, and then rising again proceeds in a straight line. On reversing the current the line of light curves upwards. Notice that the action of the magnet in this case is only local.

In a highly exhausted tube the action is quite otherwise. Such a tube is before you (Fig. 2), and in it I have carried the exhaustion to a high point (0·1). I pass the induction current and you perceive the electrified molecules, like the line of light in the first tube, also move in straight lines, and make their path apparent by impinging on a phosphorescent screen, D E. If, however, I submit them to the action of a magnet, C, their behaviour is different. The line dips down to F, but does *not* recover itself. It seems that in the tube first shown we have to do with the average behaviour of the molecules of gas in its totality. In the second case, where the gas has been greatly attenuated, we are merely concerned with the behaviour of the individual molecules of which it was originally composed.

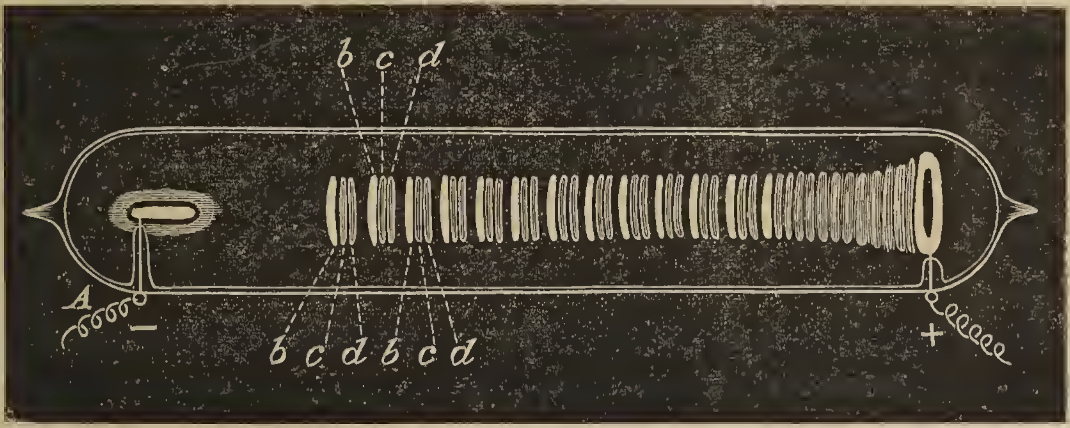

Fig. 3.—P. = 2 m.m.

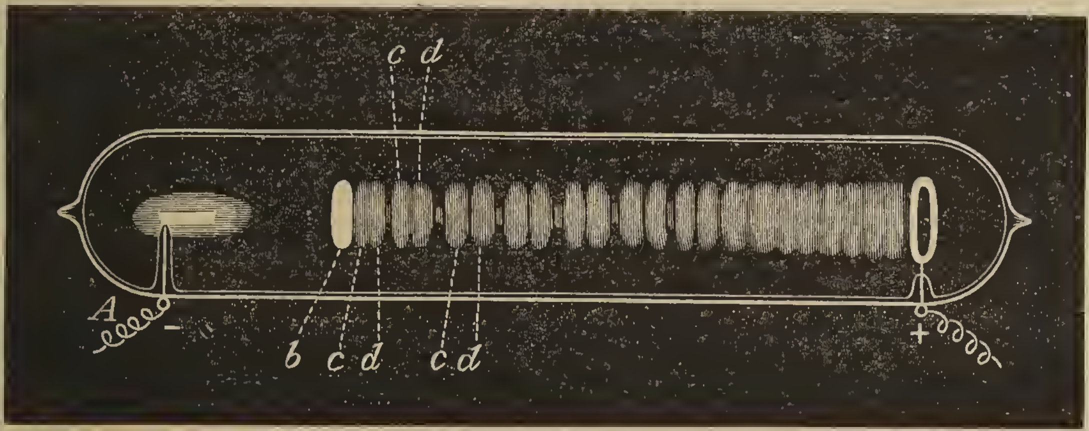

Fig. 4.—P. = 2 m.m.

The Stratified Discharge.

When the gas is rarer than is necessary to give the flexible line of light, as shown in the first experiment, the luminosity is plainly discontinuous, or, as it is termed, stratified.

A very good illustration of this fact may be taken from the moving crowd in any much frequented street—say Fleet Street. If at some time when the stream of traffic runs almost equally in both directions, we take our stand at a window from which we can overlook the passing crowd, we shall notice that the throng on the foot-way is not uniformly distributed, but is made up of knots—we might almost say blocks—interrupted by spaces which are comparatively open. We may easily conceive in what manner these knots and groups are formed. Some few persons walking rather more slowly than the average rate slightly retard the movements of others whether travelling in the same or in an opposite direction. Thus a temporary obstruction is created. The passengers behind catch up to the block and increase it, and those in front, passing on unchecked at their former rate, leave a comparatively vacant space. If a crowd is moving all in the same direction the formation of these groups becomes more distinct. With vehicles in crowded streets, the result, as everyone may have remarked, will be the same.

Hence mere differences in speed suffice to resolve a multitude of passengers into alternating gaps and knots.

Instead of observing moving men and women, suppose we experiment on little particles of some substance, such as sand, approximately equal in size. If we mix the particles with water in a horizontal tube and set them in rhythmical agitation, we shall see very similar results, the powder sorting itself with regularity into alternate heaps and blank spaces.

If we pass to yet more minute substances we observe the behaviour of the molecules of a rarefied gas, when submitted to an induction current. The molecules here are free, of course, from any caprice, and simply follow the law I seek to illustrate, and though originally in a state of rampant disorder yet under the influence of the electric rhythm they arrange themselves into well-defined groups or stratifications; the luminosities show where arrested motion with concomitant friction occurs, and the dark intervals indicate where the molecules travel with comparatively few collisions.

Party-coloured Stratifications.

As another illustration of stratifications in a moderately exhausted tube (P = 2 m.m.), I will take the case of hydrogen prepared from zinc and sulphuric acid after being passed through various purifying agents, dried in the usual manner, and exhausted with a mercury pump (Fig. 3). I pass the induction current, and we see that the stratifications are tri-coloured, blue, pink, and grey. Next the negative pole A is a luminous layer, then comes a dark interval or Faraday's dark space (see below), and after this are the stratifications, the front component (*b*) of each group blue, the next (*c*) pink, and the third (*d*) grey. The blue disks are somewhat erratic. At a certain stage of exhaustion all the blue components of the stratifications suddenly migrate to the front, forming one bright blue disk, and leaving the pink and grey components by themselves. The tube before you (Fig. 4) is at this particular stage of exhaustion, and on passing the current you observe the blue disk only (*b*) is in front. When the tube contains a compound gaseous residue of this kind, the form of stratifications can be very considerably altered by varying the potential of the discharge. This alteration in the forms of stratification was first pointed out by Gassiot (1865, "B.A. Abstracts," p. 15), who gave very full descriptions and drawings of the alterations produced by putting in resistances of various lengths of distilled water. That the alteration depends simply upon the difference of potential the following experiment pretty clearly shows:—Here is a tube giving on my coil the coloured stratification usually attributed to the presence of residual hydrogen, but which I find is due to a mixture of hydrogen, mercury, and hydrocarbon vapours. Now by altering the brake so as to produce frequent discharges of lower potential, you see the stratifications gradually change in shape and become all pink; again altering the brake so as to send less rapid discharges at a much higher potential, once more we get the coloured stratifications. When in this state, if we introduce a water resistance into the circuit so as to damp down the potential, exactly the same thing happens. The blue disk is caused by mercury; its spectrum is that of mercury only, without even a trace of the bright red line of hydrogen. Experiments not yet finished make it very probable that the pink disks are due to hydrogen, and that the grey disks indicate carbon. The tube you have just seen contains nothing but hydrogen, mercury, and a minute trace of carbon; but with all the resources at my command I have not been able to get hydrogen quite free from impurity. Indeed I do not think absolutely pure hydrogen has ever yet been obtained in a vacuum tube. I have so far succeeded as to completely eliminate the mercury, and almost completely to remove the trace of carbon. On the table is such a tube giving uniformly pink stratifications and showing no blue or grey disks with any potential of current.

(To be continued).

COMPOSITION OF BUTTER FAT.

By WILLIAM JOHNSTONE, Ph.D., D.Sc., F.I.C., F.C.S.

For some considerable time now the insoluble fatty acids of butter fat have been taken as varying from 87·5 to 89·5 per cent, and in some extreme cases even to 90 per cent. In the month of June, 1890, two samples of butter came into my hands, and in course of analysis, my attention was particularly directed to them on account of the low results obtained for insoluble fatty acids with corresponding highness in the soluble fatty acids, so I was induced to further examine them in the hope that I should be able to account for the apparent abnormal figures I had obtained, namely, 85·68 and 86·25 per cent, as they were undoubtedly genuine, the addition of cocoa-nut oil being out of the question. That investigation has resulted in establishing the fact that a butter fat yielding 85·81 per cent of insoluble fatty acids is a definite chemical compound, a compound tri-glycerin of the following formula:—

$$\left.\begin{array}{l}C_{18}H_{33}O_2\\C_{16}H_{31}O_2\\C_{10}H_{19}O_2\end{array}\right\}C_3H_5.$$

the iso-oleo-palmito capriate of glycerin.

Up to the present time it was by no means certain that butter fat did really contain normal oleic acid or stearine, and my results now confirm the accuracy of that suspicion. A butter fat, therefore, yielding 85·81 per cent of insoluble fatty acids is entirely devoid of stearine, and what was previously considered to be oleic acid now proves to be iso-oleic acid—

$$\left.\begin{array}{l}C_{13}H_{25}O\\C_4H_7O\end{array}\right\}CH_2,$$

or butro-methene, tridacotic acid.

Furthermore, genuine butter fats yielding insoluble fatty acids above 85·81 per cent do not contain stearic acid (?) as is generally supposed, but nondecatoic acid, the next higher acid of the series, as a glyceride. Butter fat then becomes a mixture of iso-oleo-palmito capriate of glycerin and tri-nondecatoic of glycerin in varying proportions, a compound complicated tri-glyceride.

The following represent a butter fat of that description:—

Fatty acids.

$$\left.\begin{array}{l}C_{18}H_{33}O_2\\C_{16}H_{31}O_2\\C_{10}H_{19}O_2\end{array}\right\}C_3H_5 \qquad 62{\cdot}47 \quad = \quad 53{\cdot}61$$

$$\left.\begin{array}{l}C_{19}H_{37}O_2\\C_{19}H_{37}O_2\\C_{19}H_{37}O_2\end{array}\right\}C_3H_5 \qquad \begin{array}{r}\underline{37{\cdot}53}\\100{\cdot}00\end{array} \quad = \quad \begin{array}{r}\underline{36{\cdot}00}\\89{\cdot}61\end{array}$$

Fatty acids actually found .. 89·95

From the above, it becomes evident that another acid radicle might replace one of nondecatoic acid, and that occurs in the following butter:—

Fatty acids.

$$\left.\begin{array}{l}C_{18}H_{33}O_2\\C_{16}H_{31}O_2\\C_{10}H_{19}O_2\end{array}\right\}C_3H_5 \qquad 53{\cdot}21 \quad = \quad 45{\cdot}66$$

$$\left.\begin{array}{l}C_{19}H_{37}O_2\\C_{19}H_{37}O_2\\C_7H_{14}O_2\end{array}\right\}C_3H_5 \qquad \begin{array}{r}\underline{46{\cdot}79}\\100{\cdot}00\end{array} \quad = \quad \begin{array}{r}\underline{44{\cdot}50}\\90{\cdot}16\end{array}$$

Fatty acids actually found .. 90·00

The radicle of œnanthylic acid replacing one of the nondecatoic acids in the tri-glyceride, and forming the di-nondecatoic-œnanthylic of glycerin.

I append the following formula in support of my theory. Thus:—

	Theory.			Theory.	Found.
$C_{13}H_{25}O$ ..	26·34	Upon saponification yield	$C_{13}H_{26}O_2$	28·60	
CH..	1·7		CH_4 ? ..	2·13	
C_4H_7O	9·45		$C_4H_8O_2$	11·76	11·70
$C_{13}H_{31}O_2$ ..	34·09		$C_{16}H_{32}O_2$	34·22	
$C_{10}H_{19}O_2$ ..	22·86		$C_{10}H_{20}O_2$	22·99	
C_3H_5	5·47		$C_3H_8O_3$	12·30	12·23
	99·98			112·00	

The ultimate separation of the fatty acids is still in hand, and I refrain from giving results until I am able to give a correct process for the separation of the same; but results have been obtained near enough to prove the correctness of the theory. Butter analysis is, therefore, now placed on a satisfactory basis, and if the analyst be fortunate enough to detect stearic acid in a sample of butter, he need have no hesitation in certifying the addition of animal fat other than butter, or at least to a fat containing stearic acid.

THE FILTRATION OF NATURAL WATERS.*

By THOMAS M. DROWN,
Member Boston Society Civil Engineers.

(Concluded from p. 48).

The surface waters used to supply London from the Thames or the Lea are filtered by the method of continuous filtration, a surface of one hundred acres being required for the purpose. The thickness of sand differs

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with the different companies supplying the city with water, from two feet at the East London and Grand Junction Companies to four and a half feet at the Chelsea Company, and the rate of filtration per hour in imperial gallons per square foot of filtering surface is two and one-sixth with the Lambeth Company, to one and a half gallons with the Southwark and Vauxhall Company. Two and a half gallons, or five vertical inches an hour (which is seldom attained), is considered the maximum consistent with good clarification. Complete analyses are made of the water supplied to the metropolis by the different companies. Some of the determinations, as for instance colour, and the amount of permanganate to oxidise the organic matter are made daily; other chemical determinations are made weekly. The monthly determinations made by Dr. Percy F. Frankland, of the bacteria in the waters of the different companies have been suspended since December, 1888. The average reduction of the number of micro-organisms present in the waters of the Thames and Lea, was in 1887 97·6 per cent in the case of the Thames, and 93·9 in the case of the Lea. "If," says the report on the metropolitan supply for December, 1888, "these figures could be accepted as at all representing the degree of security given to consumers of the waters of those rivers by preliminary filtration, it is evident that the views on this subject acquired by a consideration merely of the results of comparative chemical analysis of filtered and unfiltered waters would have to be considerably modified, and the character of the water supply would be correspondingly raised in the public estimation. Further, if the results obtained from month to month could be relied on as an index to the effect of filtration in eliminating objectionable matters from the water, the bacteriological method would seem to afford a delicate and easily applied test of the working efficiency of the filter."

The average numbers of bacteria in the water of the Thames is generally less than in the Spree at Berlin; thus during the year ending December, 1887, the highest number in November was 81,000, and the lowest in June was 2200, the average for the year being 21,492.

The only filtering plant in this country that I know of which at all compares with the plants in Europe, is that at Poughkeepsie, where the Hudson River water is converted into good clear water, though not absolutely free from colour. Mr. Fowler, the superintendent of the works, writes me with regard to the details of the filtration:—"Our usual rate of filtration is about six inches per hour, vertically, and this we regard as the maximum of efficiency, although we can sometimes do good work, so far as clarifying is concerned, at double that rate, and at other times are unable to do good work at one half that rate, although the latter condition is exceptional. Very much depends upon the condition of the water in the river. The depth of water on the sand varies from one to three or four feet, and the difference of level between the surface of the water on the beds and that in the intermediate basins is usually two to four or five feet."

The rapid filtration of water through coarse gravel is not unfrequently carried out at water works to remove the larger particles floating in the water. When a filter of this kind is cleaned, it is surprising to see the amount of fine dirt of all kinds that has been intercepted by the coarse material. Filters of this character do not pretend to purify the water in the sense of removing bacteria or in oxidising the organic matter, but they are useful just to the extent to which they clarify the water and thereby improve its appearance.

The American system of filtering large quantities of water may be said to be the mechanical filters working under pressure. These filters are composed of four or five feet of moderately fine sand (some have also a mixture of coke), enclosed generally in boiler-iron cases. They work with tremendous rapidity, sometimes over a hundred vertical feet an hour, but forty feet is said by some to be the highest rate consistent with good filtration. In this system alum is generally added to the water as a coagulent. Its effect in very small amount is quite remarkable—say a grain to a gallon, or even less—in retaining the solid matters of the water in the sand of the filter. The alum is decomposed by the carbonates in the water, and hydrate of alumina is precipitated. This is a gelatinous and slimy substance, and immediately surrounds the algæ, clay, and anything else that may be suspended in the water, and the sand retains this coagulated mass. Alumina has also the effect of taking the colour out of water, so that clear, colourless water may be obtained by this process from swampy waters full of growing algæ with almost incredible rapidity.

These filters are in very general use in paper mills and other industrial works where a clear, colourless water is needed, and where a coloured turbid river water is the only natural supply available. They have also been introduced into some cities of considerable size, as, for instance, Long Branch, Chattanooga, and Atlanta, and they are said to give water that is satisfactory to those who use it. The objection to the system is the use of alum. If all the alum used were decomposed in the few seconds that it takes the water to pass through the filter, so that no undecomposed alum passed into the filtered water, there might be no objection to its use, but this is not always the case. The amount of alum used is ordinarily small, and it is claimed that if it even all went into the filtered water it would not injure it for drinking. This may be so, but the prejudice that exists against drinking water which has been treated with "chemicals" is so strong that it is not likely that any system using a coagulent in a soluble form will find general acceptance. Under some conditions, when the water has high colour with much suspended matter, the alum has to be increased largely to give good results. I have known as high as seventeen grains to the gallon to be used with a very bad swampy water.

In this connection should be mentioned the spongy iron filter of Bischof, which gives most excellent results both in taking out suspended matters from the water, including the bacteria, and also decreases the hardness of the water. This filter has been used on the small scale in houses, and also on the large scale in Antwerp, to decolourise and otherwise purify the water of that city. The filter is composed of finely-divided metallic iron made by reducing iron ore by means of carbon at a temperature below fusion. Its action was not understood for a long time, and the mystery that surrounded it was an additional recommendation for it. The rationale of its working seems to be this, namely, that the iron being in a very finely-divided state is dissolved to a slight extent by the combined action of the oxygen and carbonic acid in the water, and the ferrous carbonate thus produced is further oxidised, forming hydrate of iron, and then this acts as a coagulent just as the alumina hydrate does. The system was said to be too expensive on a large scale, and it has now been replaced at Antwerp by the Anderson process, in which the dark water is made to pass through a long revolving iron cylinder in which there is a large quantity of fragments of cast iron. These fragments of iron in their friction one on the other are abraded, minute particles are broken off which are dissolved in the way above described. The water coming from the revolving cylinder is exposed to the air, the iron oxidises and precipitates, combines with the colouring matter in the water, encloses the solid particles, and is then filtered out through sand. The process is said to work satisfactorily and give clear, colourless water. There is no objection to this use of iron as a coagulent, provided that it is all oxidised and precipitated, and none is carried in solution into the filtered water; but this takes time.

Both alum and iron salts have a tendency to sterilise water. Their action may be both direct by killing the bacteria, and indirect by removing them with the precipitated alumina or iron hydrate. If a drop of a solution of alum or of iron chloride be added to a gallon of turbid water, it will become perfectly clear in the course of a few hours, the alumina or iron hydrate, which is formed in the water, settling to the bottom and carrying all the suspended matters with them. It has been proposed to clarify Mississippi water by adding a very small quantity of an iron solution to the water in the settling basins.

I have laid some weight on the desirability of following nature's processes in the purification of impure waters. Neither the American system, with its mighty rush of waters, or the European system, with its calm, steady, and deliberate flow, finds any analogy in nature. In the rapid-working mechanical filters a coagulent is used to grasp and hold the suspended matter; in the continuously working filter beds the bacteria are put to a novel use in retaining the solid matter on the sticky surface of the sand.

Nature uses these methods also; she removes colour by means of clay in the soil and intercepts mechanically in the bacteria-laden soil all the solid matter in the water, but she goes further than this, and, giving the bacteria full play, breaks up the organic compounds and leaves no trace of their existence behind. To do this, time is needed. "The bacteria of nitrification," as Dr. Smart has well said, in referring to the systems of rapid filtration, "cannot be harnessed to the work of artificial filtration."

The rate at which nature works may be expressed in the amount of rainfall. If we take the rainfall at fifty inches, and assume that even half of this sinks into the ground (a very high estimate), we have twenty-five inches yearly on a square foot of surface. The amount of water which goes through the Berlin filters, at a rate of four inches an hour, is more than 1250 times this amount. If we wish to imitate the process by which nature makes its springs, we must pour the water from river or lake which we wish to filter intermittently on the surface of ground which is favourable for this purpose. The favourable conditions are these:—The ground must be sufficiently porous to allow the ready flow of water through it, and it must have such relations to the strata below as will enable us to collect the water at some lower level. It would not profit us much to pour the water on to a gravel bed if we could not find it again after it had been filtered. If the natural conditions for this purpose are not favourable, drains would have to be put in at suitable depths to collect the filtered water. Water purified in this way would in no wise differ from natural spring water, provided that the amount of water applied did not exceed the capacity of the filtering area.

The question of the maintenance of the purity of the water supplies of large cities, which are dependent upon surface waters, is daily becoming more urgent in this country as the population becomes more dense on the collecting areas, and the protection of streams against pollution becomes more and more difficult. The radical remedy in such cases is to take water from another and, usually, more distant region, which, it is probable, will never become thickly settled. But in filtration, both intermittent and continuous, when intelligently conducted, we have a substitute which can give as clear, colourless, and, we have good reason also to suppose, safe drinking water.

The Production of Higher Alcohols During the Alcoholic Fermentation.—L. Lendet.—In view of the author's results, it is impossible to admit that the higher alcohols are exclusively produced by the normal fermentation of sugar, and their formation must be chiefly sought for elsewhere. Their origin may be traced to the development of a micro-organism, the action of which at the outset of fermentation is smothered by the action of the yeast, but which resumes its activity when the yeast has completed its task.—*Comptes Rendus*, vol. cxii., No. 2.

THE SPECIFIC GRAVITY OF A LIQUID, A FUNCTION OF ITS BOILING-POINT AND MOLECULAR WEIGHT.

By A. E. RICHARDSON, Assoc.Inst.Elect.Eng.

THE boiling-point of a liquid is to some extent dependent upon the molecular weight of that liquid. This fact is best observed in the case of the homologous series in organic chemistry, in which a fairly constant rise in the boiling-point occurs for a constant increase of molecular weight. Nevertheless, between *specific gravity* and the temperature of ebullition, no definite relations seem to have been observed.

If, by a new mode of procedure, some connection were found to exist between these two quantities—boiling-point and specific gravity—there is no reason to doubt that a material aid would be rendered to the solution of the more important problem, namely, the dependence of specific gravity upon molecular weight. In this paper, only those liquids which possess a specific gravity greater than unity have been examined.

Under what conditions must a liquid be placed that its specific gravity may appear as a function of its boiling-point? The boiling-points, pure and simple, apparently have no connection whatever with the specific gravities, and thus some other temperature must be considered. Imagine the case of a liquid heated to temperatures far above its boiling-point. Also conceive that ebullition has by some means been prevented. Under such circumstances it is palpable that the specific gravity of the liquid will have much decreased, taking it for granted that the liquid would continue expanding. At some temperature, constant for each liquid, the specific gravity would at last assume unit value. Here then is a new condition of liquid matter, namely, the temperature at which each given liquid attains unit specific gravity.

To arrive at these temperatures two measurements are required for every liquid. We must know (1) the specific gravity at some given temperature, and (2) the rate of expansion between 0° and the boiling-point.

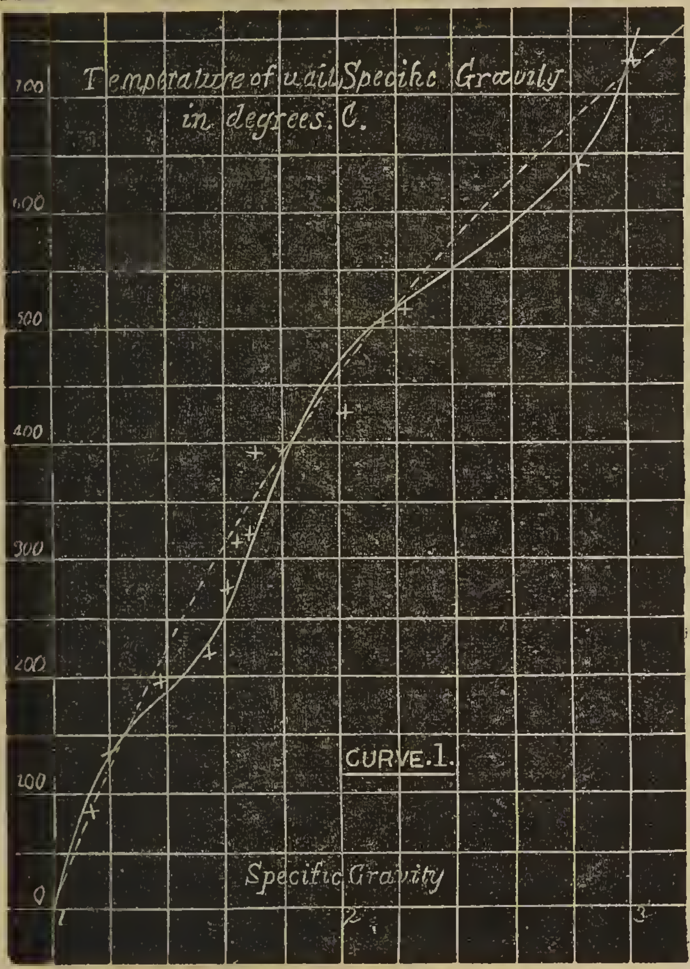
In the following tables these temperatures have been calculated for a few liquids. The specific gravities and rates of expansion were taken from Professor Thorpe's paper on specific volume (*Journ. Chem. Soc.*, 1880).

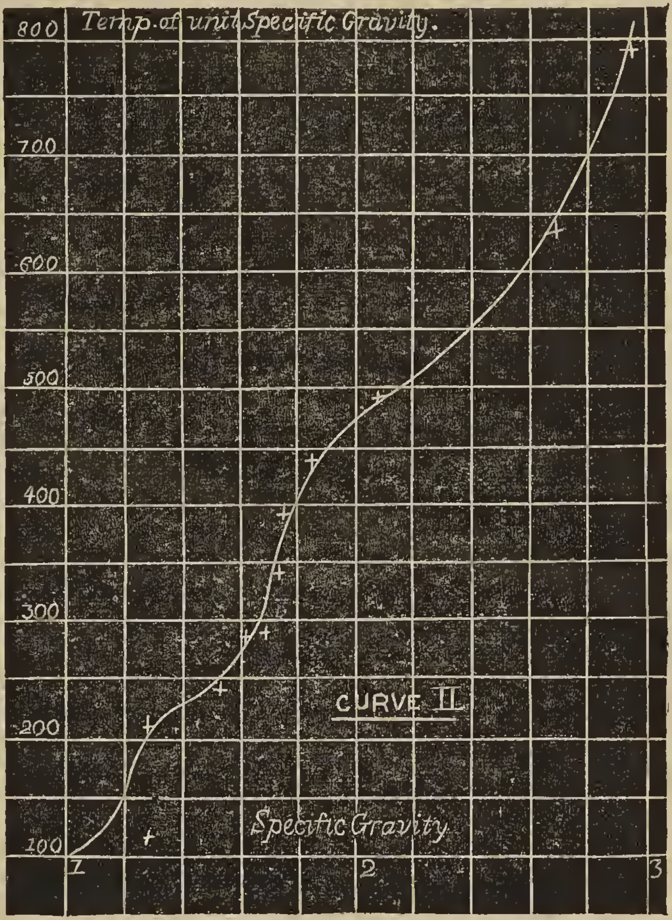
In this table m = molecular weight, T = unit specific gravity temperature (Centigrade), Ta = absolute temperature of unit specific gravity, t = boiling-point (Centigrade), and ta = absolute temperature of boiling.

With inorganic compounds we have the following results. (See Table, p. 60).

The values of T were calculated from the equation for liquid expansion, $V = 1 + at + bt^2 + ct^3$. The values of a, b, and c are given, in the paper above mentioned, for all temperatures between 0° and the boiling-point for each liquid. The equations are here assumed to hold true for temperatures *above* the boiling-points. Curves I. and II. are obtained by plotting the values of specific gravity as abscissæ, and temperatures of unit specific gravity as ordinates, from Tables I. and II. respectively. The curves show that specific gravity is a function of the temperature of unit specific gravity. Since the rates of expansion of the various liquids are so extremely variable, no such relation could have been predicted.

The values of $\frac{T}{m}$ are very uniform, and many of them closely approximate to the number 2. It seems extremely probable that if a large number of liquids were examined, they might admit of division into groups, such that for each group a constant value of $\frac{T}{m}$ would be obtained. Such a division would at first be purely empirical. The reason of such a grouping would possibly appear when a


Temperature of unit Specific Gravity in degrees C.
700
600
500
400
300
200
100
0
CURVE. I.
Specific Gravity
1
2
3


Temp. of unit Specific Gravity.
800
700
600
500
400
300
200
100
CURVE II.
Specific Gravity
1
2
3

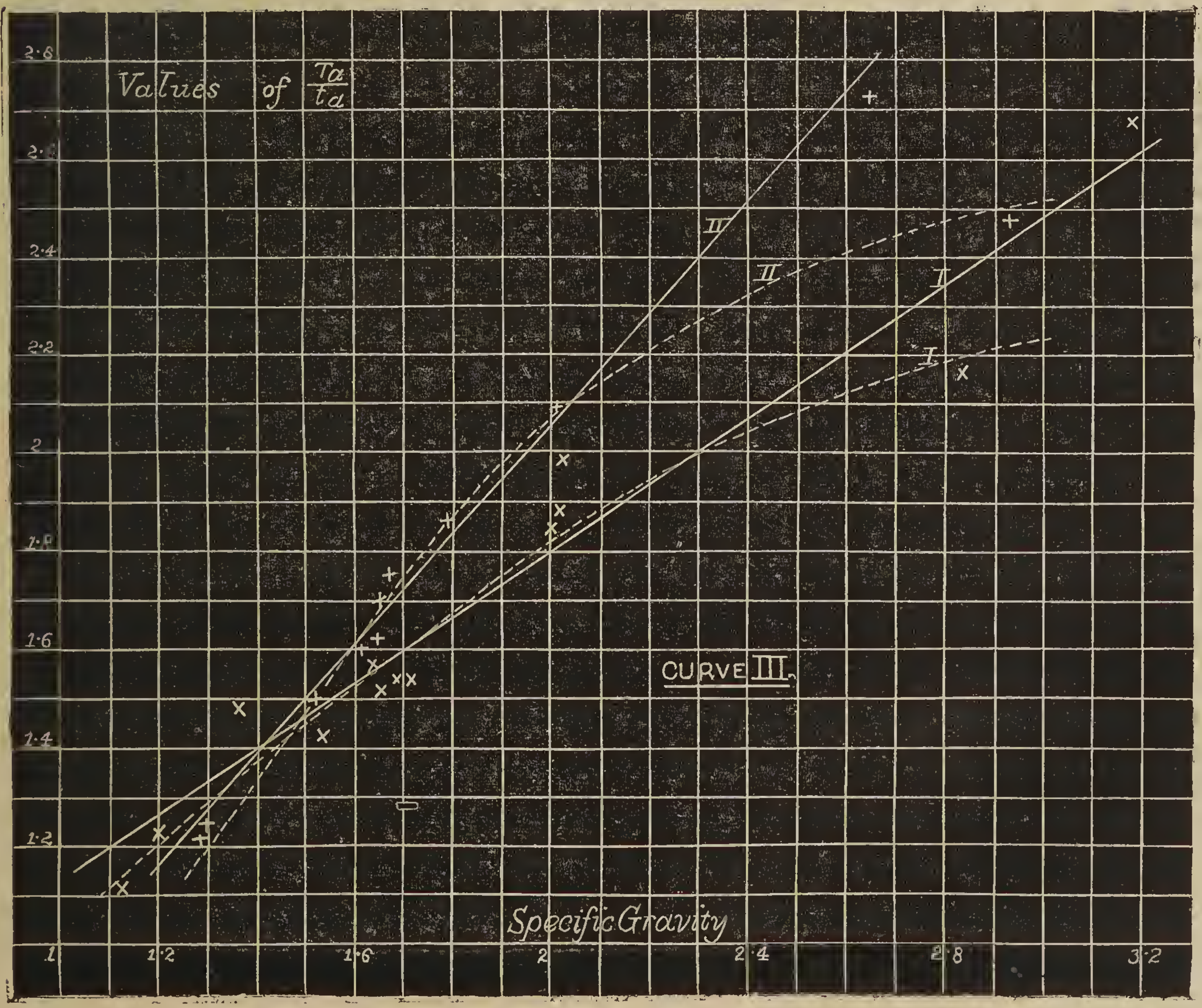

Values of $\frac{Ta}{ta}$
2·6
2·4
2·2
2
1·8
1·6
1·4
1·2
II
II
I
I
CURVE III.
Specific Gravity
1
1·2
1·6
2
2·4
2·8
3·2

TABLE I.—*Organic Compounds.*

Formula.	Molecular weight.	Unit specific gravity temp.	Specific gravity.	Boiling point.	$\frac{T}{m}$	$\frac{T}{t}$	$\frac{Ta}{ta}$
C_2H_3OCl	78·5	84°	1·13773	50·7°	1·07	1·65	1·13
CH_3CHCl_2	98·7	136	1·20394	59·9	1·37	2·27	1·23
CH_2Cl_2	84·7	198	1·37776	41·6	2·3	4·75	1·49
CCl_3COH	147	220	1·5448	97·2	1·5	2·2	1·33
CCl_4	153·4	271	1·63195	76·7	1·7	3·5	1·56
CCl_3COCl	182	322	1·6564	118	1·76	2·8	1·52
$C(NO_2)Cl_3$	164	326	1·69225	111·9	2	2·9	1·55
CCl_3CHCl_2	202·7	393	1·70893	159·1	1·9	2·47	1·55
CCl_3Br	198	425	2·05496	104·07	2·15	4·07	1·85
C_2H_4ICl	190·5	506	2·161439	140	2·6	3·6	1·88
$C_2H_4Br_2$	188	518	2·21324	131·45	2·8	3·9	1·95
$CHBr_3$	253	646	2·83413	151·2	2·56	4·3	2·16
ICl	162·5	730	3·1822	101·3	4·49	7·2	2·68
$CHCl_3$	119	246	1·52657	61·2	2·07	4·02	1·55
Br_2	160	619	3·18828	60	3·8	10·3	2·68

TABLE II.

Formula.	m.	T.	Specific gravity.	t.	$\frac{T}{m}$	$\frac{T}{t}$	$\frac{Ta}{ta}$
CS_2	76	112	1·29215	46·04	1·47	2·44	1·21
$PCl_2C_2H_5O$	146·7	210	1·30526	117·5	1·4	1·8	1·24
$SiCl_4$	169·4	244	1·52408	57·57	1·45	4·2	1·5
PCl_3	137	287	1·61275	75·95	2·1	3·78	1·6
$SOCl_2$	118·7	297	1·67673	78·8	2·5	3·77	1·62
$POCl_3$	153	345	1·7116	107·23	2·2	3·2	1·62
$TiCl_4$	189	390	1·76088	136·4	2·06	2·8	1·62
$VOCl_3$	173	440	1·8653	127·19	2·5	3·46	1·78
$POBrCl_2$	197·7	490	2·12065	137·6	2·5	3·6	2·46
AsF_3	132	635	2·6659	60·4	4·8	10·5	2·72
PBr_3	271	792	2·92311	172·9	3·7	4·6	2·39
SO_2Cl_2	135	283	1·70814	69·95	2·1	3·05	1·63
$C_6H_5PCl_2$	178·7	304	1·3428	224·6	1·7	1·36	1·16
$PSCl_3$	169	361	1·6682	125·07	2·1	2·85	1·59
$SSCl_2$	135	402	1·7094	138·12	2·2	2·9	1·64
$SnCl_4$	279	438	2·2787	113·89	1·57	3·8	1·84
CrO_2Cl_2	202·7	494	1·961	115·9	2·4	4·26	1·95
SO_2OHCl	116·5	503	1·78474	155·3	4·3	3·2	1·82

sufficient number of examples had been examined. We should thus have the following conditions:—

Specific gravity ∞ temperature of unit specific gravity. Temperature of unit specific gravity ∞ molecular weight (because $\frac{T}{m}$ approaches constant value), and hence specific gravity ∞ molecular weight.

Lastly, there is a greater uniformity between the values of $\frac{Ta}{ta}$ than between those of $\frac{T}{m}$, and consequently all that has been said with regard to values of $\frac{T}{m}$ applies with even greater force to values of $\frac{Ta}{ta}$. Moreover, it should be remarked that the numbers representing $\frac{Ta}{ta}$, regarded in general, increase with increasing specific gravities, and in fact usually assume values *very closely approximating the actual specific gravities themselves.*

Curve III. represents this relation. Although these curves are represented as straight lines, it will at once be evident that they could, with equal right, be regarded as sinuous, similar to those of Curves I. and II. (Points on Curve I. are expressed by the *multiplication* sign; those on Curve II. by the *addition* sign).

Nothing can be definitely decided until many and more varied liquids have been examined. Consequently this paper can avail nothing except to indicate a possible source of a more intimate connection between the physical properties of liquids.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1890.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

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

London January 9th, 1891.

SIR,—We submit herewith the results of our analyses of the 133 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

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

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

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

Of the 133 samples examined, the whole were found to be clear, bright, and well filtered.

It will be noticed that from the 15th to the 31st of the month, the regular examination of samples drawn from the stand-pipes day by day, was largely interfered with by the prevailing frost, which, while considerable also in severity, has not for many years past been equalled in duration, beginning as it did on December 9th, and continuing, practically without intermission, well into the present year. That this wholly exceptional frost, though offering impediments to the process of filtration and retarding the rate of filtration, did not interfere with its thoroughness, is shown by the circumstance that no one sample of water, alike among those included in the Tables, and among numerous supplementary samples submitted to examination, was found otherwise than free from colour and turbidity. Moreover, in respect to chemical characters generally, the water supply for December was found to compare favourably even with the supply of the previous summer and autumn months, as shown in the following Table of results afforded by the water distributed by the Companies taking their supply from the Thames:—

	Ratio of brown to blue tint. Means.	Oxygen required for oxidation. Means.	Organic carbon per 100,000. Means.	Organic carbon per 100,000. Maxima.
June	12·0 : 20	0·049	0·150	0·166
July	16·1 : 20	0·056	0·152	0·185
August . ..	17·1 : 20	0·065	0·150	0·175
September ..	11·5 : 20	0·044	0·147	0·170
October ..	10·4 : 20	0·040	0·136	0·160
November ..	13·1 : 20	0·045	0·142	0·158
December ..	14·8 : 20	0·045	0·136	0·148

It came to our notice, however, that some of the Thames-derived water distributed during the later part of December, and at the commencement of the present year, manifested, in the case of certain particular samples, an unpleasant faint taste associated in yet fewer instances with a corresponding odour. From our analysis of different samples, we were able to satisfy ourselves definitely that the occurrence of this taste and smell, both evanescent, did not depend on any contamination of the water with animal matter; and from a consideration of the exceptional meteorological conditions prevailing of combined frost, fog, and snow, and from our examination of various samples of snow and snow-water, we are inclined to attribute the occurrence in question to an admixture with the main supply of a small proportion of water furnished by the melting of heavily fog-laden snow, such as some of that which we had the opportunity of experimenting on.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

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. cxii., No. 2, January 12, 1891.

On a Reclamation of Priority on Behalf of M. de Chancourtois with Reference to the Numerical Relations of the Atomic Weights.—MM. Lecoq de Boisbaudran and A. de Lapparent.—Inserted in full.

Action of Sodium Phenol and of Sodium Naphthol upon Camphor Cyanide.—J. Minquin.—The author has formerly shown that sodium benzylate reacting upon camphor cyanide gives rise to a compound—

$$C_8H_{14}<^{CH_2CN}_{CO_2C_7H_7},$$

and that in the washing-waters from the preparation of this body there is found an acid—

$$C_8H_{14}<^{CH_2CN}_{COOH}.$$

Phenol and naphthol behave in a manner absolutely identical.

New Method for Detecting Olive Oil and Seed Oils Equally Applicable to Natural Butters and Oleo-Margarine. — Raoul Brullé. — The reagent employed is a solution of silver nitrate at 25 per 1000 in ethylic alcohol at 95°. About 12 c.c. of the oil in question and 5 c.c. of the reagent are placed in a test-tube. The tube is then set in a beaker of boiling water, and the changes of colour which take place in the liquids are watched through the glass. Unless the oils are perfectly limpid, they must be previously filtered. Olive oils sooner or later take a fine green colour, which is lighter in the superior qualities. Pure cotton-seed oil is turned completely black. Oil of earth nuts (*Arachis*) takes first a red-brown colour and finally turns green, losing its transparency. Oil of sesame takes a deep red colour and remains reddish. Oil of colza takes yellowish green colours and becomes turbid. Natural butter preserves its natural colour. Oleo-margarine becomes a brick-red, which colour may be detected even in samples containing as little as 5 per cent of margarine.

On the Diamond-bearing Sands Collected by C. Rabot in Russian Lapland (Valley of the Pasrig).—Ch. Vélain.—The sands in question contain the following minerals in the order of their frequency:—Garnet (almandine), zircon, amphiboles brown and green, glaucophane, disthene, pyroxene, quartz, corundum, rutile, magnetite, staurotide, andalusite, tourmaline, epidote, felspar (oligoclase), diamond. The diamonds are of the average size of 0·25 m.m.

MISCELLANEOUS.

Researches on Micro-organisms.—His Majesty the King of the Belgians has graciously accepted a copy of Dr. A. B. Griffiths's book, "Researches on Micro-organisms," which has just been published by Messrs. Baillière and Co.

Prix Montyon.—At a meeting of the Académie des Sciences, Paris, held on December 29, Dr. A. B. Griffiths, F.R.S.E., F.C.S., was awarded an "honourable mention" in connection with the Prix Montyon, which is given annually by the Academy for researches in experimental physiology and physiological chemistry.

Preparation of Metallic Manganese by Means of Manganese Chloride and Magnesium.—E. Glatzel.—Crystalline manganese chloride is dehydrated, pulverised, and 100 grms. of the mass are mixed with 200 grms. of potassium chloride in fine powder and perfectly dry. The whole is placed in a Hessian crucible, covered with its lid, and heated to near redness. When the mass is in quiet fusion 15 grms. of magnesium, broken up into fragments of 3—4 grms., are added in four or five portions. When the reaction is over the crucible is covered, and the heat is raised to the strongest redness. When cold a metallic regulus of 20—25 grms. is found at the bottom of the crucible. The metal thus obtained is harder than a steel file. It is not at all attracted by a powerful magnet. It is permanent in dry air, but rusts readily in moist air and is easily attacked by acids. It contains mere traces of magnesium.—*Journal de Pharm. et de Chemie*, Vol. xxii., No. 1.

The Chemical Society's Jubilee, 1891. — The Chemical Society, having been founded in 1841, is in the fiftieth year of its existence, and is the eldest among chemical societies. The following arrangements have been made to celebrate this important occurrence in the history of the Society on February 24th and 25th next:—On February 24th, at 3—5 o'clock p.m., a Meeting will be held at the Society of Arts, where the original meeting took place at which the formation of the Society was decided on. At this meeting various addresses will be delivered, and delegates from other Societies will be received. On the evening of the same day, at 8.30 o'clock, the President and Council will hold a Reception at the Goldsmiths' Hall, which has been most kindly placed at the disposal of the Society for the purpose by the Worshipful Company of Goldsmiths. On the evening of February 25, at 6.30 for 7 p.m., the Fellows and their friends will dine together at the Hotel Métropole. (Tickets one guinea each).

MEETINGS FOR THE WEEK.

Monday, 2nd.—Medical, 8.30.
—— Society of Chemical Industry, 8, "On Standard Sperm Candles," by W. C. Young.
—— Society of Arts, 8. "The Construction and Capabilities of Musical Instruments," by A. J. Hipkins, F.S.A.
—— Royal Institution, 5. General Monthly Meeting.
Tuesday, 3rd.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S., B.S., F.R.C.S., Fullerian Professor of Physiology, R.I.
—— Pathological, 8.30.
Wednesday, 4th.—Society of Arts, 8. "Decimal Coinage, Weights, and Measures," by J. Emerson Dowson.
—— Geological, 8.
Thursday, 5th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "The Little Manx Nation," by Hall Caine.
—— Chemical, 5.
Friday, 6th.—Royal Institution, 9. "Some Applications of Photography," by The Right Hon. Lord Rayleigh, F.R.S.
—— Geologists' Association, 7.30. (Anniversary).
—— Quekett, 8.
Saturday, 7th.—Royal Institution, 3. "Pre-Greek Schools of Art," by W. Martin Conway, M.A., F.S.A.

TO CORRESPONDENTS.

C. O'N. Williams.—Dr. Letheby died March 28, 1876.

THE CHEMICAL NEWS.
Vol. LXIII., No. 1628.

ON GASEOUS ILLUMINANTS.*

By Professor VIVIAN B. LEWES.

V.

It has been proposed to carburet and enrich poor coal gas by admixture with it of an oxy-oil gas, in which crude oils are cracked at a comparatively low temperature, and are then mixed with from 12 to 24 per cent of oxygen gas. Oil gas made at low temperature is *per se* of little use as an illuminant, as it burns with a smoky flame and does not travel well; but when mixed with a certain amount of oxygen it gives a very brilliant white light and no smoke, while, as far as experiments have at present gone, its travelling powers are much improved. At first sight it seems a dangerous experiment to mix a heavy hydrocarbon gas with oxygen; but it must be remembered that although hydrogen and carbon monoxide only need to be mixed with but half of their own volume of oxygen to produce the most explosive compound, yet as the number of carbon and hydrogen atoms in the combustible gas increases, so does the amount of oxygen needed. So that coal gas requires rather more than its own volume, and ethylene three times its volume, to yield the maximum explosive results; while these mixtures begin to be explosive when 10 per cent of oxygen is combined with hydrogen or water gas, 30 per cent with coal gas, and more than 50 per cent with oil gas of the character used. It is claimed that if this gas were used as an enricher of coal gas, 5 per cent of it would increase the luminosity of 16-candle gas by about 40 per cent. Oxygen has been obtained for some time past from the air, on a commercial scale, by the Brin process; and it is now proposed to make oxygen by a process first introduced by Tessié du Motay, which consists of passing alternate currents of steam and air over sodic manganate heated to dull redness in an iron tube. The process has never been commercially successful, for the reason that the contents of the tube fused, and, flowing over the surface of the iron, rapidly destroyed the tubes or retorts; and also, as soon as fusion took place, the mass became so dense that it had little or no action on the air passing over it, but it is now claimed that this trouble can be overcome. Cheap oxygen would be an enormous boon to the gas manager, as, by mixing 10·8 per cent of oxygen with his coal gas before purification, he could not only utilise the method so successfully introduced by Mr. Valon at Ramsgate, but could also increase the illuminating value of his gas to a slight extent.

No ordinary gas flame is in contact with the burner from which it issues, this being due to the cooling effect of the burner, but as this only affects the bottom of the flame, with a small flame the total effect is very great, with a large flame almost nil. The first point, therefore, to attend to, is that the burner should be made of a good non-conductor. In the next place, the flow of the gas must be regulated to the burner; as, if you have a pressure higher than that for which the burner is constructed, you at once obtain a roaring flame and a loss of illuminating power, as the too-rapid rush of gas from the burner causes a mingling of gas and air, and a consequent cooling of the flame, while the form of the flame becomes distorted. The tap also which regulates the flame is better at a distance from the burner than close to it, as any constriction near the burner causes eddies in the flow of the gas, which gives an unsteady flame. These general principles govern all burners.

We will now take the ordinary forms in detail. In the flat-flame burner, given a good non-conducting material and a well-regulated gas supply, little more can be done, while burning it in the ordinary way, to increase its luminosity; and it is the large surface of flame exposed to the cooling action of the air which causes this form of burner to give the lowest service of any per cubic foot of gas consumed. Much is done, moreover, by faulty fittings and shades, to reduce the already poor light afforded, because the light-yielding power of the flame largely depends on its having a well-rounded base and broad luminous zone; and when a globe with narrow opening is used with such a flame as is done in ninety-nine cases out of a hundred, the up-draught drags the flame out of shape, and seriously impairs its illuminating power—a trouble which can be overcome by having a globe with an opening at the bottom not less than 4 inches in diameter, and having small shoulders fixed to the burner which draw out the flame and protect the base from the disturbing influence of draughts.

The Argand burner differs from the flat-flame burner in that a circular flame is employed, and the air supply is regulated by a glass of cylindrical form. This kind of burner gives better service than a flat-flame, as not only can the supply of gas and air be better adjusted, but the air being slightly warmed by the hot glass, adds to the temperature of the flame, which is also increased by radiation from the opposite side of the flame itself. The chief loss of light depends upon the fact that, being circular, the light from the inner surface has to pass through the wall of flame; and careful photometric experiments show that the solid particles present in the flame so reduce its transparency that a loss amounting to about 25 per cent of light takes place during its transmission.

For many years no advance was made upon these forms of burner. But when, fifteen years ago, it was recognised that anything which cools the flame reduces its value, while anything which increases its temperature raises its illuminating power, a change began to steal over the forms of burner in use; and the regenerative burners, fathered by such men as Siemens, Grimston, and Bower, commenced what was really a revolution in gas lighting, by utilising the heat contained in the escaping products of combustion to raise the temperature of the gas and air which are to enter into combination in the flame. An enormous increase in the temperature of the solid particles of carbon in the flame is thereby obtained, and a far greater and whiter light is the result.

The only drawback to this class of burner is that it is by far the best form of gas stove as well as burner, and that the amount of heat thrown out by the radiant solid matter in the flame is, under some circumstances, an annoyance. On the other hand, we must not forget that this is the form of burner best adapted for overhead lighting, and that nearly every form of regenerative lamp can be used as a ventilating agent; and that with the withdrawal of the products of combustion from the air of the room, the great and only serious objection to gas as an illuminant disappears.

When coal gas is burnt, the hydrogen is supposed to be entirely converted into water vapour, and the carbon to finally escape into the air as carbon dioxide. If this were so, every cubic foot of gas consumed would produce approximately 0·523 cubic foot of carbon dioxide, and 1·34 cubic feet of water vapour, and the illuminating power yielded by the foot of gas will, of course, vary with the kind of burner used.

Roughly speaking, the ordinary types of burner give the following results:—

	Illuminating Power in candles per c. ft. of gas consumed.	Products of combustion per candle power.	
		Carbon dioxide.	Water vapour.
Batswing	2·9	0·18 c. ft.	0·46 c. ft.
Argand	3·3	0·16 ,,	0·40 ,,
Regenerative ..	10·0	0·05 ,,	0·13 ,,

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* Abstract of the Cantor Lectures delivered at the Society of Arts. Communicated by the Author.

So that the regenerative forms of burner, by giving the greatest illuminating power per cubic foot of gas consumed, yield a smaller amount of vitiation to the air per candle of light emitted. An ordinary room (say, 16 ft. by 12 ft. by 10 ft.), would not be considered properly illuminated unless the light were at least equal to 32-candle power; and in the following table the amount of oxygen used up, and the products of combustion formed by each class of illuminant and burner, in attaining this result, are given. The number of adults who would exhale the same amount during respiration is also stated:—

Illuminants.	Quantity of materials used.	Oxygen removed.	Products of Combustion.		Adults.
			Water vapour.	Carbon dioxide.	
	Grms.	C. ft.	C. ft.	C. ft.	
Sperm candles ..	3840	19·27	13·12	13·12	21·8
Paraffin oil.. ..	1984	12·48	7 04	8·96	14·9
Gas (London)—	C. ft.	C. ft.	C. ft.	C. ft.	
Batswing burner.	11·0	13·06	14·72	5·76	9·6
Argand ,, ..	9·7	11·52	12·80	5·12	8·5
Regenerative ..	3·2	3·68	4·16	16·0	2·6

From these data it appears, according to scientific rules by which the degree of vitiation of the air in any confined space is measured by the amount of oxygen used up and carbon dioxide formed, that candles are the worst offenders against health and comfort; oil lamps come next, and gas least. This, however, is an assumption which practical experience does not bear out. Discomfort and oppression in a room lighted by candles or oil are less felt than in one lighted by any of the older forms of gas-burner. The partial explanation of this is to be found in the fact that, when a room is illuminated with candles or oil, people are contented with a feebler and more local light than when using gas. In a room of the size described, the inmates would be more likely to use two candles placed near their books, or on a table, than 32 candles scattered about the room. Moreover, the amount of water vapour given off during the combustion of the gas is greater than in the case of the other illuminants. Water vapour, having a great power of absorbing radiant heat from the burning gas, becomes heated; and, diffusing itself about the room, causes a great feeling of oppression. The air also, being highly charged with moisture, is unable to take up so rapidly the water vapour which is always evaporating from the surface of the skin, whereby the functions of the body receive a slight check, resulting in a feeling of *malaise*. Added to these, however, is a far more serious factor, which up to the present has been overlooked, and that is that an ordinary gas-flame in burning yields distinct quantities of carbon monoxide and acetylene, the prolonged breathing of which, in the smallest traces, produce headache and general physical discomfort, while their effect upon plant life is equally marked.

Ever since the structure of flame has been noted and discussed, it has been accepted as a fact beyond dispute that the outer, almost invisible zone which is interposed between the air and the luminous zone of the flame is the area of complete combustion; and that here the unburnt remnants of the flame gases, meeting the air, freely take up oxygen, and are converted into the comparatively harmless products of combustion, carbon dioxide and water vapour, which only need partial removal by any haphazard process of ventilation to keep the air of the room fit to support animal life. I have, however, long doubted this fact; and at length, by a delicate process of analysis, have been able to confirm my suspicions. The outer zone of the luminous flame is not the zone of complete combustion. It is a zone in which luminosity is destroyed in exactly the same way that it is destroyed in the Bunsen burner—*i.e.*, the air penetrating the flame so dilutes and cools down the outer layer of incandescent gas, that it is rendered non-luminous; while some of the gas sinks below the point at which it is capable of burning, with the result that considerable quantities of the products of incomplete combustion (carbon monoxide and acetylene) escape into the air, and render it actively injurious. I have proved this by taking a small platinum pipe with a circular loop at the end—the interior of the loop being pierced with minute holes; and by making a circular flame burn within the loop, so that the non-luminous zone of the flame just touched the inside of the loop, and then by aspiration, so gentle as not to distort the shape of the flame, withdrawing the gases escaping from the outer zone, and analysing these by a delicate process which will be described elsewhere, I arrived at the following results:—

Gases Escaping from the Outer Zone of Flame.

	Luminous.	Bunsen.
Nitrogen	76 612 ..	80·242
Water vapour	14·702 ..	13·345
Carbon dioxide	2·201 ..	4·966
Carbon monoxide	1·189 ..	0·006
Oxygen	2·300 ..	1·430
Marsh gas	0·072 ..	0·003
Hydrogen	2·388 ..	0·008
Acetylene	0·036 ..	nil
	100·000	100·000

The gases leaving the luminous flame show that the diluting action of the nitrogen is so great that considerable quantities even of the highly-inflammable and rapidly-burning hydrogen escape combustion; while the products of incomplete combustion are present in sufficient quantity to perfectly account for the deleterious effects of gas-burners in ill-ventilated rooms. The analyses also bring out very clearly the fact that, although the dilution of coal gas by air in atmospheric burners is sufficient to prevent the decomposition of the heavy hydrocarbons, with liberation of carbon, and so destroy luminosity, yet the presence of the extra supply of oxygen does make the combustion far more perfect, so that the products of incomplete combustion are hardly to be found in the escaping gases.

The feeling has gradually been gaining ground in the public mind that, when atmospheric burners and other devices for consuming coal gas are employed for heating purposes, certain deleterious products of incomplete combustion find their way into the air; and that this does take place to a considerable extent is shown by the facts brought forward in a paper read by Mr. W. Thompson at the last meeting of the British Association, at Leeds (Chem. News, lxii., p. 193). Mr. Thompson attempted to separate and determine the quantity of carbon monoxide and hydrocarbons found in the flue gases from various forms of gas stoves and burners; but, like every other observer who has tried to solve this most difficult problem, he found it so beset with difficulties that he had to abandon it, and contented himself with determining the total quantities of carbon and hydrogen escaping in an unburnt condition. His experiments proved that the combustion of gas in stoves for heating purposes is much more incomplete than one had been in the habit of supposing; but they did not show whether the incompletely burnt matter consisted of such deleterious products as carbon monoxide and acetylene, or comparatively harmless gases such as marsh gas and hydrogen.

If a cold substance—metallic or non-metallic—be placed in a flame, whether it be luminous or non-luminous, it will be observed that there is a clear space, in which no combustion is taking place, formed round the cool surface, and that, as the body is heated, this space becomes gradually less, until, when the substance is at the same temperature as the flame itself, there is contact between the two. Moreover, when a luminous flame is employed in this experiment, the space still exists between the cool body and the flame; but it will also be noticed that the luminosity is decreased over a still larger area, though the flame exists. This means that in immediate contact with the cool body the temperature is so reduced that a flame cannot exist, and so is extinguished over a small area; while over a still larger space the temperature is so reduced that it is not hot enough to bring about decomposition of the heavy hydrocarbons, with liberation of carbon, to the same extent as in hotter portions of the flame.

Now, inasmuch as when water is heated or boiled in an open vessel, the temperature cannot rise above 100° C., and as the temperature of an ordinary flame is more than 1000° C., it is evident that the burning gas can never be in contact with the bottom of the vessel; or, in other words, the gas is put out before combustion is completed, and the unburnt gas and products of incomplete combustion find their way into the air, and render it perfectly unfit for respiration. The portion of the flame which is supposed to be the hottest is about half an inch above the tip of the inner zone of the flame. It is at this point that most vessels containing water to be heated are made to impinge on the flame; and it is this portion of the flame also that is utilised for raising various solids to a temperature at which they will radiate heat in most forms of gas-stove.

I have determined the composition of the products of combustion and the unburnt gases escaping when a vessel containing water at the ordinary temperature is heated up to boiling-point by a gas flame; the vessel being placed in the first case half an inch above the inner cone of the flame, and in the second at the extreme outer tip of the flame. The results are given in the following table:—

Gases Escaping during Checked Combustion.

	Bunsen flame.		Luminous flame.	
	Inner.	Outer.	Inner.	Outer.
Nitrogen	75·75	79·17	77·52	69·41
Water vapour ..	13·47	14·29	11·80	19·24
Carbon dioxide..	2·99	5·13	4·93	2·38
Carbon monoxide	3·69	nil	2·45	2·58
Marsh gas.. ..	0·51	0·31	0·95	0·39
Acetylene	0·04	nil	0·27	nil
Hydrogen	3·55	0·47	2·08	nil
	100·00	100·00	100·00	100·00

These figures are of the greatest interest, as they show conclusively that the extreme tip of the Bunsen flame is the only portion which can be used for heating a solid substance without liberating deleterious gases. This corroborates the previous experiment on the gases in the outer zone of the flame, which showed that the outer zone of the Bunsen flame is the only place where complete combustion is approached. Moreover, this work sets at rest a question which has been over and over again under discussion, and that is whether it is better to use a luminous or a non-luminous flame for heating purposes. Using a luminous flame, it is impossible to prevent a deposit of carbon, which is kept by the flame at a red heat on its outer surface; and the carbon dioxide formed by the complete combustion of the carbon already burnt up in the flame is by this reduced back to carbon monoxide. So that, even in the extreme tip of a luminous flame, it is impossible to heat a cool body without giving rise to carbon monoxide, although, acetylene being absent, gas-stoves in which small flat-flame burners are used have not that subtle and penetrating odour which marks the ordinary atmospheric burner stove with the combustion checked just at the right spot for the formation of the greatest volume of noxious products. It is the contact of the body to be heated with the flame before combustion is complete that gives rise to the great mischief. Any cooling of the flame extinguishes a portion of it; and the gases present in it at the moment of extinction creep along the cooled surface, and escape combustion.

In utilising a flame for heating purposes combustion must be completed before any attempt is made to use the heat; in other words, the products of combustion and not the flame must be used for this purpose.

I think I have said enough to show that no geyser or gas-stove should be used without ample and thorough means of ventilation being provided; and no trace of the products of combustion should be allowed to escape into the air. Until this is done, the use of improper forms of stoves will continue to inflict serious injury on the health of the people using them; and this will gradually result in the abandonment of gas as a fuel, instead of, as should be the case, its coming into general use.

Let us now consider for a moment what is likely to be the future of gas during the next half-century. The labour troubles, bad as they are and have been, will not cease for many a weary year. The victim of imperfect education—more dangerous than none at all, as, while destroying natural instinct, it leaves nothing in its place—will still listen to, and be led by the baneful influence of irresponsible demagogues, who care for nothing so long as they can read their own inflammatory utterances in the local press, and gain a temporary notoriety at the expense of the poor fools whose cause they profess to serve. The natural outcome of this will be that every possible labour-saving contrivance will be pressed into the gas manager's service, and that although coal (of a poorer class than that now used) will still be employed as the source of gas, the present retort-setting will quickly give way to the inclined retorts on the Coze principle; while instead of the present wasteful method of quenching the red hot coke, it will, as far as it can be used, be shot direct into the generator of the water-gas plant, and the water-gas, carburetted with the benzene hydrocarbons derived from the smoke of the blast furnaces and coke ovens, or from the creosote oil of the tar distiller, by the process foreshadowed in the concluding sentences of the preceding lecture, will then be mixed with the gas from the retorts, and will supply a far higher illuminant than we at present possess. In parts of the United Kingdom, such as South Wales, where gas-coal is dear and anthracite and bastard coals are cheap, water gas, highly carburetted, will entirely supplant coal gas, with a saving of 50 per cent on the prices now existing in these districts.

While these changes have been going on, and improved methods of manufacture have been tending to the cheapening of gas, it will have been steadily growing in public favour as a fuel; and if, in years to come, the generation of electricity should have been so cheapened as to allow the electric light to successfully compete with gas as an illuminant, the gas works will still be found as busy as of yore, and the holder of gas shares as contented as he is to-day; for, with the desire for a purer atmosphere and white mist instead of yellow fog, gas will have largely supplanted coal as a fuel, and gas stoves, properly ventilated and free from the reproaches I have hurled at them to-night, will burn a gas far higher in its heating power than that we now use, far better as regards its capacity for bearing illuminating hydrocarbons, and entirely free from poisonous constituents. As soon as the demand for it arises, hydrogen gas can be made as cheaply as water gas itself; and when the time is ripe for a fuel gas for use in the house, it is hydrogen and not water gas that will form its basis. With carburetted water gas and 20 per cent of carbon monoxide, we shall still be below the limit of danger; but a pure water gas, with more than 40 per cent of the same insidious element of danger, will never be tolerated in our households. Already a patent has been taken by Messrs. Crookes and Ricarde-Seaver for purifying water gas from carbon monoxide, and converting it mainly into hydrogen by passing it at a high temperature through a mixture of lime and soda-lime—a process which is chemically perfect, as the most expensive portion of the material used could be recovered.

From the earliest days of gas making, the manufacture of hydrogen by the passage of steam over red hot iron has been over and over again mooted and attempted on a large scale; but several factors have combined to render it futile. In the first place, for every 478·5 cubic feet of hydrogen made under perfect theoretical conditions never likely to be obtained in practice, 56 lbs. of iron were converted into the magnetic oxide; and as there was no ready sale for this article, this alone would prevent it being used as a cheap source of hydrogen. The next point was that, when steam was passed over the red hot iron, the temperature was so rapidly lowered that the generation of gas could only go on for a very short period. Finally, the swelling of the mass in the retort, and the fusion of some of the magnetic oxide into the side, renders the removal of the spent material almost an impossibility. These difficulties can, however, be overcome. Take a fire-clay retort 6 feet long and 1 foot in diameter, and cap it with a casting bearing two outlet tubes closed by screw valves, while a similar tube leads from the bottom of the retort. Enclose this retort, set on end, by a furnace chamber of iron, lined with fire brick, leaving a space of 2 ft. 6 in. round the retort; and connext the top of the furnace chamber with one opening at the top of the upright retort, while an air blast is led into the bottom of the furnace chamber below rocking fire bars, which start at the bottom of the retort, and slope upwards to leave room for ash holes closed by gas-tight covers. The retort is filled with iron or steel borings—alone if pure hydrogen is required, or cast into balls with pitch if a little carbon monoxide is not a drawback, as in foundry work. The furnace chamber is filled with coke, fed in through manholes or hoppers in the top; and the fuel being ignited, the blast is turned on, and the mixture of nitrogen and carbon monoxide formed passes over the iron, heating it to a red heat, while the incandescent coke in contact with the retort does the same thing. When the fuel and retort full of iron are at a cherry-red heat, the air-blast is cut off, and the pipe connecting the furnace and retort, together with the pipe in connection with the bottom of the retort, is closed. Steam, superheated by passing through a pipe led round the retort or interior wall of the furnace, is injected at the bottom of the red hot mass of iron, which decomposes it, forming magnetic oxide of iron and hydrogen, which escape by the second tube at the top of the retort, and are led away—to a carburetting chamber if required for illumination, or else direct to the gas-holder if wanted as a fuel; the mass of incandescent fuel in the furnace chamber surrounding the retort keeping up the temperature of the retort and iron sufficiently long to enable the decomposition to be completed. The hydrogen and steam valves are now closed, and the air-blast turned on; and the hot carbon monoxide, passing over the hot magnetic oxide, quickly reduces it down again to metallic iron, which, being in a spongy condition, acts more freely on the steam during later makes than it did at first, and, being infusible at the temperature employed, may be used for a practically unlimited period. What more simple method than this could be desired? Here we have the formation of the most valuable of all fuel gases at the cost of the coke and steam used—a gas also which has double the carrying power for hydrocarbon vapours possessed by coal gas, while its combustion gives rise to nothing but water vapour.

A NEW SOLVENT FOR CELLULOSE.

By C. F. CROSS and E. J. BEVAN.

Hitherto we have had no acid solvent for cellulose, but such as in dissolving it bring about marked changes in composition and properties; in dissolving, the cellulose is resolved, *e.g.*, by the action of sulphuric and phosphoric acids, into products of lower molecular weight, and cannot be recovered from the solution. Concentrated hydrochloric acid, as is well known, attacks cellulose profoundly; when digested with the acid in the cold the fibres are completely disintegrated, and the resulting modification, obtained as a white powder, manifests very different properties from the original. When warmed with aqueous solutions of the alkalies it is coloured deep yellow, and the products of hydrolysis are powerful reducing agents (aldehyds). Some of the OH groups are also so affected that they react with acetic anhydride at its boiling temperature, giving, so far as our determinations show, the diacetate of a C_{18} compound. We find, however, that on dissolving in the acid one-half its weight of zinc chloride, a solution is obtained (of specific gravity 1·44), which dissolves cellulose instantly and without sensible modification. This observation is of importance, as it enables us to investigate some points in the constitution of cellulose, for the determination of which such an acid solution is an essential condition. The solution of cellulose obtained by heating it with concentrated solutions of zinc chloride may also be diluted with hydrochloric acid without precipitating the dissolved products; but the solution by the new reagent has the double advantage of being instantaneous, and of being prepared, therefore, with the minimum of resolution of the cellulose into bodies of lower molecular weight which usually attends the somewhat prolonged heating necessary for complete solution in the aqueous solution of zinc chloride.

The reagent we also find of great value in the investigation of structural points, *i.e.*, as an aid to microscopic work in the province of the vegetable fibres. All forms of pure cellulose are rapidly dissolved by the reagent, and the various stages preceding their final disappearance may be observed under the microscope, the observation throwing much light on structural peculiarities. The raw fibres, *e.g.*, cotton and flax, are not dissolved; at least, only partially, but swell up under the action of the reagent, with the result that the structural features are brought out with great prominence. Jute and the ligno-celluloses generally are dissolved by the reagent, and many of the adipo-celluloses also. We are investigating these actions more closely, and hope shortly to publish an account of our observations. In the meantime, we commend the reagent in question to all who are engaged in the chemical or microscopic investigation of the vegetable fibres.

VOLUMETRIC ESTIMATION OF MANGANESE.

By THOMAS MOORE.

The present volumetric methods for the estimation of manganese involve so many not easily obtainable conditions that, in the great majority of cases, the gravimetric methods appear to be the only ones employed, and indeed this is not to be wondered at, as during the time spent in procuring the manganese in a suitable condition for titrating, an expert analyst would probably have finished the analysis gravimetrically. The process given below will, I hope, be found to be a decided advance both as regards time and accuracy, and trust it may be of some service to those especially who are often placed in the position to estimate rapidly and accurately the *total* amount of manganese in slags, &c.

The process depends for its principle on the conversion of the manganese into the fine violet-coloured manganic metaphosphate, MnP_3O_9, and the titration of this compound by some reducing agent, such as ferrous sulphate, *i.e.*, until the violet colour completely disappears, thus indicating the complete reduction to manganous metaphosphate and end of the reaction.

For the oxidation of the manganese to the manganic state, I have found potassic chlorate to be the most effective and convenient; nitric acid also gives a complete oxidation, but the formation of nitrites at a later stage of the process exercises a reducing effect, and gives results considerably below the truth.

The substance to be examined is dissolved in a suitable solvent, and the solution concentrated until only 2 or 3 c.c. remain; then add 10 to 20 c.c. syrupy phosphoric acid, or the substance may (as is not unfrequently the case), be dissolved directly in the phosphoric acid. The acid most suitable for the above purpose is that known as syrupy phosphoric acid, having a specific gravity of about 1·75. A few crystals of potassic chlorate are now added to the mixture, and the whole gently warmed until the action, at first rather energetic, becomes quieter; the heat may now be increased and the solution left to itself until all odour of chlorine has vanished. The addition of the potassic chlorate causes the liquid to become of a dirty pink colour; this, however, on the continued application of heat, gradually changes to a magnificent deep violet, strongly resembling that of a solution of potassic permanganate. The thick syrupy liquid after cooling is then dissolved in about 100 c.c. water, and titrates direct by means of a solution of ferrous sulphate, continuing the addition of the latter until the violet colour is dissipated, or add at once a known quantity of the iron solution, and titrate back the excess by means of potassic permanganate in the usual manner. Having found by either method the amount of iron oxidised, a simple calculation will give the quantity of manganese present. Thus, considering the metals present only as oxides, we have—

$$Mn_2O_3 + 2FeO = 2MnO + Fe_2O_3.$$

Hence, 1 part of Fe represents 1·4108 parts Mn_2O_3.

Everything considered, the best reducing agent is probably the ferrous sulphate, as it may be prepared when required from metallic iron, besides giving a sharper and more decided reaction than oxalic acid, &c.

In testing this method with such compounds as the sulphate, the carbonate, or the pyrophosphate of manganese, the results obtained were excellent, and in the analysis of some minerals, slags, &c., the figures found agreed so well with those by the gravimetric method that it would be difficult to decide in which process the error lay.

As far as my experience has gone, the only metal which interferes is chromium; this being oxidised by the potassic chlorate, passes into solution, and, oxidising the iron, gives a false number. Cobalt, which under the circumstances might be supposed to pass into a higher state of oxidation, does not interfere, provided care is taken that all free chlorine is expelled before proceeding to titrate; nevertheless, appearances seem to indicate the formation of a somewhat similar compound at lower temperatures, the liquid assuming a deep brown colour. Inasmuch as the rose colour of the cobalt marks the end of the decomposition, it is best first to add an excess of the iron solution, then, after neutralising the cobalt colouration by the addition of sufficient nickelous sulphate, titrate back the excess of iron by permanganate of potassium.

In conclusion it may be observed that phosphoric acid is a powerful solvent for certain silicates, and even glass is strongly attacked when the temperature is raised sufficiently.

Thio, New Caledonia,
December 1, 1890.

THE ACTION OF THE SILENT DISCHARGE OF ELECTRICITY ON CHLORINE.

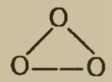
By H. M. VERNON.

Arguing from the fact that oxygen gas, when subjected to the silent discharge of electricity, partially undergoes condensation into ozone, it seemed possible that other elementary gases, as chlorine and bromine vapour, might undergo an analogous change when subjected to the same treatment. Accordingly, a glass tube, with a U-shaped index of fine-bore glass tubing, similar to those used by Andrews and Tait in their experiments on ozone (*Phil. Trans.* 1860, 113), was filled with purified and dried chlorine. After passing a current of the gas through the tube for some time, the end was sealed in the blowpipe flame. The tube was then warmed slightly, and a few bubbles of gas thus driven out. The end of the index tube dipped under strong sulphuric acid saturated with chlorine gas, so that, on cooling, a short column of the acid was drawn up. This served as an index for any changes of volume which might take place in the chlorine in the tube.

A silent discharge of electricity from a large induction coil connected with four Grove's cells was then passed between the platinum wires sealed in the tube. The volume of the gas was soon observed to increase slightly, but after this the volume remained quite constant even after the discharge had been passed for several hours. The discharge from a single cell and a smaller induction coil produced the same effect, except that the initial increase of volume was not quite so large. We may therefore conclude that no allotropic change takes place when chlorine gas is subjected to the silent discharge of electricity, the initial increase of volume being merely due to the heating effect the discharge has upon the gas.

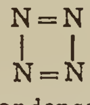
Into another similar tube, filled with chlorine, was introduced a small quantity of liquid bromine. The tube thus contained chlorine saturated with bromine vapour. The silent discharge, on being passed through this tube, did not produce any different effect than for chlorine alone, so we may conclude that bromine vapour also does not undergo any allotropic condensation when subjected to the influence of a silent discharge of electricity. If a contraction of volume had taken place, it would have been necessary to have made experiments with bromine vapour unmixed with chlorine; for such a contraction might be due to the formation or condensation of a chloride of bromine. The fact of no contraction taking place proves, however, that the bromine underwent no change. If bromine vapour alone were used, it would have been necessary to heat the tube to above the boiling-point of bromine before passing the discharge, and as it would be difficult to keep the temperature so constant as at ordinary temperatures, the experiment was not made.

The fact that oxygen gas is capable of undergoing condensation while chlorine and bromine are not, is easily explained. The oxygen atom being divalent is capable of uniting itself to two other atoms of oxygen or other elements, and thus with oxygen forming ozone



The atoms of chlorine and bromine, however, being only monovalent, have all their affinity satisfied when they are united to a single other atom of chlorine and bromine, thus, Cl—Cl, Br—Br. It is not possible, therefore, that condensation can take place if the atoms remain monovalent. Hydrogen gas and iodine vapour are in a similar manner debarred from undergoing condensation.

The atoms of nitrogen being trivalent are theoretically capable of undergoing condensation and forming molecules with four or more atoms, thus—



They cannot, however, condense to molecules with three atoms without the existence of free affinities. Looking at the great stability of the nitrogen molecule, and the instability of the ozone molecule, which contains only three atoms of oxygen, it does not seem probable that such a modification is capable of existing. The possibility of such a condensation taking place is, however, proved by the existence of the similarly constituted molecules of phosphorus and arsenic vapours.

The hexatomic molecules of sulphur and selenium, known to exist at temperatures not far removed from the boiling-points of these elements, are another example of the condensation of polyvalent atoms when situated under suitable conditions. Inasmuch as these molecules are dissociated into diatomic molecules at higher temperatures, it would not be possible to re-form them by the action of the silent discharge upon the diatomic molecules. The very slight affinity that atoms of metallic elements have for each other when in the state of vapour is too well-known to need comment. We therefore come to the conclusion that it is not probable that any other elements but oxygen will be found capable of undergoing molecular condensation when, in the gaseous state, subjected to the silent discharge of electricity.

ELECTRICITY
IN TRANSITU:
FROM PLENUM TO VACUUM.*

By WILLIAM CROOKES, F.R.S.,
President of the Institution of Electrical Engineers.

(Continued rom p. 56).

The Dark Space.

AFTER the stratification stage is passed we come to a very curious phenomenon, the so-called "Dark Space." Studying electrical phenomena in gases, in the year 1838, Faraday† pointed out a break in the continuity of the luminous discharge separating the glow of the positive electrode from that of the negative. This he called "the dark space." It is seen in tubes containing gas only slightly rarefied, as in this tube (Fig. 5, P. = 6 m.m.), where you will observe that the positive glow, extending as a pink streak from the positive electrode, B, ends about ten millimetres before the spot of blue light, C, representing the negative glow. This gap, or non-luminous hiatus, D, is Faraday's "dark space." Separating the negative glow from its electrode is another space. In this tube it is so small that the glow appears to be in actual contact with the electrode, but on exhausting a little further it rapidly separates; and in the next tube (Fig. 6), containing air at a little less pressure (P. = 3 m.m.), this dark space, E, has extended so as to remove the negative glow about four millimetres from the electrode, A. It is with this second dark space that I particularly wish to deal to-night. Therefore I shall refer to it as the "dark space," meaning always that in the negative glow.

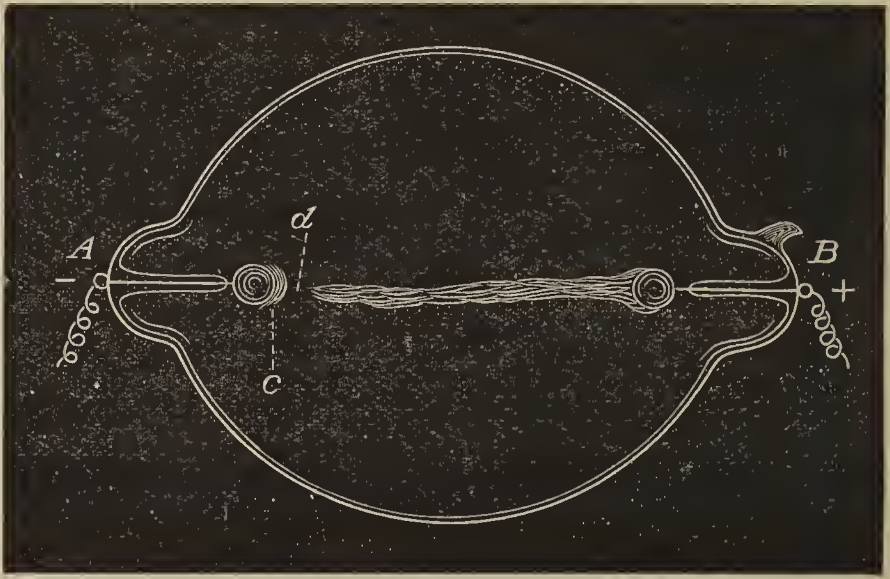


FIG. 5.—P. = 6 m.m.

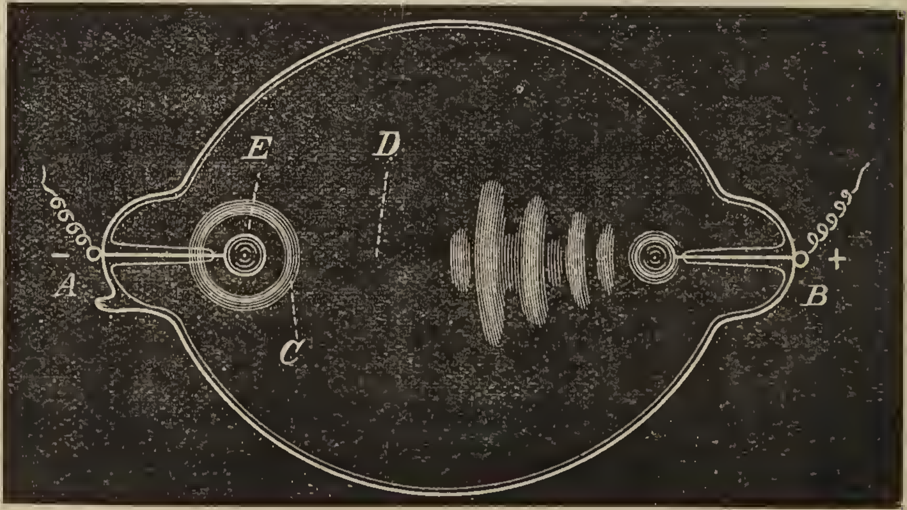


FIG. 6.—P. = 3 m m.

In the experiments just shown with hydrogen stratifications the contents of the tube under the electric discharge still obey the laws following from the average properties of an immense number of molecules moving in every direction with velocities of all conceivable magnitudes. But if I continue exhausting, the dark space, E, round the negative pole, A, becomes visible, grows larger and larger, and at last fills up the entire tube. The molecules at this stage are in a condition different from those in a less highly exhausted tube. At low exhaustions they behave as gas in the ordinary sense of the term, but at these high exhaustions, under electric stress, they have become exalted to an *ultra-gaseous* state, in which very decided properties, hitherto masked, come into play.

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* Inaugural Address delivered January 15th, 1891.

† "Experimental Researches in Electricity," 1838, par. 1544.

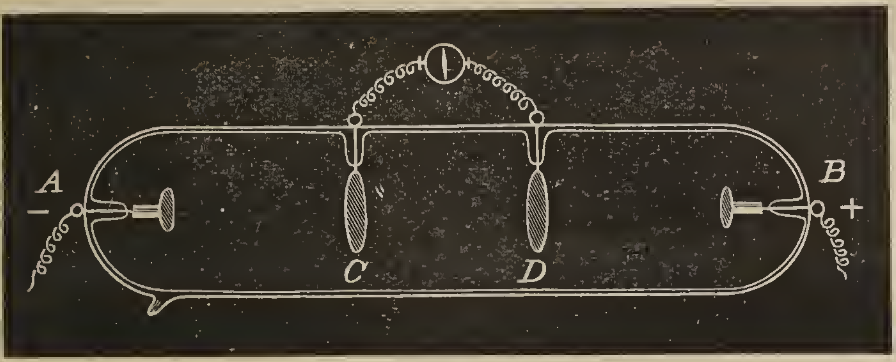

Fig. 7.

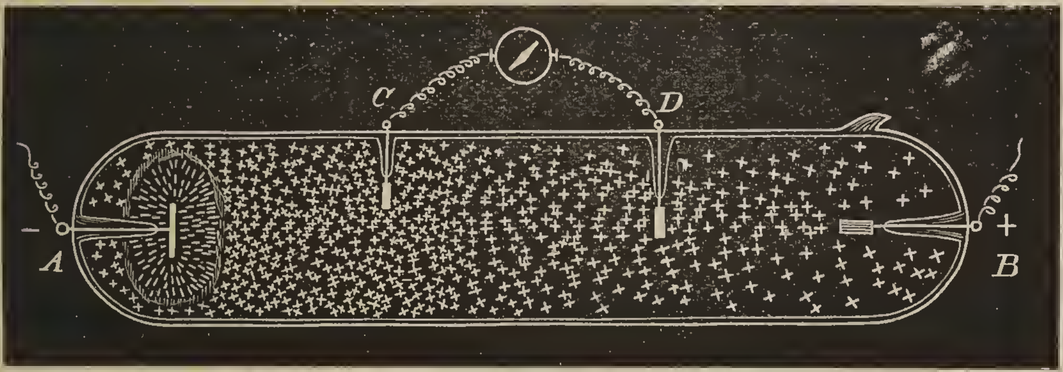

Fig. 8*a*.—P. = 0·25 m.m.

Fig. 8*b*.—P. = 0·25 m.m.

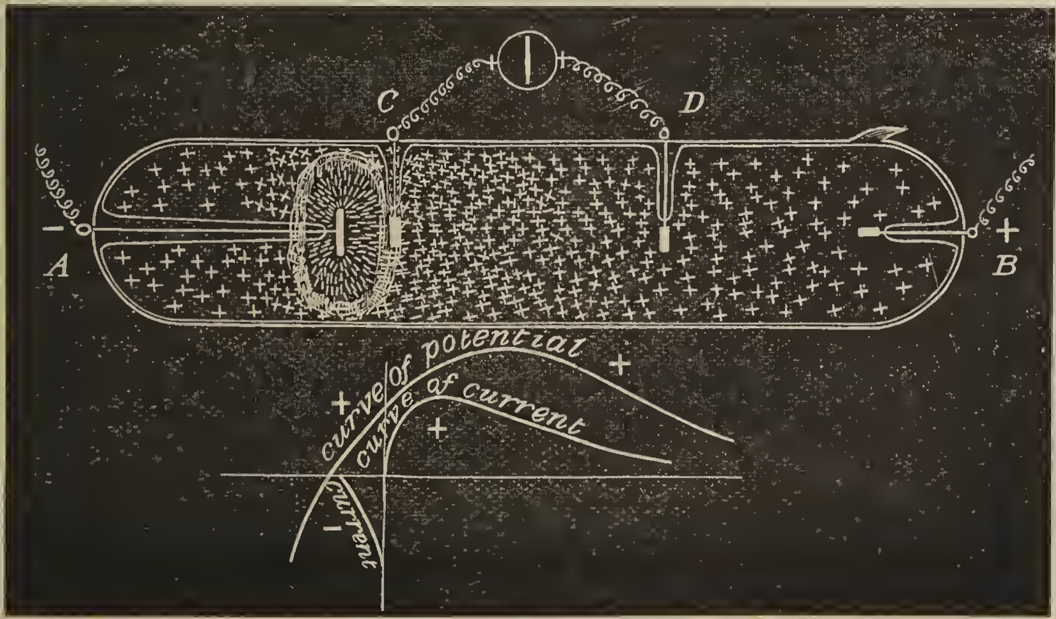

Fig. 8*c*.—P. = 0·25 m.m.

The radius of the dark space varies with the degree of exhaustion, with the kind of gas in which it has been produced, with the temperature of the negative pole, and to a less extent with the intensity of the spark.

It has been erroneously assumed that I ever said the thickness of the "dark space" represents the mean free path of the molecules in their ordinary condition, and it has been pointed out that the radius of the dark space is decidedly greater than the calculated mean free path of the molecules. I have taken accurate measurements of the radius of the dark space at different pressures, and compared it with the calculated mean free path of the gaseous molecules at corresponding pressures when not under the influence of electrical energy, and I find that they do not bear a constant relation one to the other. The length of the dark space is not 20 times the mean free path, as some have estimated, but a gradually increasing multiple must be taken as the exhaustion becomes greater.

Exploration with Idle Poles.

Wishing to learn something of the electrical condition of the matter within and without the dark space, I made a tube (Fig. 7), having besides the positive and negative terminals, A B, two extra intermediate poles, C and D; the tube showed that when the exhaustion was such that both the idle poles were outside the dark space, on passing the current through the tube, there was a considerable difference of potential between them when measured on the galvanometer. If the exhaustion was carried so high that one of the extra poles was just on the border of the dark space, then no current passed between them. When the exhaustion was still further increased so as to inclose one of the extra poles fully in the dark space, again there was a great difference of potential between them, but the direction was reversed, the pole at highest potential now being the one formerly at lowest potential.

When the dark space has been further explored by means of a movable negative pole, I found that the effects did not depend essentially on the exhaustion, and were really due to the position occupied by the extra pole with regard to the dark space.

These phenomena are difficult to understand from mere description, and the experiments themselves are not easy to carry out so as to be visible to many at a time. I have here, however, a working model of an apparatus which will make these puzzling indications clear to all.

A cylindrical tube (Fig. 8, *a*, *b*, and *c*, P.=0·25 m.m.), furnished with the usual poles, A, B, at the ends, has two extra or idle poles near together at C and D. The pole A is movable along the axis of the tube, so that when exhausted the dark space can be brought to any desired position with respect to the idle poles C and D. The shading and + and − marks roughly show the distribution of positive and negative electricity inside the tube. I start with the negative pole A as far as possible from either idle pole (Fig. 8, *a*). Turning on the coil you see the dark space surrounding the pole A, and the idle poles quite outside.

The shading shows that each idle pole is in the positive area, and on testing with a gold leaf electroscope it will be seen that each is charged with positive electricity. But the shading also shows more positive at C than at D, and on connecting C and D with a galvanometer the needle indicates a rush of current from C to D, D being negative to C.

The dark space is next brought to such a position that the pole C is well within it (Fig. 8, *b*). A change has now come over the indications. The galvanometer shows a reverse current to that which was seen on the former occasion. C is now negative and D positive, but the gold leaves still tell us both poles are positively electrified.

At a certain position of the dark space, when its edge is on the pole C (Fig. 8, *c*), a neutral state is found at which the gold leaves still show strongly positive electrifications, and no current is seen on the galvanometer. The curves below (Fig. 8, *c*), roughly show the rise and fall of negative and positive current at different parts of the tube, whilst the potential curve keeps positive.

When a substance that will phosphoresce under electrical excitement is introduced into the tube, the position of greatest luminosity is found to be at the border of the dark space, just where the two opposing armies of negative and positive atoms meet in battle array and re-combine. Later on I shall refer to this phenomenon in connection with the phosphorescence of yttria.

(To be continued).

KEEPING OF "NESSLER" STANDARDS.

By W. P. MASON.

Standard tubes containing 0·01, 0·02, 0·03, 0·04, 0·05, 0·06, 0·07, 0·08, and 0·09 m.grm. NH_3 in 50 c.c. water were prepared for use. Three days afterward they were compared with fresh standards of above values. It was observed that 0·03, 0·05, and 0·07 had not changed, and the remainder had darkened to a very slight degree—less than 0·0025 in each case.

Standards made in the morning may be thoroughly relied upon for working during the day.

NOTICES OF BOOKS.

An Introduction to the Study of Metallurgy. By Professor Roberts-Austen, C.B., F.R.S. London: Charles Griffin and Co., 1891.

Professor Roberts-Austen's students have long hoped that he would give them in the form of a book his introductory Lectures on Metallurgy, in which he has for many years treated the subject in an original way. It was to be expected that he would take great pains in the preparation of such a volume, but we were hardly prepared to find so large a mass of information compressed into the small compass of a crown octavo volume.

His guiding principle seems to be that it is more important at the outset for the student to know what was the scope of mind of the early practisers of metallurgy, and to see what kind of aid the art may be expected to receive in future from the sciences, rather than to acquire familiarity with complicated details of processes and appliances. With this end in view he traces at some length the development of chemistry as a science from the very ancient metallurgical process of cupelling lead to extract the precious metals, and the opinions are given of prominent metallurgists and chemists from Geber in the eighth century to Lavoisier in the eighteenth, with abundant references to authorities.

Much space is devoted to a description of the action of minute quantities of elements on masses of metals, for Professor Roberts-Austen rightly considers the study of such questions to be the distinguishing feature of modern metallurgy. Indeed his own generalisation that the influence of "traces" on masses of metal is directly proportional to the atomic volume of the added element has been recognised as being the most important application from an industrial point of view which we have as yet had of the Periodic Law.

The number of curves he gives in illustration of this portion of his subject will be of great value to the student. Many of these have been specially prepared for this volume. Of similar value are the schemes showing the course adopted in conducting smelting operations. The scheme (p. 250) of the processes adopted in the great metallurgical district of Freiberg in Saxony for smelting complex ores, and the scheme (p. 242) for smelting ores of copper, deserve special mention.

A comprehensive classification of processes, and of the methods adopted in extracting metals from their ores, is given to show that the art of metallurgy is capable of being far more systematically treated than has hitherto been the case in this country. In dealing with typical metallurgical processes the author has hardly permitted himself sufficient space, and this portion of the volume, which is at present the least satisfactory, will, it may be hoped, be greatly extended in later editions.

The author considers that in the immediate future the most marked technical advance may be expected to arise, not from improvements in smelting operations, but from the study of the properties of metals and alloys as influenced by thermal and mechanical treatment, and by the presence of foreign matter. In this connection we welcome the introduction into the volume of Professor Austen's lecture delivered at Newcastle, on the "Hardening and Tempering of Steel," the merit of which has been so widely recognised. Its long array of references to authority will be found very serviceable; indeed, throughout the whole book the list of references is most complete.

From the point of view of the student the main question is, perhaps, how does this book differ from other books on the same subject? This we have to some extent already indicated, but it may be further pointed out that no text-book with which we are acquainted—at least no English text-book—at all approaches this one either in its method of treatment, its general arrangement, or in the completeness with which the most modern views on the subject are dealt with. The art of metallurgy is so rapidly changing from a more or less empirical application of chemistry and physics to an art of which both chemists and physicists are now looking for the explanation of many important but at present doubtful theoretical questions, that it is evident that a book of the nature of Professor Austen's volume will be invaluable, not only, as the author modestly describes it, to the student of metallurgy —using the term in its ordinary sense—but also to those whose knowledge of the art is far advanced.

Contributions of Alchemy to Numismatics. By Henry Carrington Bolton, Ph.D. Read before the New York Numismatic and Archæological Society. Author's Edition: New York.

We have here a curious and interesting work, evidently the outcome of prolonged and careful research, the purport of which might have perhaps been more clearly understood had it been entitled "Contributions of Numismatics to the History of Alchemy." The author, though plainly no believer in the pretensions of the adepts, gives us some striking pictures of the alleged gold-makers of the seventeenth century.

There exist, it appears, a number of coins, medals, &c., said to have been stamped from bullion obtained by the Hermetic art. Many more such are recorded as having formerly existed. Of these pieces, forty-three are here particularly described. One of the most successful alchemists is said to have been Raymond Lully (Ramon Lulli, 1235 to 1315). This worthy is said to have transmuted base metals into gold, in the Tower of London and in Westminster Abbey, in such quantity that six million nobles, each exceeding £3 in value, were coined from the product. These coins, called "Raymond" or Rose-nobles, are mentioned by Camden and Selden, and are said to have been of purer gold than that generally coined in the thirteenth century. Even if any of these pieces were still existent, there would be no evidence that they had been actually obtained from alchemical gold. The author quotes J. F. Buddeus to the effect that hermetic symbols upon a coin are no conclusive proof as to its origin. Reyher cites Monconys, to the effect that "The apothecary Strobelperger told me that a certain merchant of Lubeck, not very successful in business, but who knew how to 'fix' lead and convert it into gold, presented to the King of Sweden a mass of gold weighing 100 lbs., prepared by himself through hermetic art. Gustavus Adolphus caused ducats to be made of this gold, bearing his likeness on one side and the Royal Arms, with the symbols of mercury and sulphur, on the other. He gave me (continues Monconys) one of these ducats, and said that after the death of the merchant, who did not seem very wealthy and had long since discontinued trade, 1,700,000 crowns were found in his house." This is a fine case of hearsay evidence!

Some of the leading alchemists of the seventeenth century were for a time successful, if not in making gold at least in obtaining it from their patrons. Wenzel Seyler was ennobled as Baron von Reinburg. Dr. Bolton has examined a medallion made from his gold in 1677. It is brassy in colour, and its specific gravity is only 12·67. Baron Krohnemann, a profligate and impudent swindler, was at length detected in fraud and was hanged by order of the Margrave of Brandenburg. Domenico Manuel, after a career of roguery, had the honour of being hanged on gilded gallows at Küstrin, in 1709.

Even the present century is not without its claimants of alchemical skill. Francois Cambriel, in 1843, undertook to teach the secret of transmutation in a course of 19 lessons. About the same time there was inserted in a leading London literary organ an advertisement offering to teach the "Hermetic art" for a fee of 100 guineas. In 1889 appeared in Paris the second edition of a work entitled "L'Or et la Transmutation des Metaux," by G. Théodore Tiffereau. He permitted one of the assayers of the Paris Mint to make an experiment according to his system. The result was negative. It is not likely that we shall have any more alchemists. Fraud and gullibility have entered upon novel phases.

CORRESPONDENCE.

REFERENCES TO ORIGINAL PAPERS.

To the Editor of the Chemical News.

Sir,—In your issue of October 3rd, 1890 (vol. lxii., p. 177, col. 2), "An Abstractor" justly complains of the carelessness of some authors in omitting the dates of publication of volumes to which references are made, and points out that vol. and page are insufficient.

Your correspondent remarks that the desired date can only be obtained by those who have "immediate access to a library round whose walls all journals ever published were properly ranged."

I cordially endorse his views as to the desirability of affixing dates to references, and beg leave to direct his attention to a compilation I published several years ago, which will enable him to determine the date of issue of any volume of each of 500 scientific periodicals without leaving his writing-desk. I refer to the extensive Chronological Tables accompanying my "Catalogue of Scientific and Technical Periodicals (1665-1882)," published by the Smithsonian Institution, as No. 514 of the Smithsonian Miscellaneous Collections, Washington, 1885. This catalogue forms an 8vo. volume of 773 pages, and comprises full titles of more than 5000 scientific periodicals in about twenty languages. Pages 618-707 contain the Chronological Tables, by the aid of which the year of publication of each volume of about 500 periodicals can be readily found, or, if the date be known, the number of the volume can be found. The sequence of several series, when a periodical has changed its name, or absorbed other journals, is also clearly indicated. These Chronological Tables have a separate index. I venture to describe this work here because I suspect all working *savants* are not familiar with this convenient hand-book. The Tables commence with the year 1728, and come down to the year 1880. The data for the decade just closed are more easily obtained, and there are fewer irregularities of publication than in the earlier years. If your correspondent will send me his name and address, I shall be pleased to present him with a copy of my catalogue.—I am, &c.,

H. Carrington Bolton.
University Club, New York City.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 1.

The Great Chemical Industries at the Exhibition of 1889.—M. P. Kienlen.—An account of the manufacture of sulphuric acid, and of the extraction of copper from the burnt ores.

On the Condensation of Gaseous Carbons under the Influence of the Effluve (Continued).—P. Schützenberger.—The gases which here come in question are carbon monoxide, cyanogen, mixtures of cyanogen and hydrogen, acetylene, and the vapour of benzene.

The Spontaneous Purification of Rivers with reference to the Waters of the Rhône.—P. Cazeneuve.—The spontaneous purification of rivers is a fact of constant occurrence. The Wupper is abominably contaminated at Elberfeld. Some miles lower down at Opladen it is pure, and serves for the most delicate uses of the dye works, which require very pure waters. The Isar receives at Munich the filth of forty-nine sewers. Below Munich the river rapily becomes pure, as is proved by the analysis of Schelhass, Brunner, and Emmerick. The Derle receives the waste waters of Lille, coming from paper-mills, distilleries, and starch works. The water takes an impure character visible to the naked eye, but which gradually disappears. The same phenomenon of purification is seen in the Rhône. The dyers of the Quay Saint Clair turn into the river their waste liquors, and when they empty their becks the waters are coloured all the length of the quay for a breadth of 25 or 30 metres. A kilometre lower down at the Morand Bridge, the Rhône is perfectly limpid. When hypochlorites or *Cocculus indicus* is thrown into a river at 2 or 3 kilometres lower down the fishes are not injured. The two drains of Clichy and St. Denis pour into the Seine 3 cubic metres per second of polluted water, whilst at Meudon every trace of infection has disappeared.

Influence of Silicon on the Properties of Iron and Steel.—Th. Turner.—From the *Journal of the Chemical Society.*

The Use of Fluor-spar in Metallurgy.—Dr. Foehr. An abridgment from the *Chemiker Zeitung.*

Quantities of Zinc and Lead Contained in the Gases of Blast Furnaces.—Albert Nita (*Zeitschrift Angewandte Chemie*).—The quantity of zinc thus carried off corresponds to 27 per cent of the total amount in the ore. The loss of lead is only 9 per cent.

Metallurgy in the West of America.—R. Pearce.—An account of the operations of the Boston and Colorado Smelting Company.—*Chemiker Zeitung.*

Mercury Mine at Nikitowka, in Russia.—C. Ernst (from the *Chemiker Zeitung*).—The yield of mercury was in 1887 63,967 kilos., and in 1888 it had risen to 164,790 kilos.

The O'Brien Process for the Extraction of Gold and Silver from Pyrites.—(*Chemiker Zeitung*).—The ore is roasted, treated for twenty-four to thirty hours with sulphurous anhydride, washed with water, and amalgamated in the ordinary manner. The quantity of silver extracted is much more considerable than by the chloruration process. The sulphurous acid is obtained by roasting the ore.

Analysis of Manganese by Means of Hydrogen Peroxide.—A. Baumann (*Zeit. Angewandte Chem.*).—If manganese peroxide in powder is allowed to act upon hydrogen peroxide in a neutral or alkaline solution, the hydrogen peroxide is decomposed, oxygen is set at liberty, but the manganese is not attacked. If the hydrogen peroxide is in an acid solution and in excess, the manganese dioxide is reduced to the state of a salt of the monoxide, and oxygen is given off proportionate to the weight of MnO_2 present; 86·72 MnO_2 yield 31·92 of oxygen. Three methods may be founded upon this reaction: gravimetric, volumetric, and the direct determination of the gas given off.

Detection of Sodium Thiosulphate in Sodium Bicarbonate.—J. Lüttke (*Chemiker Zeitung*).—If we add a few c.c. of a solution of barium nitrate to a solution of sodium bicarbonate previously saturated with hydrochloric acid and not containing sulphuric acid, no turbidity or precipitate ought to be occasioned. If a thiosulphate is present, there is formed a turbidity or a precipitate on adding a drop of permanganate, which transforms the thiosulphate into a sulphate.

Use of the Nitrometer for Titrating Chloride of Lime, Manganese, and Permanganate.—G. Lunge (*Zeit. f. Angewandte Chem.*).—The method, which was described some years ago, is founded on the use of oxygenated water. In the case of chloride of lime a volume of oxygen is evolved equal to the volume of the active chlorine contained in the chloride—

$$CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2.$$

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.

Magnesium Chloride.—Can any reader inform me how chloride of magnesium, used for sizing purposes in Lancashire, is manufactured?—W. H. B.

MEETINGS FOR THE WEEK.

Monday, 9th.—Medical, 8.30.
—— Society of Arts, 8. "The Construction and Capabilities of Musical Instruments," by A. J. Hipkins, F.S.A.
Tuesday, 10th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S., B.S., F.R.C.S., Fullerian Professor of Physiology, R.I.
—— Photographic, 8 (Anniversary).
—— Royal Medical and Chirurgical, 8.30.
—— Society of Arts, 8. "Sgraffito," by Heywood Sumner.
Wednesday, 11th.—Society of Arts, 8. "The Proposed Irish Channel Tunnel," By Sir Robert Lethbridge, M.P.
—— Pharmaceutical, 8.
Thursday, 12th.—Royal, 4.30.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "The Position of Lulli, Purcell, and Scarlatti in the History of the Opera," by Professor C. Hubert H. Parry, Mus. Doc. M.A.
Friday, 13th.—Royal Institution, 9. "Some Results of Recent Eclipse Expeditions," by Professor A. Schuster, Ph.D., F.R.S., F.R.A.S.
—— Astronomical, 3. (Anniversary).
—— Physical, 5. Annual General Meeting. (1) "Discussion of Prof. Minchin's Paper on Photo-electricity;" (2) The Change in the Absorption Spectrum of Cobalt Glass Produced by Heat," by Sir John Conroy, Bart., M.A.
Saturday, 14th.—Royal Institution, 3. "The Forces of Cohesion," by The Right Hon. Lord Rayleigh, M.A., D.C.L., F.R.S.

THE CHEMICAL NEWS.

Vol. LXIII., No. 1629.

NOTE ON ALDEPALMITIC ACID, THE CHIEF CONSTITUENT OF THE BUTTER OF THE COW

By J. ALFRED WANKLYN.

On the 19th of last month I had the honour of laying before the Society of Chemical Industry a short account of my investigations into the nature and constitution of butter, and made the announcement that the commonly received views of the constitution of butter are erroneous. It does not consist mainly of olein, palmitin, and stearin, but of something quite different from the common animal and vegetable fats.

The chief acid in butter soap is not palmitic acid, but a new acid to which I have given the name aldepalmitic acid. This acid differs from palmitic acid by containing less hydrogen (as was shown by a combustion of the substance), and by its equivalent being smaller (shown by most careful investigation of its baryta-salt).

Its formula appears to be $(C_{16}H_{30}O_2)_n$; but it does not belong to the oleic series of acids. I expect that its molecule will turn out to be very complex, and that the n in the formula will be at least 2.

Between the properties of the new acid and those of palmitic acid obtained from palm oil the differences are very striking.

The specific gravities are different and the melting-points different, and nothing could well be more striking than the behaviour of the two acids towards alcohol of 85 per cent strength.

At ordinary temperatures the solubility of the acids is very nearly the same, but as the temperature rises the differences appear. The solubility of palmitic acid increases, comparatively slowly, as the temperature rises; but the solubility of aldepalmitic acid jumps up suddenly, so that at 25° C. this acid passes into perfect solution in about its own weight of alcohol. When the alcoholic solution is cooled down to common temperatures, the entire solution solidifies or gelatinises, and in that manner aldepalmitic acid can solidify five times its weight of alcohol. Part of the alcohol is retained mechanically and part chemically.

On the other hand, palmitic acid possesses no power of combining with alcohol. Some of the salts of aldepalmitic acid combine readily with a large proportion of alcohol. In fine, aldepalmitic acid is a most distinct substance endowed with most characteristic properties.

LOSS OF CARBON IN RUSTED PIG-IRON.

By J. G. DONALD, M.A.

Recently the writer was engaged in determining the graphite and carbon in two samples of pig-iron. The drillings weighed off for treatment with cuprammonium chloride were brushed into beakers which were wet, having been rinsed with distilled water. At this point, and before the solvent had been added, he was called away. On returning to the work, after the lapse of nearly a week, the drillings in the beakers were of course found to be much rusted.

The idea occurred to him that it would be interesting to learn to what extent there had been loss of carbon through the rusting of the drillings. To this end the rusted portions as well as portions of the original samples were treated with the solvent, and the carbon sponge submitted to combustion, with the following results for total carbon:—

	No. 1.	No. 2.
Rusted drillings	1·941	1·332
Original sample.. ..	2·282	2·132

The combined carbon in each of the samples was found to be as follows:—

No. 1.	No. 2.
0·378	0·336

It will thus be seen that in the case of No. 2 the rusting has caused a disappearance of a portion of the graphite. No. 2 was in much finer drillings than No. 1, and to this fact is doubtless due in part at least the greater loss of carbon in No. 2.

124, St. James Street,
Montreal, Cananda, January 21, 1890.

THE POTASSIUM CYANIDE ASSAY OF LEAD ORES.

By WALTER J. COOPER.

Referring to the article on "The Potassium Cyanide Assay of Lead Ores" (Chemical News, vol. lxii., p. 30). I notice that in the experiments (15 and 16), made with the ores containing pyrites, the author does not say what becomes of the copper present, and the general wording of the article seems to state that the reduced lead was obtained as a clean weighable button, which result I cannot reconcile with my own experience.

During last autumn I made some experiments with galena and pyrites bearing quartz from North Wales, of which the following is the average analysis—

SiO_2	83·05	
$Fe_2S_3Cu_2S$	10·639	
FeS_2	2·967	
PbS	3·001	
Au..	Trace	(Not estimated.)
Fe_2O_3	0·343	
	100·000	

Among other experiments I tried the reduction of the ore by means of potassium cyanide. The ordinary commercial cyanide was used, being mixed with the ore in very large excess. A Battersea crucible was taken, and a thick layer of cyanide well rammed into the bottom; the mixed ore and cyanide were then introduced, and the whole well covered with cyanide. The charge was heated at a moderate red heat till the evolution of gas had nearly ceased, and the whole then raised to a bright red heat for a further five minutes and allowed to cool.

The crucible was then broken, and the slag which was black and very hard removed by boiling with water. The fine black mud (Fe) was then washed carefully away and a small button of lead with numerous scales of copper remained in the bottom of the beaker. The button was rather hard and the surface covered with strongly adhering copper scales. On analysis it proved to contain all the lead with a considerable quantity of copper and a little iron.

The above results seem to point out that with lead ores containing other reducible metals, the assay by means of potassium cyanide offers no advantages over the ordinary means of estimation by the wet method, as the resulting button has to be carefully analysed in order to ascertain the actual quantity of lead present.

High Street, Mitcheldean.

BORAX.

By E. L. FLEMING.

Borax is now so generally and extensively used amongst the industries of the world, and such advances have been made during the last thirty years, both in new discoveries of the mineral itself, or of material from which it can be manufactured, that some account is rendered necessary of its consumption and production.

It is employed in various branches of the hardware, earthenware, textile, leather, chemical, and food industries.

In the capacity of a flux for the reduction of the precious metals and in soldering gold it was known to the ancients under the name of crysacolla; it is used for brazing copper, for welding steel and iron together, for enamelling both copper and iron, and for lining between the inner and outer shells of fireproof safes.

Mixed with other ingredients it forms a very fusible glass or frit necessary for glazing china, earthenware, bricks, and tiles. It is used in the manufacture of glass, and also in the production of those cements that take a polish after setting.

It is employed in dissolving shellac in the manufacture of hats, in dissolving the glutinous matter adhering to raw silk by silk weavers, in calico-printing, and fire-proofing delicate fabrics, in the fabrication of paper, in starch glazing linen, and the preparation of candle wicks. It is used in dyeing leather, curing hides and skins, and the chemical tanning of leather.

In the chemical industries it is employed in the production of borate of chromium (Guignet's green), borate of manganese (a drier), in the manufacture of soap, in the formation of toning baths for silver prints, by photographers, and in several pharmaceutical preparations.

As a food preservative it is now very largely used by American pork packers as an antiseptic, many thousands of tons of bacon and hams being so preserved annually.

Borax occurs in its native state, from which source probably one-third of the borax used throughout the world comes, and it is manufactured from (*a*) boracic acid, (*b*) borate of lime, (*c*) double borate of lime and soda; there are several other minerals from which it could be manufactured.

The borate of lime, like carbonate of lime, occurs in three varieties; one like marble, another like calc spar or Iceland spar, and the third like chalk; in outward apppearance it often so closely resembles the carbonate as often to be mistaken for that body. The principal deposits of crude borax occur in North America, Northern India, and Southern Thibet.

In North America there are ten deposits or borax marshes, as they are called, and a description of the Saline Valley marsh, situated in Inyo county, California, will afford a general idea of the whole, although the Saline Valley, by competent authorities, is considered the richest.

Saline Valley is on the Eastern slope of the Sierra Nevada Mountains, eleven miles from the line of the Carson and Colorado Railroad Company, and its topographical aspect is best described by comparing it to an immense oval saucer.

The crude borax there covers the plain, which is eighteen miles long by twelve miles wide, for an area of over one thousand acres with a depth of from six to eighteen inches.

Surrounding the plain are a complete circle of mountainous hills, with here and there a copse of mesquit, manzanita, or shellac-wood; and looking over the dry and arid marsh, towards the mountains, small streams of pure fresh water may be observed, affording not only a pleasant relief to the eye, but a great boon to those employed in the industry of refining the borax.

The colour of the crude material as it lays upon the plain is of a peculiar greyish yellow; the borax is mixed with sand, sulphate of soda, carbonate of soda, and salt. The material varies in richness from 10—90 per cent of borax, the formation being a conglomeration of sand and small crystals of a loose and friable nature.

Samples taken from different portions of the marsh are shown in the Table appended.

Below the surface of the marsh, at a depth of four feet, liquor is found highly impregnated with borax; this liquor upon evaporation yields a salt, the composition of which is—

From an Analysis by Prof. T. Price, San Francisco.

*Anhydrous biborate of soda ..	7·43
Chloride of sodium	32·89
Sulphate of soda..	39·07
Carbonate of soda	15·59
Water	5·02
	100·00

* Equivalent to 20·3 per cent crystallised borax.

The process of refining the crude material is an extremely simple one. The surface of the marsh is removed to a depth of eighteen inches and the material carted to the refinery. There the crude borax is dissolved in boiling water in large wrought-iron pans, capable of holding four or five thousand gallons; the contents are allowed to settle, and the clear liquor containing the borax, carbonate, sulphate of soda, and salt, is run into galvanised iron vats holding two thousand gallons; the borax crystallises out first, and the mother liquor is concentrated and again allowed to crystallise, after which the solution being strongly impregnated with the foreign salts is run to waste.

There is such an abundance of the crude material testing over 50 per cent of borax that no attention is paid to the borax liquors laying below the surface of the marsh, though these, in years to come, will be utilised.

No sooner has the crude borax been removed from the marsh than a second growth begins to form, doubtless owing to capillary attraction, when the liquor on reaching the surface, becoming exposed to the heat of the sun, is naturally evaporated to dryness.

In that portion of the marsh where the borax is the richest are found the "Tincal beds" these beds consisting of layers of borax crystals some two feet in thickness.

The Composition of the Crude Material.

	1.	2.	3.	4.	5.	6.	7.	8.
Biborate of soda	30·30	38·3	2·1	53·08	1·9	33·3	6·52	45·2
Water..	37·68	40·8	14·08	39·24	25·7	25·88	16·46	43·8
Insoluble matter	18·00	10·9	12·8	1·20	33·0	2·4	8·8	7·15
Carbonate of soda	6·10	5·3	16·1	5·50	34·3	13·7	18·3	2·75
Sulphate of soda	0·26	0·1	19·1	0·35	0·5	8·25	20·2	—
Chloride of sodium	0·50	0·4	34·6	0·50	0·7	15·4	28·2	0·4
Carbonate of lime	3·28	2·4	0·7	—	2·0	0·6	0·8	0·3
Carbonate of magnesia	2·26	0·4	0·3	—	0·6	0·3	0·5	0·3
Oxide of iron and alumina	1·62	1·4	0·22	0·13	1·3	0·17	0·2	0·1
	100·00	100·0	100·0	100·0	100·0	100·0	100·0	100·0

The crystals are large and well-formed and differ in size; they lie about two feet below the level of the marsh under a crust composed of sulphate of soda, carbonate of soda, and salt, and are pure enough for roasting, containing 95 per cent of borax, and yielding when calcined 180 per cent borax.

The geological formation of the surrounding hills consists of granite, marble, dolomite, black lava, and felspar; the sand of the valley is mixed with volcanic ash and decomposed lime rock. Many theories have been laid down as to the formation of the borax. Sesquiborate of lime ($Ca_2B_6O_{11}$), is slightly soluble in water, and when treated with carbonate or bicarbonate of soda, may be converted into borax.

Sesquiborate of lime ($Ca_2B_6O_{11}$), with five molecules of water, is the composition of different varieties of borate of lime that are at present used in the manufacture of borax. When this is heated in a current of steam, boracic acid passes off; in fact, when heated by itself the steam arising from the water of combination is sufficient to carry with it free boracic acid.

In California, as in Asia Minor, beds of this sesquiborate of lime are found which crop out on the surface, or are found at different depths below the surface. This sesquiborate of lime may consequently be the source from which the boracic acid comes.

In Saline Valley there are depressions or circular holes which have the appearance of extinct fumaroles, where subterranean gases and vapours may have passed into the waters of the lake. It is possible that vapours carrying boracic acid, as we find is the case in the Tuscan boracic acid lagoons, may have percolated into the waters of the lake, which, being strongly alkaline, have converted the boracic acid into borax, and the lake subsequently drying up the borax was left. Or the borax may have been formed by the direct action of alkaline waters of the lake on the borate of lime found within the area covered by the lake.

The formation or manufacture of borax by artificial means is an industry carried on in different parts of the world. The material most extensively used is the sesquiborate of lime, $Ca_2B_6O_{11}5aq$, known as pandermite, colemanite, boracite, or priceite. When this material is decomposed with carbonate of soda, which may be done by bringing them together in contact with water, double decomposition takes place—

$$Ca_2B_6O_{11}+2Na_2CO_3=2CaCO_3+Na_2B_4O_7+2NaBO_2.$$

The borate of soda, $NaBO_2$, crystallises from syrupy solutions in needle-shaped crystals, having the formula $NaBO_24H_2O$, and the composition being—

Boracic acid, B_2O_3	25·3
Soda, Na_2O	22·5
Water, H_2O..	52·2
	100·0

Borate of soda may be formed by mixing the concentrated solutions of borax and caustic soda in their equivalent quantities and evaporating to a syrupy consistency, $Na_2B_4O_7+2NaHO=4NaBO_2+H_2O$. Borate of soda is decomposed by carbonic acid, forming borax and carbonate of soda, $4NaBO_2+CO_2=Na_2B_4O_7+Na_2CO_3$.

In the conversion of sesquiborate of lime into borax by means of carbonate of soda, large quantities of this borate of soda are formed.

As borax is frequently tested volumetrically, and the boracic acid calculated accordingly, it is well to prove the absence of the borate of soda in the first place, as the higher percentage of soda the borate of soda contains might lead to erroneous results.

The following comparative table of the crystalline and anhydrous salts will show the relative difference between the two:—

	Biborate of soda.	Borate of soda.	Biborate of soda, crystal'd.	Borate of soda, crystal'd.
Boracic acid, B_2O_3 ..	69·05	53·03	36·6	25·3
Soda, Na_2O	30·95	46·97	16·2	22·5
Water, H_2O	—	—	47·2	52·2
	100·00	100·00	100·0	100·0

ON CUPRIC OXYBROMIDE.[*]

By THEODORE WILLIAM RICHARDS.

A CAREFUL examination of the basic bromide of copper precipitated by the solution of dried cupric bromide in water being an essential consideration in the preceding research upon the atomic weight of copper, a quantity of the substance was gradually collected from successive preparations for the purpose of analysis.

The only mention of the preparation of a definite oxybromide of copper in chemical literature is that by Et. Brun,[†] who obtained a crystalline salt by the slow oxidation of a solution of cuprous bromide in aqueous potassic bromide, as well as by the action of the latter salt upon ammoniacal cupric sulphate. He describes his new preparation as consisting of very small dark green crystals totally insoluble in water, and gives several analyses of different samples which agree with the formula—

$$Cu_2Br(OH)_3, \text{ or } 3CuO{\cdot}CuBr_2,3H_2O.$$

It seemed very probable that the substance under discussion was identical with this body, although prepared in a very different manner.

The oxybromide so often mentioned in the foregoing description of the research upon the atomic weight of copper crystallises in very beautiful doubly-terminated prisms which undoubtedly belong to the trimetric system, and have the varying habit shown in the accompanying sketch. When precipitated by the rapid addition of water to solid slightly basic copper bromide, the prisms appear as extremely thin plates (Fig. 1), often united in radiating groups; but on more gradual crystallisation from stronger brown solutions, the crystals develop nearly equally in all axial directions (Figs. 2 and 3). The only angle even approximately measured with success by means of the microscope was that of the two domes upon each other, giving an inclination of about 94½° between the normals. This value affords us the means of calculating the axial ratio, $x:z=1:1{\cdot}08$; and the two figures suggest the angle 96° 38′ and axial ratio 1 : 1·123 observed in atacamite.[‡] Indeed, the general resemblance in habit and in emerald green colour between the two substances is very marked, and has already been noticed by Brun.[§]

Crystallised cupric oxybromide which has been dried in the air does not lose weight over sulphuric acid. It is, of course, very soluble in mineral acids and in ammonia, as well as in strong acetic acid. The mode of formation of the salt shows that it must be slightly soluble also in very concentrated solutions of the normal cupric bromide, and that dilution diminishes, or perhaps wholly destroys, this solubility. The proof of its total insolubility in water being of great importance in the preceding research, the following experiment was made.

Two hundred c.c. of water were digested for four days at 25° with a tenth of a grm. of very fine crystals of copper oxybromide, the mixture being occasionally shaken. The liquid was then filtered, and 30 c.c. contained in a

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[*] Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, Vol. xxv.

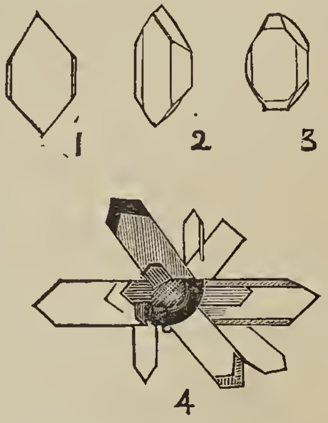
[†] *Compt. Rend.*, vol. cix., p. 66 (1889). Löwig and Berthemot describe an indefinite substance. *Liebig's Handw. Ch.*, iv. 714; *Ann. de Chim. et de Phys*, [ii.] xliv. 385.

[‡] *Zepharovitch*, *Wien. Akad. Sitzungsber.*, 1871 ol. lxiii., Part i., p. 6.

[§] *Loc. cit.*

long tube were tested for copper with ammonia, giving an absolutely negative result. 130 c.c. of the same liquid were evaporated to dryness, and the apparently clean dish was rinsed with a few drops of dilute nitric acid, to which was then added an excess of ammonia. An exceedingly faint tinge only of blue was apparent, much less than that produced by one-tenth of a m.grm. of copper under the same circumstances.

Being thus essentially insoluble in water, the oxybromide could hardly be present, even in traces, in the very dilute solution of cupric bromide used for the determination of the atomic weight; but for certainty upon this point the normal state of this solution was tested by experiments with methyl orange. These experiments, which have already been described,* settled the question in a wholly satisfactory manner.



Magnified 250 diameters.

The salt is decomposed by continued boiling with water into the normal bromide and a dark insoluble compound of uncertain composition. Brun has already pointed out the fact that the crystals are quite decomposed when heated to 250°.

On account of the very small amount of substance at hand, the analysis was undertaken with all possible care.

I. 0·20003 grm. of copper oxybromide yielded, on evaporation with nitric and sulphuric acids and subsequent electrolysis, 0·09823 grm. of metallic copper.

II. 0·0828 grm. of copper oxybromide yielded, on solution in ammonia, acidification with nitric acid, and precipitation by silver nitrate, 0·0606 grm. of argentic bromide.

Analysis of Cupric Oxybromide.

	Theory, $Cu_2(OH)_3Br$.	Found. I.	Found. II.	Average of Brun's results.
Copper	49·27	49·11	—	49·19
Bromine	30·98	—	31·15	31·05

The results agree with the theoretical as well as could be expected, considering the small quantities of substance used.

By the very slow oxidation of cuprous bromide, kept under water in the dark for six months, groups of emerald green radiating prisms over a tenth of a m.m. in length were obtained (Fig. 4), which, by their terminal angles, colour, and general appearance, showed themselves to be identical with the compound whose analysis has just been given. The amount of these crystals was so small that it was impossible to determine their percentage composition, but there can be no doubt of its agreement with that given above. The crystalline salt was also obtained by the long-continued action of cupric oxide upon a strong solution of cupric bromide.

It will be seen that the formula—

$$Cu_2(OH)_3Br, \text{ (or } 3CuO{\cdot}CuBr_2{\cdot}3H_2O)$$

does not exactly correspond to that of any one of the known oxychlorides, containing only three-fourths as much water as atacamite ($3CuO{\cdot}CuCl_2{\cdot}4H_2O$). It is a noteworthy fact, however, that many of the more definite basic salts of copper contain, as these do, three molecules of copper oxide to every single molecule of the normal compound.

CIRCULAR ON ATOMIC WEIGHTS.

By request of the Committee of Revision and Publication of the Pharmacopœia of the United States of America, Prof. F. W. Clarke, Chief Chemist of the U.S. Geological Survey, has furnished a Table of Atomic Weights, revised upon the basis of the most recent data, and his latest computations. The Committee has resolved that this Table be printed and furnished for publication to the professional press. The Committee also requests that all calculations and analytical data which are to be given in reports or contributions intended for its use or cognisance, be based upon the values in the Table. It would be highly desirable that this Table be adopted and uniformly followed by chemists in general, at least for practical purposes, until it is superseded by a revised edition. It would only be necessary for any author of a paper, &c., to state that his analytical figures are based upon "Prof. Clarke's Table of Atomic Weights, of Dec. 6th, 1890," or some subsequent issue.

Charles Rice,
Chairman of the Committee of Revision, &c.

New York, Dec. 20, 1890.

TABLE OF ATOMIC WEIGHTS.

(Issued December 6, 1890).

Revised for the Committee of Revision and Publication of the Pharmacopœia of the United States of America.

By F. W. CLARKE,
Chief Chemist of the United States Geological Survey.

This Table represents the latest and most trustworthy results, reduced to a uniform basis of comparison, with oxygen = 16 as starting-point of the system. No decimal places representing large uncertainties are used. When values vary, with equal probability on both sides, so far as our present knowledge goes, as in the case of cadmium (111·8 and 112·2), the mean value is given in the Table.

The names of elements occurring in pharmacopœial, medicinal, chemicals, are printed in italics.

Name.	Symbol.	Atomic weight.
Aluminum	*Al*	27·
Antimony	*Sb*	120·
Arsenic	*As*	75·
Barium	*Ba*	137·
Bismuth	*Bi*	208·9
Boron	*B*	11·
Bromine	*Br*	79·95
Cadmium	Cd	112·
Cæsium	Cs	132·9
Calcium	*Ca*	40·
Carbon	*C*	12·
Cerium	*Ce*	140·2
Chlorine	*Cl*	35·45
Chromium	*Cr*	52·1
Cobalt	Co	59·
*Columbium	Cb	94·
Copper	*Cu*	63·4
†Didymium	Di	142·3
Erbium	Er	166·3
Fluorine	F	19·
Gallium	Ga	69·
Germanium	Ge	72·3

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* *Proceedings*, vol. xxv., page 201.

Name.	Symbol.	Atomic weight.
‡Glucinum	Gl	9·
Gold	*Au*	197·3
Hydrogen	*H*	1·007
Indium	In	113·7
Iodine	*I*	126·85
Iridium	Ir	193·1
Iron	*Fe*	56·
Lanthanum	La	138·2
Lead	*Pb*	206·95
Lithium	*Li*	7·02
Magnesium	*Mg*	24·3
Manganese	*Mn*	55·
Mercury	*Hg*	200·
Molybdenum	Mo	96·
Nickel	Ni	58·7
Nitrogen	*N*	14·03
Osmium	Os	191·7
§*Oxygen*	*O*	16·
Palladium	Pd	106·6
Phosphorus	*P*	31·
Platinum	Pt	195·
Potassium	*K*	39·11
Rhodium	Rh	103·5
Rubidium	Rb	85·5
Ruthenium	Ru	101·6
Samarium	Sm	150·
Scandium	Sc	44·
Selenium	Se	79·
Silicon	*Si*	28·4
Silver	*Ag*	107·92
Sodium	*Na*	23·05
Strontium	Sr	87·6
Sulphur	*S*	32·06
Tantalum	Ta	182·6
Tellurium	Te	125·
Terbium	Tb	159·5
Thallium	Tl	204·18
Thorium	Th	232·6
Tin	Sn	119·
Titanium	Ti	48·
Tungsten	W	184·
Uranium	U	239·6
Vanadium	V	51·4
Ytterbium	Yb	173·
Yttrium	Yt	89·1
Zinc	*Zn*	65·3
Zirconium	Zr	90·6

* Has priority over niobium.
† Now split into neo- and praseo-didymium.
‡ Has priority over beryllium.
§ Standard, or basis of the system.

Researches on Alizarin Oil.—M. Scheurer-Kestner.—The author arrives at the following conclusions:—The oil for red tones is formed of sulphoricinoleic acid, a compound which is definite and permanent at the ordinary temperature. It is accompanied by polyricinic acids, the condensation of which extends as far as to di-ricinic acids. The molecular weights, which the author has found by Raoult's method, employing the substance dissolved in acetic acid, indicate a mixture of mono- and di-ricinic acids. The sulpho-fatty compound is hydrated, and is stable in the hydrous state. It looses its water of hydration completely at about 120 and becomes insoluble. It is resolved into hydrated sulphuric acid and an oily acid. From the tinctorial point of view, the author has recognised an interesting fact:—That the sulphonic compound gives shades inclining to a yellow, whilst the polymerised fatty acids give a carmine shade verging more towards a blue.—*Comptes Rendus*, Vol. cxii., No. 3.

On Sizing Paper according to the Most Recent Practical Experience.—Dr. E. Muth (*Dingler's Journ.*).—A very full account of the preparation and application of the sizes used by paper-makers, those especially in which resin soaps play a leading part.—*Monit. Sci.*

ELECTRICITY
IN TRANSITU:
FROM PLENUM TO VACUUM.*

By WILLIAM CROOKES, F.R.S.,
President of the Institution of Electrical Engineers.

(Continued from p. 70).

Radiant Matter.

By means of this tube (Fig. 9), I am able to show that a stream of ultra-gaseous particles, or Radiant Matter, does not carry a current of electricity, but consists of a succession of negatively electrified molecules whose electrostatic repulsion overbalances their electro-magnetic attraction, probably because their speed along the tube is less than the velocity of light. The tube has two negative terminals, A, A′, close together at one end, enabling me to send along the tube two parallel streams of radiant matter, rendered visible by impinging them through holes in a mica diaphragm on a screen of phosphorescent substance. It is exhausted to a pressure of 0·1 m.m. I connect one of the negative poles, A, with the induction coil and the luminous stream darts along the tube from C to D parallel with the axis. I now connect the other negative pole, giving a second parallel stream of radiant matter. If these streams are in the nature of wires carrying a current they will attract each other, but if they are simply two streams of electrified molecules they will repel each other. As soon as the second stream is started you see the first stream jump away in the direction C, E, showing strong repulsion, proving that they do not act like current carriers, but merely like similarly electrified bodies. It is, however, probable that were the velocity of the streams of molecules greater than that of light, they would behave differently, and attract each other, like conductors carrying a current.

To ascertain the electrical state of the residual molecules in a highly exhausted tube such as you have just seen, I introduced an idle pole or exploring electrode between the positive and negative electrodes in such a manner that the molecular stream might play upon it. The intention was to ascertain whether the molecules on collision with an obstacle gave off any of their electrical charge. In this experiment (Fig. 10, P.=0·0001 m.m., or 0·13 M.†) it was found that an idle pole, C, placed in the direct line between the positive and the negative poles, A, B, receiving in consequence the full impact of the molecules shot from the negative pole, manifested a strong *positive* charge. In a variety of other experiments made to decide this question, the electricity obtained was always found positive on testing with the gold leaf or Lippman's electrometer, and when the idle pole was connected to earth through a galvanometer a current passed as if this pole were the copper element of a copper-zinc cell, indicating leakage of a current to earth, the idle pole being positive. If, instead of sending this current to earth, the wire was connected to the negative pole of the tube, a much more powerful current passed in the same direction.

The Edison Effect.

An exactly parallel experiment has been made by Mr. Edison, Mr. Preece, F.R.S., and Prof. Fleming, using, instead of a vacuum tube, an incandescent lamp. They found that from an idle pole placed between the ends of the filament the electricity always flowed as if the pole were the zinc element of a copper-zinc cell; having repeated their experiments I entirely corroborate them. I get a powerful current in one direction from an idle pole placed between the limbs of an incandescent carbon filament, and one in the opposite direction from an idle pole in an highly exhausted vacuum tube. This discrepancy

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* Inaugural Address delivered January 15th, 1891.

† M. = one-millionth of an atmosphere.
1,000,000 M. = 760 m.m.
„ = one atmosphere.

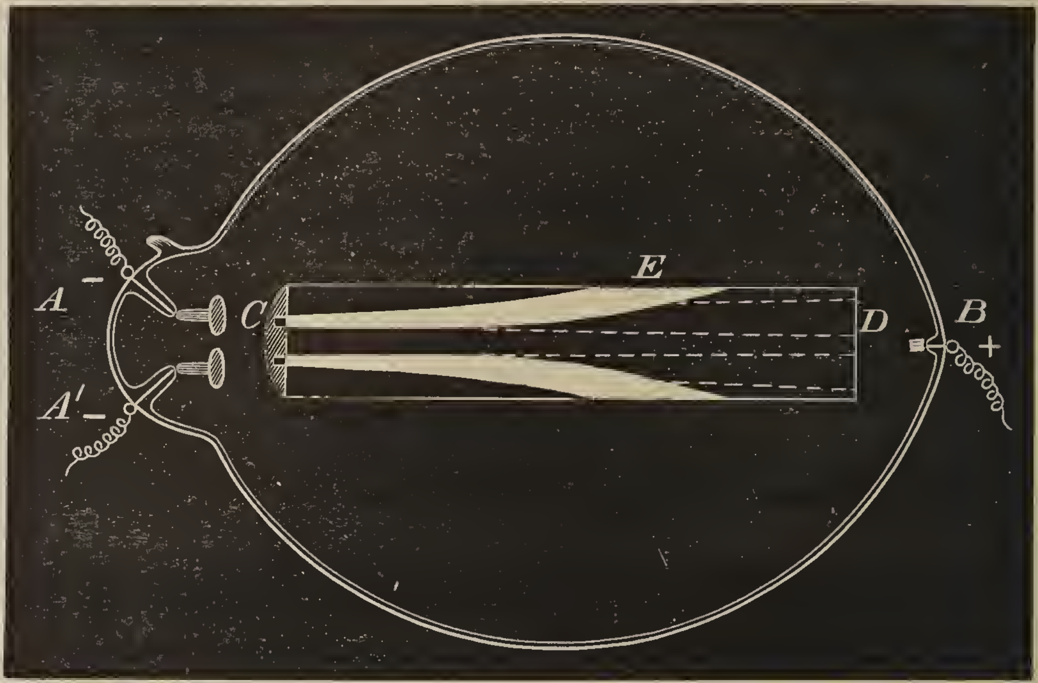


Fig. 9.—P. = 0·1 m.m.

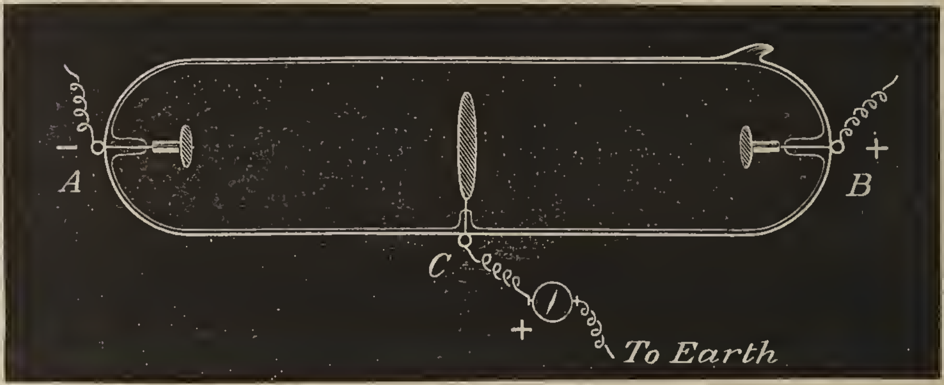


Fig. 10.—P. = 0·0001 m.m., or 0·13 M.

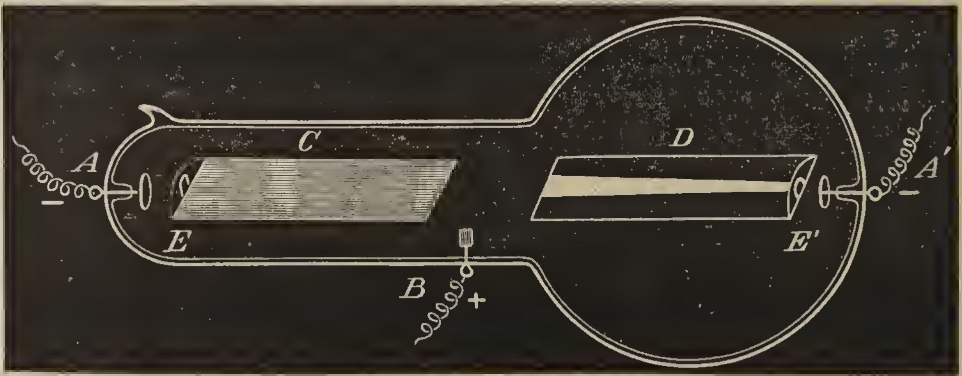


Fig. 11.—P. = 0·001 m.m., or 1·3 M.

was extremely puzzling, and I tested, with a similar result, very many experimental tubes made in different ways. The electricity obtained from an idle pole placed between the positive and negative terminals in a highly exhausted tube was always strongly *positive*, and it is only recently that continued experiment has cleared the matter up.

Some of the contradictory results are due to the exhaustion not being identical in all cases. In my vacuum tubes the directions of current between the idle pole and the earth changes from negative to positive as the exhaustion rises higher. Testing the current when exhaustion is proceeding, there is a point reached when the galvanometer deflection—hitherto negative—becomes nil, showing that the potential at this point is zero. At this stage the passage of a few more drops of mercury down the pump tube renders the current positive. This change occurs at a pressure of about 2 m.m.

After this point is reached, when the induction current is passed through the tube, the walls rapidly become positively electrified, probably by the friction of the molecular stream against the glass, and this electrification extends over the surface of any object placed inside the tube. I will show you how this electrification of the inner walls of the tube acts on the molecular stream at high

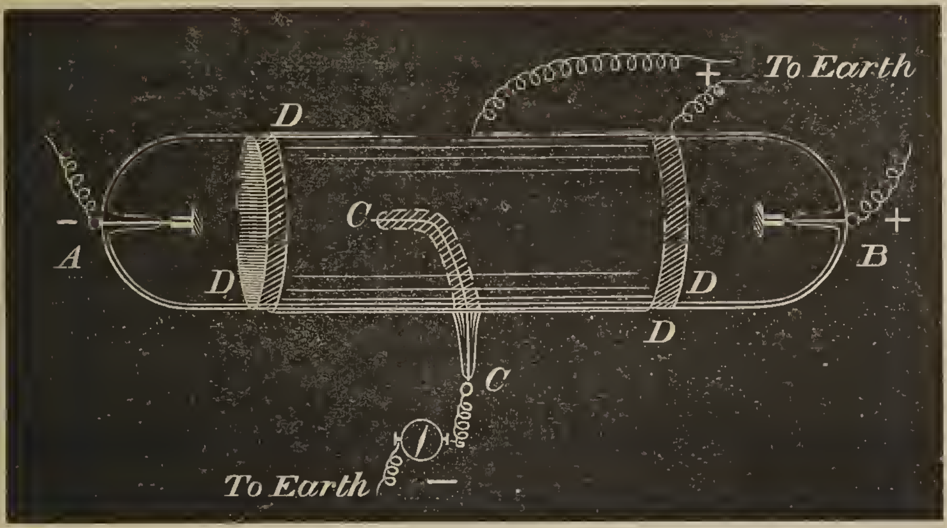


FIG. 12.—P. = 0·0001 m.m., or 0·13 M.

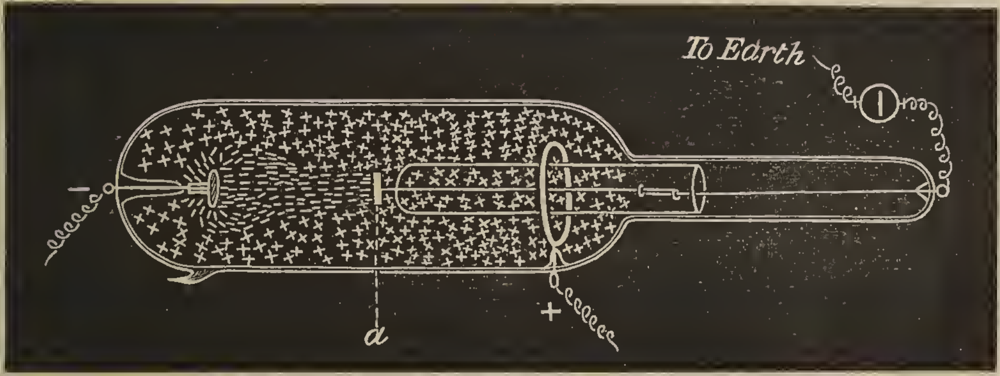


FIG 13*a*.—P. = 0·0001 m.m., or 0·13 M.

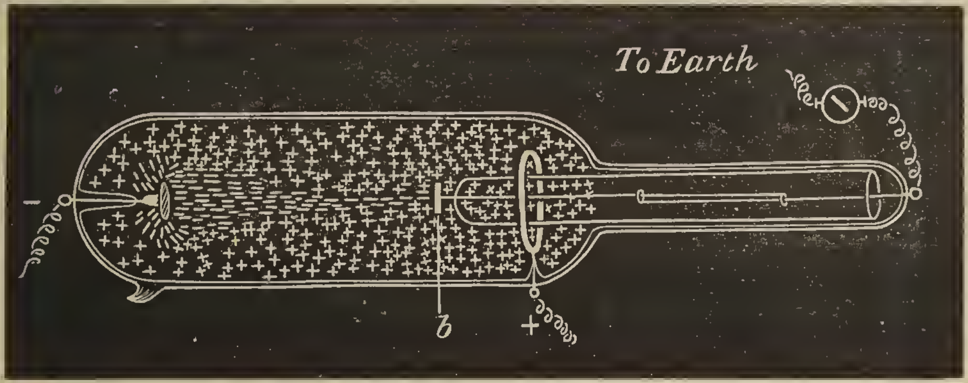


FIG. 13*b*.—P. = 0·0001 m.m., or 0·13 M.

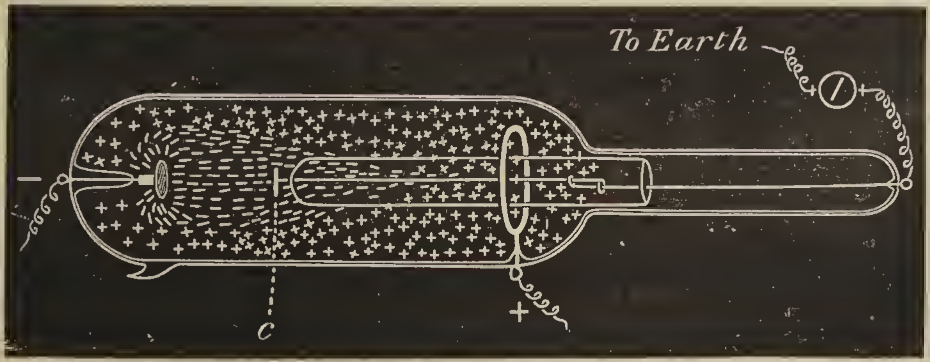


FIG. 13*c*.—P. = 0·0001 m.m., or 0·13 M.

vacua. In this tube, Fig. 11 (P.=0·001 m.m., or 1·3 M.), are fixed to exactly similar phosphorescent screens, C and D; at one end of each is a mica gate, E, E′, with a negative pole, A, A′, facing it. One of the screens, C, is in the cylindrical part of the tube and close to the walls; the other, D, is in the spherical portion, and therefore far removed from the walls. On passing the current the screen D in the globe shows a narrow sharp streak of phosphorescence, proving that here the molecules are free to follow their normal course straight from the negative pole. In the cylindrical part of the tube, however, so great is the attraction of the walls that the molecular stream is widened out sufficiently to make the whole surface of the screen, C, glow with phosphorescent light.

If an idle pole, C, C, Fig. 12 (P.=0·0001 m.m., or 0·13 M.), protected all but the point by a thick coating of glass, is brought into the centre of the molecular stream in front of the negative pole A, and the whole of the inside and outside of the tube walls are coated with metal, D, D, and "earthed," so as to carry away the positive electricity as rapidly as possible, then it is seen that the molecules leaving the negative pole and striking upon the idle pole C on their journey along the tube carry a negative charge, and communicate negative electricity to the idle pole.

This tube is of interest since it is the one in which I was first able to perceive how in my earlier results I always obtained a positive charge from an idle pole placed in the direct stream from the negative pole. Having got so far, it was easy to devise a form of apparatus that completely verified the theory, and at the same time threw considerably more light upon the subject. Fig. 13, *a*, *b*, *c*, is such a tube, and in this model I have endeavoured to show the electrical state of it at a high vacuum by marking a number of + and − signs. The exhaustion has been carried to 0·0001 m.m., or 0·13 M., and you see that in the neighbourhood of the positive pole, and extending almost to the negative, the tube is strongly electrified with positive electricity, the negative atoms shooting out from the negative pole in a rapidly diminishing cone. If an idle pole is placed in the position shown at Fig. 13 *a*, the impacts of positive and negative molecules are about equal, and no decided current will pass from it, through the galvanometer, to earth. This is the *neutral* point. But if we imagine the idle pole to be as at Fig. 13 *b*, then the positively electrified molecules greatly preponderate over the negative molecules, and positive electricity is shown. If the idle pole is now shifted as shown at Fig. 13 *c*, the negative molecules preponderate, and the pole will give negative electricity.

As the exhaustion proceeds, the positive charge in the tube increases, and the neutral point approaches closer to the negative pole, and at a point just short of non-conduction so greatly does the positive electrification preponderate that it is almost impossible to get negative electricity from the idle pole, unless it actually touches the negative pole. This tube is before you, and I will now proceed to show the change in direction of current by moving the idle pole.

I have not succeeded in getting the "Edison" current in incandescent lamps to change in direction at even the highest degree of exhaustion which my pump will produce. The subject requires further investigation, and like other residual phenomena these discrepancies promise a rich harvest of future discoveries to the experimental philosopher, just as the waste products of the chemist have often proved the source of new and valuable bodies.

(To be continued).

New Process of Bleaching.—This process depends on the decolourising action of certain products of the distillation of bituminous shales upon all fibrous matters with which they are boiled. The quantity of oil used per ton varies from 4·5 to 9 litres, according to the quality of the material.—*Moniteur Scientifique*, iv., Part 1.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 15th, 1891.

Dr. W. J. Russell, F.R.S., in the Chair.

Certificates were read for the first time in favour of Messrs. Henry Austin Appleton, 19, South Street, Middlesbro'; John Charles Aydans, 44, Crescent Road, Plumstead, S.E.; Clayton Beadle, Beadonwell, Belvedere, Kent; Thomas Byrne, Glenville, Dundrum, co. Dublin; Arthur Cole, B.A., Holmleigh, Charles Street, Berkhamsted; Reginald Lorn Marshall, 25, Lancaster Park, Richmond; Tom Kirke Rose, 9, Royal Mint, E.; R. Greig Smith, Springwells, New Street, Musselburgh; Howard C. Sucré, Breeze House, Higher Broughton, Manchester; Matthew Carrington Sykes, Sykeshurst, Barnsley, Yorks; W. Will, Ph.D., 1, Beethoven Strasse, Berlin, N.W.

The following papers were read:—

1. "*Magnetic Rotation.*" By W. Ostwald.

The magnetic rotation of organic compounds, according to Perkin, is an additive function of their composition and equal to the sum of the rotations of the components, but this is not the case with the rotation of inorganic compounds, which is usually found greater than that calculated on such an assumption. In the case of hydrogen chloride, for instance, the calculated value is about 2·18, and as a matter of fact the value obtained for hydrogen chloride dissolved in an organic solvent, isoamyl oxide, is 2·24, but when dissolved in water the value found is from 4·05 to 4·42, increasing with the dilution. The author points out that these exceptional values are only obtained in the case of electrolytes, and that they must therefore be referred to a fundamental difference existing between the constitution of electrolytes and that of non-conductors. That such a difference exists has been already deduced from other considerations, and has led Arrhenius to the formulation of the theory of electrolytic dissociation. The author claims that the facts established with regard to magnetic rotation are in perfect accordance with this theory, and that any exceptional values in the magnetic rotations of electrolytes are due to the occurrence of electrolytic dissociation.

Discussion.

Mr. Pickering said that in Professor Ostwald's attempt to appropriate Dr. Perkin's results on the magnetic rotation of solutions of electrolytes in support of the dissociation theory, no attempt was made to explain what connection should exist between the magnetic rotation and the supposed dissociation into ions, but it was boldly stated that if, as in the case of hydrogen chloride, the magnetic rotation and dissociation both increased with dilution, the result proved the truth of the dissociation theory, while equal support to this latter theory was afforded if, as in the case of sulphuric acid, dilution diminished the rotation and increased the dissociation; and the most astonishing part of the argument appeared to be that the nearly double magnetic rotations obtained in some cases should be brought forward as a proof of dissociation, when the observations were made on solutions so strong that the dissociation theory represents them as containing hardly any dissociated substance at all. Surely the natural conclusion to draw from such a doubling when it occurs in the absence of dissociation would be that it could not be explained by dissociation.

2. "*The Vapour Density of Ammonium Chloride.*" By Frank Pullinger, B.A., B.Sc., and J. A. Gardner, B.A.

The authors have made experiments at various temperatures on the vapour density of ammonium chloride. The apparatus used was that of Victor Meyer. In view of the well-known results of Wurtz concerning the vapour density of phosphorus pentachloride, it was decided to vapourise the ammonium chloride into an atmosphere of ammonia—one of the products of dissociation. In the first instance the experiments were conducted at a moderate red heat, and the salt was vapourised into air. The mean result of five experiments was 0·926; the calculated value for complete dissociation is 0·921.

At 1040° C. (the temperature of boiling zinc), Deville and Troost, using Dumas's method, found the vapour density to be 1·000.

Boiling sulphur was next used, giving a temperature of 448° C. The salt was first vapourised into air. The values found were 0·983 and 0·932. The air was then displaced by ammonia, and the values obtained were 0·939, 0·994, and 1·009.

At a temperature of 360° C. (that of boiling anthracene), the relative density in an atmosphere of air was 0·944, while in an atmosphere of ammonia it was 1·128 and 1·141.

It is evident that in this latter case the ammonium chloride was not wholly dissociated.

It was found impossible to vapourise the salt into ammonia at 300° C. in a bath of boiling α-naphthylamine. In one case, 0·0175 grm. of ammonium chloride was heated for forty minutes, but the loss in weight during that time was only 0·0045 grm., and the volume of ammonia expelled from the apparatus was only 0·91 c.c. In another experiment, 0·0037 grm. was taken, and the loss during forty minutes was 0·0021 grm., no gas being expelled. The vapourisation into air, however, goes on with comparative rapidity at this temperature, and the values found were 0·982, 0·986, and 0·985. The time taken for expulsion of the air was ten to twelve minutes.

At a temperature of 354° C., Deville and Troost, using a bath of mercury vapour, found that the vapour dehsity was 1·01. The authors propose to continue their experiments at temperatures between 300° and 360°.

3. "*Chlorinated Phenylhydrazines.*" By J. T. HEWITT, B.A., B.Sc.

The author describes the following compounds:—

Orthochlorophenylhydrazine, $ClC_6H_4{\cdot}NH{\cdot}NH_2$, and its hydrochloride.

Orthochlorophenylsemicarbazide,—
$ClC_6H_4{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$.

Orthochlorophenylphenylsemithiocarbazide,—
$ClC_6H_4{\cdot}N_2H_2{\cdot}CS{\cdot}NHPh$.

Orthochlorophenylhydrazinepyruvic acid,—
$ClC_6H_4{\cdot}N_2H_2{\cdot}CMe{\cdot}CO_2H$.

Parachlorophenylphenylsemithiocarbazide.

Formylparachlorophenylhydrazine,—
$ClC_6H_4{\cdot}NH{\cdot}NH{\cdot}COH$.

Parachlorophenylhydrazine parabanate,—
$C_3O_3N_2H_2{\cdot}2C_6H_7N_2Cl{\cdot}OH_2$.

Diparachlorophenylurea, $CO(NH{\cdot}C_6H_4Cl)_2$.

The compounds formed by interaction of aldehyds or ketones and orthochlorophenylhydrazine, according to the author, are very unstable.

4. "*A New Modification of Phosphorus.*," By H. M. VERNON, Scholar of Merton College, Oxford.

Observations on the rate of rise of temperature of phosphorus and other experiments have led the author to the conclusion that one or other of two different modifications of phosphorus may result when fused phosphorus solidifies; the new variety is formed when the phosphorus is cooled below its solidifying point and then solidified, and has an undefined melting-point; the ordinary variety of well-defined melting-point being formed when solidification of the phosphorus sets in directly the point of solidification is reached without the temperature sinking below this point. From examination of crystals under the microscope, the author considers that the new variety crystallises in rhombic prisms, the ordinary crystallising in octahedral; he summarises the properties of the two modifications in the following table:—

Octahedral variety.	Rhombic variety.
Has a definite melting-point at 44·3°.	Has no well-defined melting-point; melts at about 45·3°.
Relative density at 13°, 1·8177.	Relative density at 13°, 1·8272
Has a considerably greater latent heat of fusion than rhombic variety.	
Solidifying point, 43·8°.	Solidifying point, 43·8°.

DISCUSSION.

Mr. PICKERING thought that Mr. Vernon's conclusions must be accepted at present with great reserve. A difference of 1° in the melting-points, especially where one of these melting-points was undefined, might easily be accounted for by the presence of dissolved matter, accidental impurity, products of oxidation, or some of the oil used to cover the molten phosphorus. Mr. Vernon's curves seem to prove conclusively that this was the case, for that portion which represented the temperature of the substance while it was melting was very much curved, instead of being horizontal as it would be if the phosphorus had been pure. The small difference in the densities—0·01— was equally unsatisfactory, and even if any conclusion could be drawn from a superficial examination of the crystals under the microscope, it would be invalidated by the fact that the specimens examined had both been dissolved in, and re-crystallised from, benzene, for, since fusion had been shown to render the two supposed varieties identical, it was more than probable that dissolution would do the same. It was noticeable that although the two modifications were supposed to be obtained by cooling fused phosphorus, yet the fused phosphorus solidified in each case at the same temperature, a temperature which was not identical with the melting-points of either of the supposed varieties.

Mr. TUTTON concurred with Mr. Pickering in considering that such an important conclusion as to the existence of a new variety of phosphorus was not justified by the data brought forward. It is well known that phosphorus is a substance which exhibits the property of superfusion in a high degree, and the thermal disturbance caused by the sudden solidification of a superfused mass would be likely to influence the results of a determination of melting-point made after solidification under such circumstances. In the speaker's own experiments on the fusion of phosphorous oxide, which also exhibits superfusion in a very marked manner, a determination of melting-point after such solidification from a state of superfusion frequently yielded values differing sometimes by a whole degree from the true melting-point of the substance. It is not at all surprising that a difference of a degree should have been observed by Mr. Vernon, but this fact in itself could scarcely be said to furnish proof of the existence of two modifications. The speaker also took exception to the arbitrary manner in which, from a microscopical examination of which absolutely no details are given, it was concluded that the supposed new modification crystallised in rhombic prisms. Remembering that many really isotropic substances frequently exhibit polarisation colours, owing to their deposition probably in a slight state of strain, it would not be surprising if regular crystals of phosphorus were to exhibit polarisation. It is certainly necessary to have at least data concerning the mode of extinction of the crystals and their behaviour in convergent light before any conclusion can be arrived at as regards their crystalline system.

Means of Recognising the Kind of Size Used in Paper.—W. Herzberg.—Resin-size is evenly distributed in the entire mass of the sheet of paper. Animal size forms two layers entirely separated from each other by the body of the paper. Hence, if the paper is well rubbed and bruised, any characters traced upon it penetrate through if an animal size has been used.—*Mon. Scientifique.*

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

Sir,—We are instructed to ask you to allow the following facts to be made known through your columns to the Fellows of the Chemical Society.

As stated in a former letter, after having carefully considered the suggestions and large number of letters forwarded to us in response to our circular, the following letter was sent by our Committee to the Council of the Chemical Society:—

[Copy.]

4, Lombard Court,
Oct. 31, 1890.

Gentlemen,—We are requested, and therefore beg to call your attention to the enclosed circular relating to the present method of electing Fellows of the Chemical Society which has been sent by us to every Fellow resident in the United Kingdom.

A wide-felt opinion as to the necessity of reform led to the issue of this circular, and the answers received thereto shows that it meets with the emphatic support of the Fellows. We therefore trust the subject may receive the immediate and careful attention of the Council.

We are authorised to state that the Council will receive full support in any endeavour they may make to bring about the ends which we have in view. We therefore append from among the additional suggestions which have been sent to us, some which appear worthy of consideration. May we express the hope that you will favour us with an early reply which may be communicated to the Fellows.—We are, &c.,

(Signed) F. J. Lloyd.
F. L. Teed.

Twelve suggestions, additions to those contained in our original circular, were appended to this letter.

On November 6th Professor Thomson formally acknowledged the receipt of this letter, which came before the Council on November 20th. Subsequently, we received the following official reply:—

[Copy.]

Chemical Society, Burlington House,
December 10, 1890.

Dear Sirs,—The President and Council having under consideration the Memorial addressed to them by you, of date October 31st, would like to be informed who are the body and the individual Fellows by whom you say you are requested to call the attention of the Council to the matters set forth in your Memorial, and are further authorised to state what will be their future contingent action. I shall be obliged if you will please afford me this information, which would obviously be of much weight in guiding the Council to a conclusion on the different matters submitted to them.

Yours faithfully,
(Signed) Henry E. Armstrong.
Messrs. Lloyd and Teed.

By the instruction of our Committee, the following reply was sent:—

4, Lombard Court,
Dec. 17. 1890.

Henry E. Armstrong, Esq., Ph.D., F.R.S., &c.

Dear Sir,—In accordance with our letter of the 13th inst., we have laid your communication before the Committee under whose instructions we act, and we are requested to say, in reply, that all Fellows of the Society being equal as to status in the Society, the names of the members of the Committee have nothing to do with the question of the proposed reform in the mode of admission to the Chemical Society.

Further, in view of the very large support which our circular to the Fellows has obtained, we are requested once more to strongly urge upon the Council the necessity of taking the matter in hand immediately.

As to the steps which our Committee and its supporters would take in the future, these certainly depend upon the action of the Council. We have stated, and do so again, that all steps which the Council may take in the direction of reform will be cordially supported by us, our sole aim being the welfare of the Society itself. At the same time, the Committee request us to state that they feel themselves fully strong enough, if necessary, to act without the support of the Council.

(Signed) F. J. Lloyd.
F. L. Teed.

No answer has as yet been received to this letter, and we should therefore be justified in supposing that the Council did not consider it their duty to study the wishes of the Fellows, were it not that the recent number of the *Proceedings*, by containing the names *and particulars* of the candidates to be balloted for at the next election, shows that our efforts at reform have already had some effect on the Council.

We think it only right that Fellows should be acquainted with our action in the past, that they may form a correct judgment of our action in the future.—We are, &c.,

Fredk. J. Lloyd.
Frank L. Teed.

London, Feb. 9, 1891.

AN UNSUSPECTED SOURCE OF ERROR.

To the Editor of the Chemical News.

It is usually held by the well-informed, on more or less satisfactory evidence, that there is a special providence charged with the care of midshipmen and fools; but I have never heard the suggestion ventured that chemists enjoy any such privilege of protection. This being so, it all the more behoves us to seize every opportunity of working out our own salvation. The matter about which I am now writing you is a very simple one, and without doubt has come under the notice of most of your readers at some time or other; but since it refers to a danger that might at any time entrap the unwary and lead to a very serious error in analysis, I think it only right to point this out, deeming it probable that I may thus draw the attention of some few readers of the Chemical News to a source of error that they might otherwise chance to overlook. Moreover, I think that any danger incident to the use of certain apparatus should not be pointed out once for all, since an occasional repetition of the warning may often meet the eyes of those who have failed to notice an earlier intimation. This is my excuse for troubling you on such a simple matter.

I lately had occasion to determine some saponification equivalents, and proceeded of course in the usual manner, using a conical (Erlenmeyer's) flask in the process. The determination gave me a saponification equivalent of 10·29 per cent KHO. A duplicate in *another flask* gave me 9·18. This difference was sufficiently disturbing in all conscience; and, in addition, the equivalent was far higher than I had reason to expect it would come. Under these circumstances it was suggested to me by a friend that possibly an error had been introduced by the use of *new flasks*, owing to a reaction, that is, between the alkali and the silica of the glass. I therefore repeated my determination, *using again No. 1 flask*, and this time I obtained the saponification equivalent 6·90! A fourth determination in the same flask gave me 6·88—obviously a very close agreement. Under these circumstances, therefore, it seems to me indubitable that in the first two determinations a large quantity of the alkali was used up by reacting with the new glass; after this had taken place the flask was fit for use without fear of any further error from such source. The moral, therefore, is obvious: never to trust a saponification result obtained by the use of a *new* flask.—I am, &c.,

F. H. P. C.

P.S.—It has occurred to me that this warning is the more necessary, since—if I recollect rightly—Mr. Hehner, in his well-known researches on the constitution of beeswax, details a blank experiment made by him to determine whether or no any alkali were consumed by the glass of the flask. He found that *none* was; but evidently this conclusion must only apply to a seasoned flask, although, of course, I cannot say whether *all* new flasks would behave as mine did: glass is variable, and some glass may not require such "seasoning."

ALLOYS OF SODIUM AND LEAD.

To the Editor of the Chemical News.

Sir,—Some weeks ago we published a brief note (Chemical News, vol. lxii., p. 314), on some "Alloys of Sodium and Lead" that appear to be definite compounds, giving the observed densities of the alloys and the densities that they should have theoretically as mixtures. In your issue of January 2nd, W. J. A. B. alleges that our calculated densities are erroneous, saying that "the authors give . . . figures which it is difficult to see how they obtain."

Our figures are correct, and it is not difficult to see how W. J. A. B. has blundered. He has calculated for 10, 19·5, and 31·7 *volumes* of sodium made up to one hundred *volumes* by lead. We have followed the universal custom of giving analytical results in percentages by *weight*.

If W. J. A. B. will go over his calculations in the light of this explanation he will doubtless see his error, and we will be glad to see his retraction.—We are, &c.,

Greene and Wahl.

Philadelphia, January 30, 1891.

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. cxii., No. 3, January 19, 1891.

On the Presence of Sulphur, and on its Part in Vegetation.—MM. Berthelot and André.—Plants take up sulphur incessantly until they flower, the relative proportion of this element being greater by one-third during the first period of vegetation. The sulphur in the state of organic compounds reaches its maximum during inflorescence, and then declines. It seems as if the sulphates derived from the soil were reduced at first and then regenerated after flowering in consequence of an internal oxidation. Still, this supposes that the sulphur is entirely derived from the soil in the state of sulphates, whilst a portion may well be derived directly from organic sulphur-compounds which exist in plenty in the soil. This latter opinion is supported by the fact that organic sulphur is found in quantity in the roots except at the commencement of flowering. Towards the end of flowering it abounds at once in the roots and the stems.

Determination of the Mineral Matters Contained in Vegetable Soils, and on the Part which they Play in Agriculture.—MM. Berthelot and André.—The authors announce that a complete account of their method for determining the constituents of arable soils will be given in a future communication, and they refer to their memoirs in the *Annales de Chimie et de Physique*, Series 6, vol. xv., pp. 86—133; and vol. xiii., p. 74. They affirm that neither the phosphorus nor the total sulphur in a plant or in an arable soil can be determined by the action of acids or by simple incineration. At present they consider chiefly the determination of alkalies and oxides. They effect this, as far as the alkalies are concerned, by a preliminary elimination of the silica by treatment with ammonium fluoride and sulphuric acid, and as for alumina and ferric oxide, by fusion with potassa. The following comparative table shows the results obtained by their exact method, by digestion in the cold with dilute hydrochloric acid, by treatment for several hours with hot concentrated hydrochloric acid, and by treatment with the same acid after incineration. The results refer to 1 kilo:—

	Exact.	Cold HCl.	Hot strong HCl.	Do. after incineration
Potassa ..	8·86	0·21	1·49	1·76
Soda	2·11	0·24	0·33	0·42
Magnesia ..	0·87	0·33	—	0·67
Lime	11·6	8·79	11·20	10·6
Alumina ..	39·5	1·02	10·09	26·31
Ferric oxide..	21·5	2·96	14·01	16 78

Influence of Solvents upon the Rotatory Power of the Camphols and Iso-camphols: a Study of the Chloral Bornylates.—A. Haller.—The author's results show that, excepting methylic alcohol, the influence of which is manifest, all the other solvents exert no action upon the rotatory power of the lævo-rotatory camphol α. The influence of the different liquids upon levo-iso-camphol varies with their function or constitution, but it remains the same for each homologous series.

On the Constitution of the Albumenoids.—Dr. H Arnaud.—There are three orders of immediate essential principles forming constituent parts of organised matter: hydrocarbons, fatty bodies, and ammonium cyanate. The albumenoids are merely a combination in various proportions of the three immediate principles just enumerated; they contain potentially all three, and it is easy to isolate them. We may consequently consider the albumenoids are true polycyanates of compound ammonia, or of compound polyureas, into the structure of which there enter radicles of hydrocarbons and of fatty acids, replacing the same number of atoms of hydrogen. It may, perhaps, be also admitted that the albumenoids contain in their tissue other radicles still unknown.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 1.

Determination of Sulphur in Coal.—G. H. Bailey (*Journal of Gas-lighting*).

Analysis of Metallic Tungsten, Tungstic Irons and Steels, and Chromo Irons and Steels.—A. Zeigler (*Dingler*).—This paper will be inserted as early as possible.

Electric Bleaching of Paper.—Two English manufacturers, Evans and Overs, bleach paper electrically, rendering it perfectly white without injury to its strength The process depends on the use of a solution of magnesium chloride, which is decomposed by the action of a powerful current into chlorine and oxygen on the one hand, and into magnesium and hydrogen on the other. The electrodes are plates of platinum.

Microscopic Examination of Paper.—W. Herzberg.—From the *Zeit. fur Anal. Chem.*

New Process for Utilising the Oxygen of the Air.—Georges Kassner (from *Dingler*).—The process turns mainly on the use of the plumbates of the alkaline earths.

Industrial Society of Mulhouse.—Session of April 9, 1890.—The proceedings turned chiefly on the reception and opening of certain "sealed papers."

Revue Universelle des Mines et de la Metallurgie.
Vol. xii., No. 1.

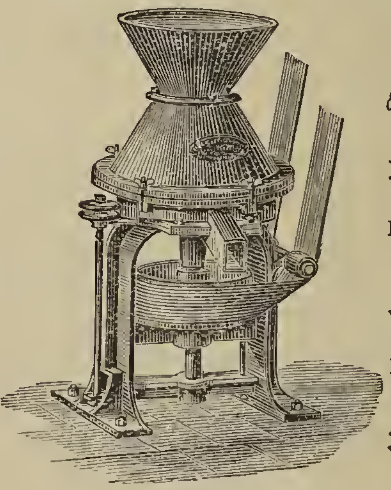
This issue contains no chemical matter.

MEETINGS FOR THE WEEK.

Monday, 16th.—Medical, 8.30.
—— Society of Arts, 8. "The Electric Transmission of Power," by Gisbert Kapp.
Tuesday, 17th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley.
—— Society of Arts, 4.30. "Chartered Companies in Africa," by Commander V. Lovett Cameron.
Wednesday, 18th.—Society of Arts, 8. "Methods and Processes of the Ordnance Survey," by Colonel Sir Charles Wilson.
—— Meteorological, 7.
—— Microscopical, 8.
Thursday, 19th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "The Position of Lulli, Purcell, and Scarlatti in the History of the Opera," by Professor C. Hubert H. Parry.
—— Chemical, 8. Ballot for the Election of Fellows. "On $\alpha\alpha'$-Diacetylpentane" and "Synthesis of Dimethyldihydroxyheptanethylene," by Prof. Perkin and Dr. Kipping.
Friday, 20th.—Royal Institution, 9. "Infectious Diseases, their Nature, Cause, and Mode of Spread," by Edward Emanuel Klein., M.D., F.R.S.
—— Geological, 3. (Anniversary).
—— Quekett, 8. (Anniversary).
—— Society of Arts, 4 30. "The Science of Colour," by Captain Abney.
Saturday, 21th.—Royal Institution, 3. "The Forces of Cohesion," by The Right Hon. Lord Rayleigh.

TO CORRESPONDENTS.

G. S. Brewer is advised to read more accurately the passage he professes to criticise.



THE CHEMICAL NEWS.

Vol. LXIII., No. 1630.

NOTE ON AN IRON CHROMIUM SOIL FROM THE ANDAMAN ISLANDS, EAST INDIES.

By C. J. H. WARDEN,
Chemical Examiner to the Government of Bengal.

The sample of soil to which the following analysis refers was kindly placed at my disposal by Dr. G. King, F.R.S., C.I.E., Superintendent Royal Botanic Gardens, Calcutta, who had collected it during a recent visit to the Andaman Islands. Few, if any, analyses of soils from these Islands have been made, and but little information is extant in connection with these general physical characters. The only facts I have been able to obtain on these points are recorded by Mr. S. Kurz, a late curator of the Herbarium, Royal Botanic Gardens, Calcutta, in his Report on the vegetation of the Andaman Islands. Mr. Kurz remarks:—"The diversity of soil, considering the smallness of the Islands, is great. Generally, however, the different kinds of soils may be brought under the following heads, which correspond with the three principal formations, viz.:—

"1. The brick coloured soil, extending over the decomposed serpentine rocks.

"2. The yellowish clay, following the sandstone formation, and therefore the most extensive and important kind of soil.

"3. A greyish or blackish soil, characterised by the considerable quantity of siliceous particles it contains, and covering the indurated chloritic or green-stone rock. A black humous soil is predominant in the level valleys, especially along the eastern coasts and on Termoklee Island, where the *kuppalee* trees—Mimusops Indica—grow beautifully."

Mr. Kurz further adds:—"According to the greater or smaller amount of moisture, these different kinds of soil are more or less mingled with decayed vegetable matter, and accordingly are more or less fertile." Mr. Kurz also states that "oxide of iron is indicated everywhere by the rusty colour of some sandstones and other rocks, and iron pyrites not unfrequently occur in the chloritic and serpentine rocks."

The sample of soil received from Dr. King had been collected from the plantation of Liberian Coffee, and was of a chocolate colour, probably corresponding with the "brick coloured soil" of Mr. Kurz's classification. On mechanical analysis, the following results were obtained:—

		Fixed substances.	Combustible or volatile matter.
0·191	Gravel retained by a sieve with 30 meshes to the linear inch	0·167	
	Organic matter		0·024
0·168	Gravel retained by 50 meshes	0·148	
	Organic matter		0·020
57·980	By elutriation, coarse sand ..	49·520	
	Organic matter		8·460
41·661	Fine sand and soil	37·201	
	Organic matter		4·460
100·000		87·036	12·964

Stones retained by a sieve with 18 meshes	0·57 per cent.
Organic matter, consisting of bits of stick, fragments of leaves, &c. ..	0·004 ,,

The largest fragment of mineral separated weighed only 0·2 grm.

The following determinations of the physical properties of the soil were made:—

The specific gravity was 3·06, calculated on the dry soil, water at 15·5° C. being taken as unity.

The Porosity.—61 per cent by volume of the soil was found to be capable of being occupied by air.

Absolute Weight.—One cubic foot of the air-dried soil, containing 11·341 per cent of moisture, weighed 429,300 grms.

Capacity for Water.—When saturated with water, the soil was found capable of holding 52·6 per cent.

Evaporation of Moisture.—The soil saturated with moisture lost on exposure to air—

After 21 hours 10 mins. exposure	18·0 per cent.
,, 45 ,, 10 ,, ,, ...	33·5 ,,
,, 69 ,, 30 ,, ,, ...	43·6 ,,

These results may also be stated in a different way:—

The saturated soil retained after exposure to air for—

21 hours 10 mins.	34·6 per cent of moisture.
45 ,, 10 ,, ...	19·0 ,, ,,
69 ,, 30 ,, ...	9·0 ,, ,,

In these experiments the dry bulb thermometer varied between 88°—89° F., and the wet bulb 83°—84° F.

The absorptive power of the soil in an atmosphere saturated with moisture, the temperature being 83—89° F., was as follows:—The soil dried at 100° C. took up in eleven days 20·801 per cent of moisture.

On chemical analysis the following results were obtained, which have been calculated on the air-dried soil. The reaction of the soil was acid, and was not due to CO_2.

Moisture lost at 100° C.		11·3410
Loss on ignition, 12·9640 per cent. Organic carbon, 2·5643 per cent.	Anhydrous humus .. .. Calculated from organic carbon	10·4459
	Nitrogen as nitric acid ..	0·00129
	Organic nitrogen and ammonia	0·24080
	Chemically combined water, not evolved at 100° C.	2·27730
Soluble in H_2O and concentr'ed HCl. Sp. gr. 1·187.	CaO	0·2941
	Fe_2O_3	35·4326
	Al_2O_3	10·4914
	MgO	0·1094
	Traces of chromium . ..	—
	Mn_3O_4	0·4174
	Na_2O	0·4554
	K_2O	0·8633
	Cl	0·0061
	P_2O_5	0·4004
	SO_3	0·1386
	Traces of CO_2	—
	SiO_2	0·0455
Containing— SiO_2 .. 12·3681 Al_2O_3 .. 0·0776	Residue from HCl, soluble in alkalies	14·4819
Containing— Fe_2O_3 .., Al_2O_3 .., Cr_2O_3 .. 2·4250 CaO .. 0·1212 MgO .. 0·1107	Residue insoluble in alkalies, decomposable by concentrated H_2SO_4 ..	2·6569
Residue not decomposable by H_2SO_4, containing sand, iron, and chromium in traces .		9·2558
		100·35509

The total amount of chromium present in the soil calculated as Cr_2O_3 was 1·6139 per cent. It will be of interest to ascertain whether the ash of coffee plants grown on this soil contains any trace of chromium or not.

NOTE ON THE ESTIMATION OF GREASE.

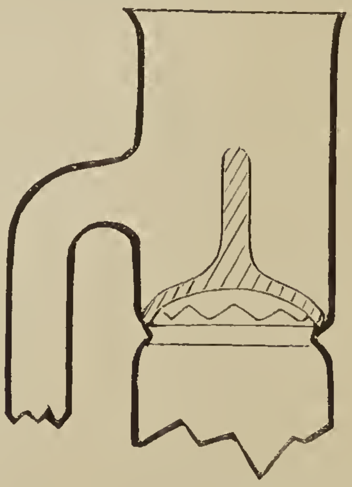
By W. LAWRENCE GADD F.I.C., and S. LEES, F.C.S.

THE authors have devised a simple modification of the ordinary Soxhlet tube for fat extraction, when used for extracting very light or finely-powdered substances, which gives excellent results in their hands, and which, they believe, may be of service to other chemists under similar circumstances.

The samples under examination were very fine, floury deposits, which, when agitated even slightly with the ether employed for their extraction, were thrown up into suspension and subsided again only very slowly; and one sample was so light that great care was necessary in handling the weighed quantities, as a slight motion was sufficient to cause clouds of dust to arise from the substance.

As the samples, when treated with ether, passed entirely through both glass and cotton-wool plugs placed at the bottom of the Soxhlet tube, the weighed quantity for each estimation was carefully placed in an ordinary star filter, previously extracted with ether, and the filter and its contents pushed down the tube until it rested on the plug of glass wool at the bottom.

The modified tube used was specially made with an annular projecting inside ring, on which rested an inverted glass cup, provided with a short stem to facilitate removal, and having cut in its periphery a number of channels or grooves, as shown in the sketch.



SECTION

PLAN

The down rush of ether from the condenser, when the syphoning action took place, was received by this glass cup, and, passing through the channels above mentioned, flowed quietly down the sides of the tube without in the least disturbing the material in the filter, which was rapidly and thoroughly extracted without any of the powder passing into the tared flask; whilst previous attempts to use the ordinary extractor had resulted in the whole of the material being speedily washed out of the filter and finding its way into the weighed flask.

The authors have repeatedly used their modified tube for extracting a variety of substances, with very satisfactory results, and they believe it can be made without adding materially to the cost of the ordinary Soxhlet extractor.

Chemical Laboratory and Assay Office,
55 and 56 Barton Arcade, Manchester, February, 1891.

THE USE OF DRY REACTIONS IN QUALITATIVE ANALYSIS.

By W. TATE, Assoc.R.C.S.

THE accompanying table was drawn up by the author to facilitate and systematise the use of the more characteristic dry reactions in qualitative analysis. Use with large classes has shown that these tests can be most advantageously applied to the separated group precipitates, as time is economised by this method.

The tests given have been culled from various sources, and modified as required by the charcters of the precipitates to be tested.

Table of Dry Reactions.

The group precipitates may be tested during the operation of washing by the reactions arranged in this table, the adhering mother-liquor not affecting the results.

GROUP I.

Precipitate may contain $AgCl$, Hg_2Cl_2, $PbCl_2$. If lead be present it is preferable not to examine for silver in the dry way.

1. Take up a minute portion of the precipitate on an asbestos thread,[*] and hold it in the upper reducing flame of a Bunsen burner. Support an evaporating basin, nearly filled with water, a little above the thread.

   A grey sublimate on the bottom of the dish indicates *mercury*. This sublimate, on exposure to the fumes of HI,[†] becomes brilliantly coloured, streaky red and yellow, from formation of HgI_2.
2. Heat a small portion of the precipitate on charcoal till the Hg_2Cl_2 has been driven off. If there be a residue add to it a mixture of KI and sulphur, and heat strongly; a yellow incrustation indicates *lead*.
3. If lead be absent fuse a portion of the precipitate with Na_2CO_3 on charcoal.

   A white malleable metallic bead not marking paper indicates *silver*.

GROUP II.—*Copper Sub-Group.*

Residue of sulphides after digestion with NaOH; it may contain CuS, CdS, Bi_2S_3, PbS, HgS.

4. Drive off HgS on charcoal, and heat the residue with KI+S. (See 2.) A fine red to reddish-brown incrustation indicates *bismuth*, yellow *lead*.

   If bismuth be present the lead incrustation may be masked, though the presence of both metals may be recognised with practice.
5. Asbestos thread sublimate in R.F. (See 1.)

   Grey sublimate indicates *mercury*; confirm as before. A brownish-black sublimate nearer the centre of the dish indicates Bi, Pb, or Cd.
6. Heat a portion of the precipitate in a closed tube with Na_2CO_3 and KCy.

   A grey metallic mirror, rubbing into minute globules when stroked with a match, indicates *mercury*.
7. Make a clear borax bead, add a little of the precipitate, and fuse in the oxidising flame of the Bunsen burner.

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[*] The asbestos thread may be wrapped round the end of an iron wire.

[†] Most readily, by saturating an asbestos plug with a strong alcoholic solution of iodine, igniting the alcohol, and holding the flame beneath the basin

Green to blue bead indicates *copper*; confirm by adding a trace of a tin salt, and holding in R.F. for one minute; a red opaque bead indicates copper.

Arsenic Sub-Group.

Sulphides precipitate from NaOH solution on addition of HCl and passage of a few bubbles of H_2S; it may contain As_2S_3, Sb_2S_3, and SnS or SnS_2.

8. Colour a borax bead faintly with Cu, hold in R.F. of Bunsen burner for one minute; the bead should remain clear blue. Add a trace of the sulphides precipitate, oxidise till the bead is once more clear blue, and then hold in R.F. for one minute.

   An opaque red bead indicates *tin*.

9. Sublimate (from asbestos) on porcelain in R.F. (See 1.)

   Sublimate is black and soluble in solution of NaOCl, *arsenic*. Sublimate is black and insoluble in solution of NaOCl, *antimony*. If both antimony and arsenic be present the stain will be dissolved round the edges.

10. Obtain sublimate as in 1, but hold thread in the oxidising flame, and the porcelain basin some little distance above the flame.

    A white sublimate of oxides almost invisible on the porcelain is obtained.

    Touch the sublimate with one drop of $AgNO_3$ solution, and expose the moistened spot to the gas evolved from strong solution of ammonia.

    If the moistened sublimate blackens, *antimony* is present; a yellow or yellowish-red stain indicates arsenic. (Both may often be distinguished together.)

    The black stain is insoluble, the yellow stain soluble, in ammonia solution.

11. Dry a small portion of the precipitate, mix it with twice its bulk of SiO_2 and a little dry sodium acetate; heat the mixture (in a fume chamber), in a tube closed at one end, placing a finger over the open end of the tube. If the finger, on removal, possesses the characteristic and disgusting odour of cacodyl, *arsenic* is present.

Group III.—*Iron Sub-Group.*

There may be present $Fe_2(OH)_6$, $Al_2(OH)_6$, $Cr_2(OH)_6$.

12. Borax bead in O.F.

    Yellowish red bead indicates *iron*.

    Bright green bead indicates *chromium*.

    Brown olive-green bead would be caused by Fe together with Cr.

13. Fuse a part of precipitate with Na_2CO_3 and KNO_3 on a piece of platinum foil.

    A yellow mass indicates *chromium*. (Green, Mn partly precipitated here.)

14. If 12 and 13 give no colour tests, and the precipitate be white, heat a portion strongly on charcoal, moisten with cobalt nitrate solution, and again heat strongly before the blowpipe.

    Blue earthy (not glassy) mass proves the presence of *aluminium*.

Zinc Sub-Group.

The precipitate may contain ZnS, MnS, CoS, NiS.

15. Borax bead in O.F.

    Blue, *cobalt*; reddish brown, *nickel*.

16. Fuse with Na_2CO_3 and KNO_3 on clean platinum foil. A green mass indicates *manganese*.

17. If CO and Ni be absent, test, as in 14, with $CO(NO_3)_2$ on charcoal.

    A green mass indicates *zinc*.

Group IV.

The precipitate may contain $BaCO_3$, $SrCO_3$, $CaCO_3$.

18. Take up a minute portion of the precipitate on platinum wire, moisten with HCl, and hold wire in Bunsen flame.

    The flame is coloured green for *barium*, crimson for *strontium*, brick-red for *calcium*.

Group V.

19. Flame reaction as in 18.

    Flame is brilliantly yellow, *sodium*; flame is violet, *potassium*.

    If sodium be present view the flame through an indigo prism; the violet potassium flame may then be distinguished, but is not to be much relied on.

THE PHOTOGRAPHY OF COLOURS.

By G. LIPPMANN

The author undertook to obtain upon a photographic plate the image of the spectrum, with its colours, so that the image should remain afterwards fixed and might be indefinitely exposed to full daylight without change.

He has been able to solve the problem by operating with the sensitive materials, the developers, and the fixing agents currently used in photography, and merely modifying the physical conditions of the experiment.

The essential conditions for obtaining colours in photography are the continuity of the sensitive layer and the presence of a reflecting surface behind this layer. By continuity is to be understood the absence of granules. The silver iodide, bromide, &c., must be disseminated within a film of albumen, gelatin, or some other transparent or inert material in a uniform manner, and without forming granules visible even under the microscope. If there are any particles they must be of dimensions which may be neglected in comparison to the length of a luminous wave.

The use of the coarse emulsions used at present is therefore excluded. A continuous layer is transparent, save generally for a slight blue opalescence. The author uses as support albumen, collodion, and gelatin; as sensitive matters, silver iodide and bromide. All these combinations give good results.

The plate, when dry, is supported by a hollow frame into which mercury is poured; this mercury forms a reflecting layer in contact with the sensitive film. The exposure, the developing, and the fixation are done as if it were intended to obtain a black negative of the spectrum, but the result is different. When the proof is finished and dried the colours appear.

The proof obtained is negative by transmitted light; that is to say, that each colour is represented by its complementary. By reflected light it is positive, and we see the colour itself which may be obtained very brilliant. To obtain in this manner a positive, the impression must be strengthened in such a manner that the photographic deposit has a bright colour, which is obtained by the use of acid liquids.

The fixation is effected by means of hyposulphite, followed by careful washings. The author has ascertained that the colours then resist the most intense electric light.

The theory of the experiment is very simple. The incident light which forms the image in the camera interferes with the light reflected by the mercury. There is consequently formed in the interior of the sensitive film a system of fringes, *i.e.*, of luminous maxima and dark minima. The maxima alone act upon the plate; at the close of the photographic operations these maxima remain masked by deposits of silver, more or less reflective, which occupy their place. The sensitive layer is divided by these deposits into a series of thin laminæ, the thickness of which is the interval which separates two maxima; that is to say, a half wave-length of the incident light. These slender laminæ have, therefore, precisely the thickness necessary to reproduce the incident wave-length by reflection.

The colours visible upon the proof are exactly of the same nature as those of soap bubbles. They are even more pure and brilliant, at least if the photographic operations have yielded a deposit which reflects well. In this case there are formed in the thickness of the sensitive film a very great number of superimposed slender films; about 200 if the film, *e.g.*, is $\frac{1}{20}$ in thickness. For the same reason, the reflected colour is so much the purer as the number of reflecting films is increased. These layers form in fact a sort of screen in depth, and for the same reason, that in the theory of screens by reflection the purity of the colours increases with the number of elementary mirrors.—*Comptes Rendus*, cxii., p. 274.

ON THE

CURIOUS BEHAVIOUR OF CERTAIN ZINC-SULPHIDE COMPOUNDS.

By JOHN CAWLEY,
Associate Royal School of Mines, England.

Some years ago I promised to send to the Chemical News a communication on the subject named in the heading of this article. Important business considerations prevented my fulfilling the promise at that time; I do not think, however, it is too late to do so now should the Editor deem the matter of sufficient interest to occupy his valuable space.

My long experience as a manufacturer of colours enables me to speak very positively respecting the industrial importance of this subject. Unfortunately, the experiments herein recorded, and many hundred others not so recorded, were made in the midst of considerable business worry; they were consequently not always well considered, and worse than all, lead to no very well-defined conclusions. They may, however, suggest to some ambitious young chemist an interesting and not unprofitable line of research. It will make what follows more intelligible if I give here a brief description of the method generally employed in preparing zinc-sulphide pigments.

Zinc sulphate, or chloride freed from iron, manganese, lead, tin, &c., is precipitated by an alkaline or alkaline-earthy sulphide; the precipitate consisting of hydrated zinc-sulphide alone or in admixture with a sulphate of an alkaline earth, is dried and ignited at a red heat; the red-hot product is thrown into water, levigated, washed, dried again, and reduced to fine powder. The pigment is then ready for grinding in oil as a paint.

This process, simple in outline, requires considerable skill and experience to carry it out successfully, but if well carried out it produces a pigment superior to the best white-lead in respect of whiteness, body, and covering power. It is, moreover, relatively innocuous, and is not discoloured by gases containing SH_2.

In general, however, it is subject to the grave defect of darkening when exposed to sunlight, the darkening apparently being due not only to light, but also dependent on the condition of the atmosphere, in respect of moisture-contents, &c. I have prepared pigments so sensitive as to be turned almost black when exposed to bright sunlight for one or two minutes. A curious thing to be noted in this connection is that the darkened pigment will completely regain its whiteness when placed in the dark for a few hours, and when so bleached it appears to be somewhat less sensitive than it was originally. It would be too long a story to go into all the details of experiments made by me in connection with this matter. I will therefore content myself by giving a brief account of the more important observations, interpolating here and there remarks of an explanatory character.

1. The dried hydrated zinc-sulphide, before ignition, is not altered by exposure to light; after ignition it darkens readily.

2. The whitest and purest zinc blende obtainable was levigated and exposed to light. No darkening was observed, but the same blend, calcined so as to slightly oxidise it, was readily darkened.

3. Zinc-sulphide was prepared in a very finely-divided condition and free from hydration, by burning zinc in an atmosphere of sulphur vapour, and collecting the product in a chamber, the temperature of which was high enough to prevent the condensation of sulphur. This sulphide was unchanged by light, but like the blende, darkened readily after slight calcination.

In connection with the observations above named, I may say I had been struck by the resemblance which the colour developed in the pigment by light bore to that of the finely-divided metal deposited from certain metallic solutions. I found, too, as might have been expected, that in the ignition of hydrated zinc-sulphide, even when air is excluded, oxidised zinc compounds are always formed, and in this way the idea was suggested to me that light might be able, under certain conditions, to effect the reactions which, as is well known, heat does. These reactions may be expressed by the equations—

$$ZnS+2ZnO=Zn_3+SO_2,$$
$$ZnS+ZnSO_4=Zn_2+2SO_2.$$

According to this hypothesis the darkening is due to the formation of a film of metallic zinc, which, owing to its finely-divided condition, would readily oxidise in the absence of light; the bleached pigment would therefore be less sensitive than it was originally, as it would be protected somewhat by a film of non-sensitive zinc oxide. This theory explained easily all the observed facts for a time, but was afterwards found to be untenable.

4 Noting that the pigment moistened with water was more sensitive than when in a dry condition, a sample was dried at 120° C., and, while warm, was placed in a glass tube which was sealed before the blowpipe. Result —no discolouration after one year's exposure. A sample placed in a sealed tube without extra drying was readily darkened.

An attempt was made to practically apply this observation by thoroughly drying the pigment *immediately before* grinding in linseed oil, the latter being as free from water as possible, the idea being that the oil would exercise a protective effect similar to that of the sealed tube. Result not satisfactory.

5. Taking a sample of pigment not very sensitive, *per se*, it was noted that its sensitiveness was enormously increased by moistening it with a weak solution of zinc sulphate, from which it was inferred that the sensitiveness might be due to imperfect washing. The most thorough washing, however, would not remove the basic zinc sulphate formed in the process of ignition.

6. Attempts were made to decompose this basic sulphate into zinc oxide, and an inert sulphate by treating the pigment with solutions of the hydrates of potassium, sodium, barium, and calcium; the first three were rejected, as they appeared to act on the zinc-sulphide itself. Lime-water exercised for a short time a decidedly protective effect; afterwards it seemed to lose its power of making the pigment resistant to light.

The best results were obtained by mixing with the zinc-sulphide precipitate about one-half of 1 per cent of *freshly precipitated* magnesium hydrate. The resulting pigment was fairly resistant to light, but the presence of magnesia somewhat impaired its general qualities. In this connection I may remark that I have noticed a certain amount of incompatibility as regards zinc-sulphide pigments between the quality of light resistance and other desirable qualities, such as extreme whiteness, softness, and opacity. In igniting hydrated sulphide of zinc, even when the utmost care is used, it is almost impossible to avoid a certain amount of fritting of the particles of the substance; and when this is excessive the pigment is worthless, as it becomes yellow, stony, and wanting in opacity. This tendency to fritting was overcome by mixing the dried precipitate, before ignition, with about 5 per cent of common salt. The latter, at the temperature of the furnace, fuses and appears to form a glaze round the particles of the pigment. This glaze immediately dissolves when the red-hot pigment is thrown into water, and the product resolves itself into a soft mass of great whiteness and opacity. Unfortunately, the product so obtained, while excellent in most respects, is extremely sensitive to light.

After several years' experience I succeeded in manufacturing on a large scale a pigment which stood the severest tests of exposure to light under all sorts of atmospheric conditions, but the process was a little uncertain, as one or two batches, for some unknown reason, were more or less sensitive.

The improved process was conducted as follows:—The zinc-salt and barium sulphide were made as concentrated as was practicable, the sulphide being used at a boiling temperature. The precipitate formed, consisting *mainly* of zinc-sulphide and sulphate of barium in equivalent proportions, was very readily filterable. To the vat containing the precipitate was added one half of 1 per cent of magnesium hydrate *freshly* made, and an amount of common salt in fine powder. The filtration carried away considerable quantities of the salt added, but enough remained to produce the anti-fritting effect above mentioned. The waste of salt was a trifling matter in comparison with the convenience of getting perfect admixture with a minimum of labour. The precipitate, after drying, was crushed to the size of small beans and mixed with 3 per cent ammonium chloride before ignition.

The way in which the ammonium chloride acts I do not attempt to explain, nor do I know why in a few instances the above mentioned failed to produce a stable pigment.

About the time we had fairly perfected our process, a combination of business circumstances made it expedient for us to abandon the manufacture. Since that time I have had little opportunity of giving the matter any attention, though I have often had it in my mind to call the attention of readers of the Chemical News to a phenomenon which, as far as I am aware, is little known, and has never been scientifically investigated. I am not without hope that I may be able in the near future to make a systematic investigation of it myself; in the meantime I trust this brief account may not be found quite uninteresting.

278, Passaic Street, Newark, N.J.,
Jan. 28, 1891.

Electro-Metallurgy of Aluminium.—Adolphe Minet.—Recent researches on the electrolysis of aluminium fluoride in a state of fusion have enabled the author to increase the yield of the system. He has succeeded in producing 32 grms. of metal by the expenditure of a quantity of energy equivalent to 1 horse-power. The losses, however, are still 30 per cent.—*Comptes Rendus*, vol. cxii., No. 4.

Chemical Theory of the Coagulation of Blood.—MM. Maurice Arthus and Calixte Pagès.—The author's experiments complement the theories of Alexander Schmidt and Hammarsten by showing the fibrinoplastic action of the salts of calcium. If we receive 225 c.c. of blood in 25 c.c. of a solution of potassium oxalate at 0·9 per cent, the blood will not coagulate spontaneously, whatever is the temperature or the time of action. For the potassium oxalate there may be substituted the corresponding sodium or ammonium salts, or a fluoride, a silicate, or an alkaline soap. These substances may be employed either in strong or weak solution or in fine powder. On the other hand the subsequent addition to the blood of a solution of calcium chloride restores its coagulating power.—*Comptes Rendus*, vol. cxii., No. 4.

ELECTRICITY
IN TRANSITU:
FROM PLENUM TO VACUUM.*

By WILLIAM CROOKES, F.R.S.,
President of the Institution of Electrical Engineers
(Continued from p. 80).

Properties of Radiant Matter.

One of the most characteristic attributes of Radiant Matter—whence its name—is that it moves in approxi-

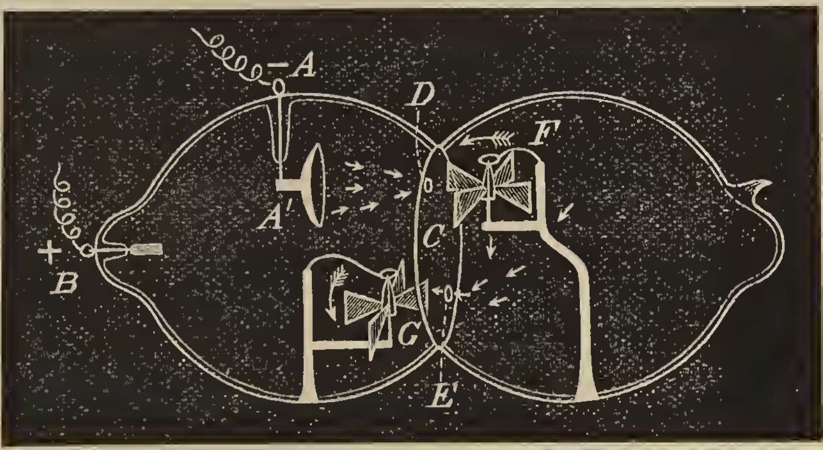

Fig. 14.—P. = 0·001 m.m., or 1·3 M.

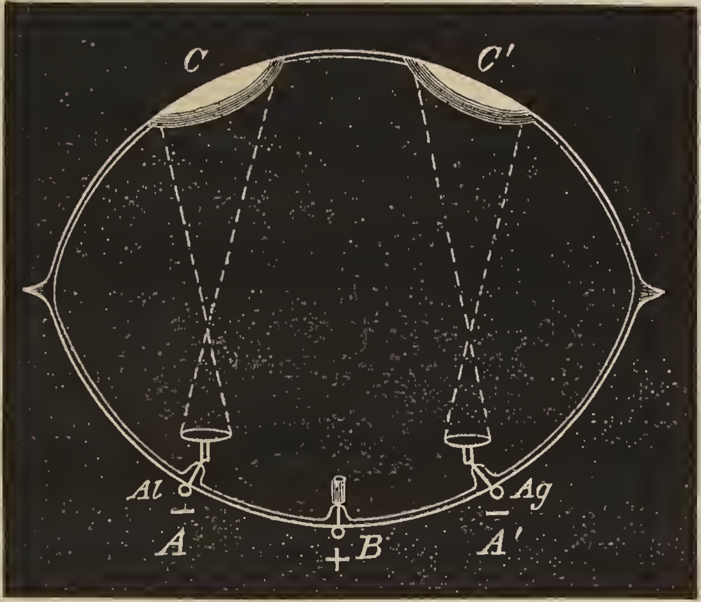

Fig. 15.—P. = 0·00068 m.m., or 0·9 M.

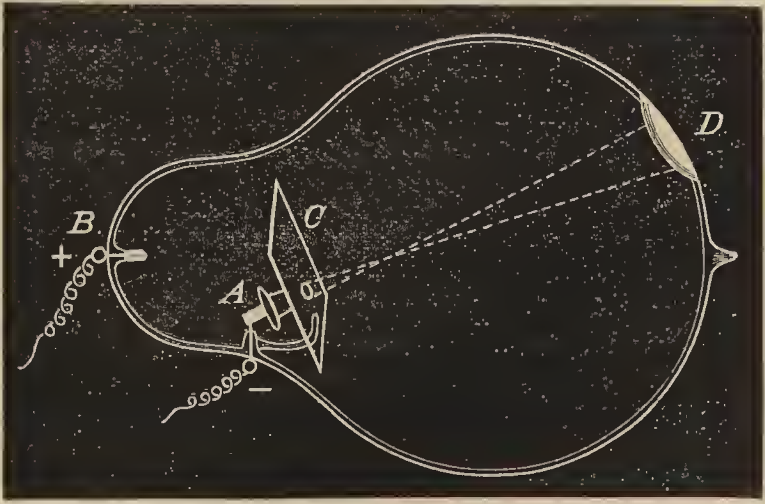

Fig. 16.—P. = 0·00068 m.m., or 0·9 M.

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* Inaugural Address delivered January 15th, 1891.

Fig. 17.—P. = 2 m.m.

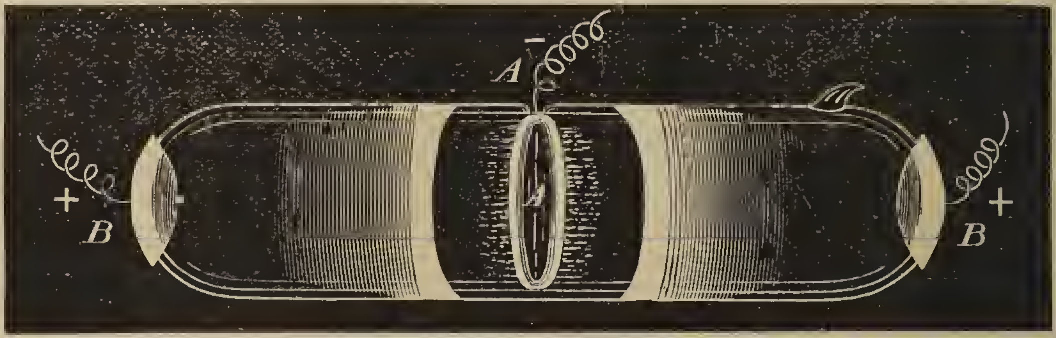

Fig. 18.—P. = 0·076 m.m., or 100 M.

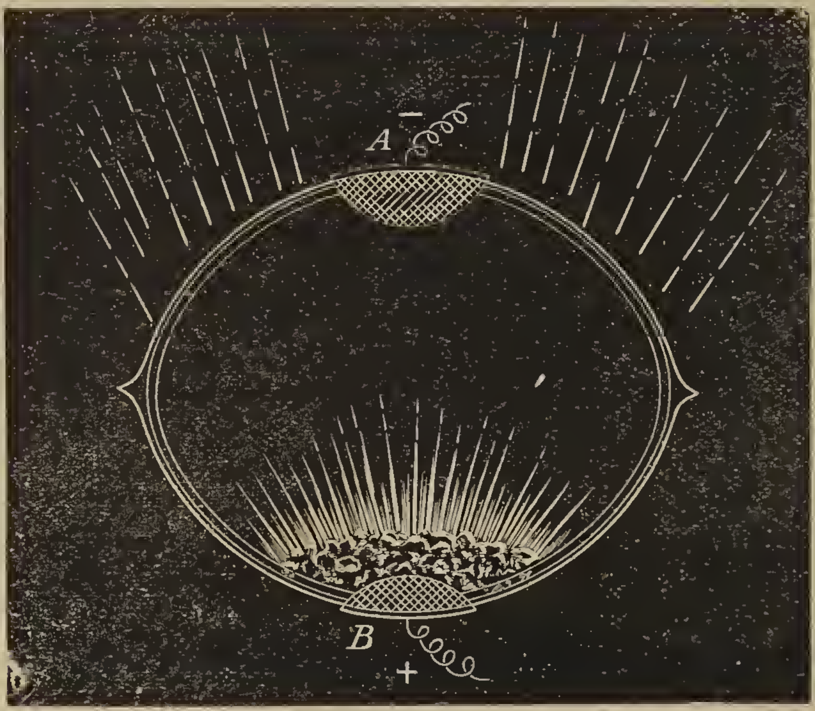

Fig. 19.—P. = 0·00068 m.m., or 0·9 M.

mately straight lines and in a direction almost normal to the surface of the electrode. If we keep the induction current passing continuously through a vacuum tube in the same direction, we can imagine two ways in which the action proceeds; either the supply of gaseous molecules at the surface of the negative pole must run short, and the phenomena come to an end, or the molecules must find some means of getting back. I will show you an experiment which reveals the molecules in the very act of returning. Here is a tube (Fig. 14) exhausted to a pressure of 0·001 m.m., or 1·3 M. In the middle of the tube is a thin glass diaphragm, C, pierced with two holes, D and E. At one part of the tube a concave pole, A′, is focussed on the upper hole, D, in the diaphragm. Behind the upper hole and in front of the lower one are movable vanes, F and G, capable of rotation by the slightest current of gas through the holes.

On passing the current with the concave pole negative, the small vanes rotate in such a manner as to prove that at this high exhaustion a stream of molecules issues from the lower hole in the diaphragm, whilst at the same time a stream of freshly charged molecules is forced by the negative pole through the upper hole. The experiment speaks for itself, showing as forcibly as an experiment can show that so far the theory is right.

This view of the ultra-gaseous state of matter is advanced merely as a working hypothesis, which, in the present state of our knowledge, may be regarded as a necessary help to be retained only so long as it proves useful. In experimental research early hypotheses have necessarily to be modified, or adjusted, or perhaps entirely abandoned, in deference to more accurate observations. Dumas said, truly, that hypotheses were like crutches which we throw away when we are able to walk without them.

Radiant Matter and "Radiant Electrode Matter."

In recording my investigations on the subject of radiant matter and the state of gaseous residues in high vacua under electrical strain, I must refer to certain attacks on the views I have propounded. The most important of these questionings are contained in a volume of "Physical Memoirs," selected and translated from foreign sources under the direction of the Physical Society (vol. i., Part 2). This volume contains two memoirs, one by Hittorff on the "Conduction of Electricity in Gases," and the other by Puluj on "Radiant Electrode Matter and the So-called Fourth State." Dr. Puluj's paper concerns me most, as the author has set himself vigorously to the task of opposing my conclusions. Apart from my desire to keep controversial matter out of an address of this sort, time would not permit me to discuss the points raised by my

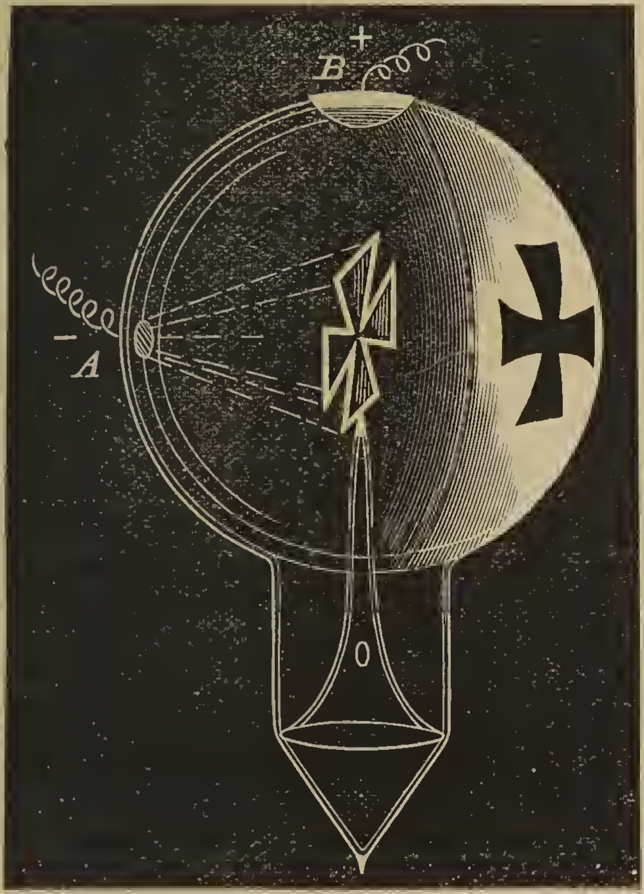

FIG. 20.—P. = 0·00068 m.m., or 0·9 M.

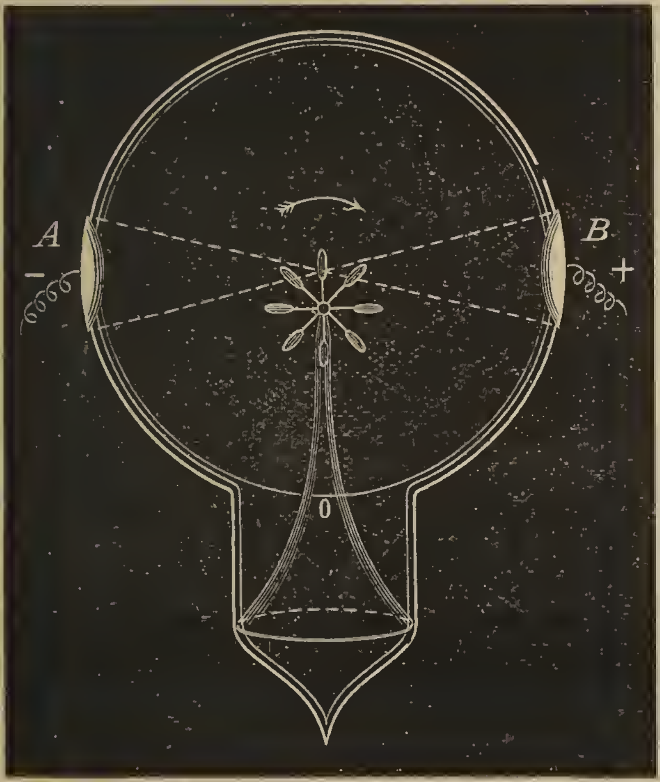

FIG. 21.—P. = 0·001 m.m., or 1·3 M.

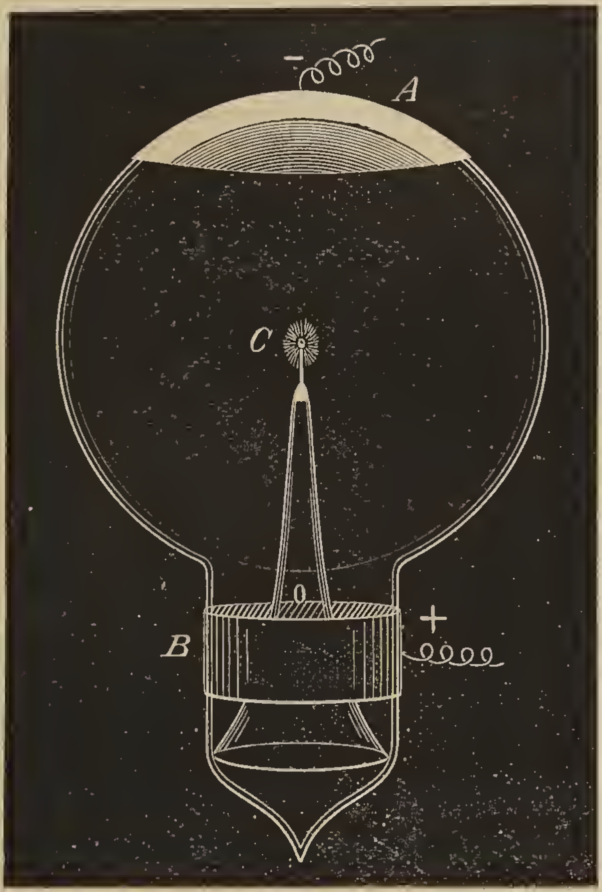

FIG. 22. P. = 0·000076 m.m., or 0·1 M.

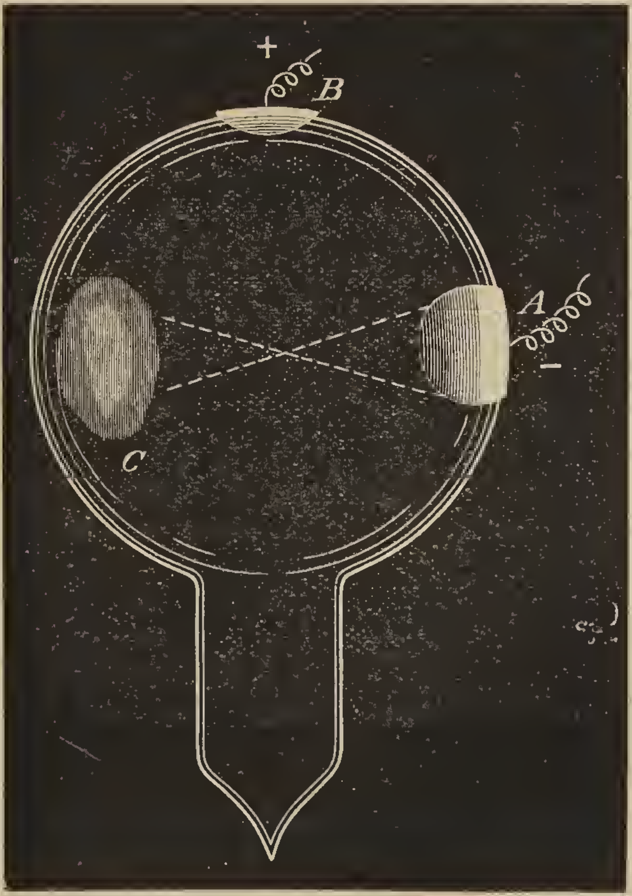

FIG. 23.—P. = 0·00068 m.m., or 0·9 M.

critic. I will therefore only observe in passing that Dr. Puluj has no authority for linking my theory of the fourth state of matter with the highly transcendental doctrine of four dimensional space.

Reference has already been made to the mistaken supposition that I have pronounced the thickness of the dark space in a highly-exhausted tube, through which an induction spark is passed, to be identical with the natural mean free path of the molecules of gas at that exhaustion. I could quote numerous passages from my writings to show that what I meant and said was the mean free path as amplified and modified by the electrification.[*] In this view I am supported by Professor Schuster,[†] who in a passage quoted below distinctly admits that the mean free path of an electrified molecule may differ from that of one in its ordinary state.

The great difference between Puluj and me lies in his statement that[‡] "*the matter which fills the dark space consists of mechanically detached particles of the electrodes which are charged with statical negative electricity, and move progressively in a straight direction.*"

To these mechanically detached particles of the electrodes, "of different sizes, often large lumps,"[§] Puluj attributes all the phenomena of heat, force, and phosphorescence that I from time to time have described in my several papers.

Puluj objects energetically to my definition "Radiant Matter," and then proposes in its stead the misleading term, "Radiant Electrode Matter." I say "misleading," for while both his and my definitions equally admit the existence of "Radiant Matter," he drags in the hypothesis that the radiant matter is actually the disintegrated material of the poles.

Puluj declares that the phenomena I have described in high vacua are produced by his irregularly shaped lumps of Radiant Electrode Matter. My contention is that they are produced by Radiant Matter of the residual molecules of gas.

Were it not that in this case we can turn to experimental evidence I would not mention the subject to you. On such an occasion as this controversial matter must have no place; therefore I content myself, at present, by showing a few novel experiments which demonstratively prove my case.

Let me first deal with the Radiant Electrode hypothesis. Some metals, it is well known, such as silver, gold, or platinum, when used for the negative electrode in a vacuum tube, volatilise more or less rapidly, coating any object in their neighbourhood with a very even film. On this depends the well-known method of electrically preparing small mirrors, &c. Aluminium, however, seems exempt from this volatility. Hence, and for other reasons, it is generally used for electrodes.

If, then, the phenomena in a high vacuum are due to the "electrode matter," the more volatile the metal used the greater should be the effect.[*]

Here is a tube (Fig. 15, P.=0·00068 m.m., or 0·9 M.), with two negative electrodes, A, A', so placed as to project two luminous spots on the phosphorescent glass of the tube. One electrode, A', is of pure silver, a volatile metal, the other, A, is of aluminium, practically non-volatile. A quantity of "electrode matter" will be shot off from the silver pole, and practically none from the aluminium pole; but you see that in each case the phosphorescence, C, C', is identical. Had the Radiant Electrode Matter been the active agent the more intense phosphorescence would proceed from the more volatile pole.

A drawing of another experimental piece of apparatus is shown in Fig. 16. A pear-shaped bulb of German glass, has near the small end an inner concave negative pole, A, of pure silver, so mounted that its inverted image is thrown upon the opposite end of the tube. In front of this pole is a screen of mica, C, having a small hole in the centre, so that only a narrow pencil of rays from the silver pole can pass through, forming a bright spot, D, at the far end of the bulb. The exhaustion is about the same as in the previous tube, and the current has been allowed to pass continuously for many hours so as to drive off a certain portion of the silver electrode, and upon examination it is found that the silver has all been deposited in the immediate neighbourhood of the pole, whilst the spot, D, at the far end of the tube that has been continuously glowing with phosphorescent light is practically free from silver.

The experiment is too lengthy for me to repeat it here, so I shall not attempt it, but I have on the table the results for examination.

The identity of action of silver and aluminium in the first case, and the non-projection of silver in this second instance, in themselves are sufficient to condemn Dr. Puluj's hypothesis, since they prove that phosphorescence is independent of the material of the negative electrode. In front of me is a set of tubes that to my mind puts the matter wholly beyond doubt. The tubes contain no inside electrodes with the residual gaseous molecules, and with them I will proceed to give some of the most striking radiant matter experiments without any inner metallic poles at all.

In all these tubes the electrodes, which are of silver, are on the outside, the current acting through the body of the glass. The first tube contains gas only slightly rarefied and at the stratification stage. It is simply a closed glass cylinder, with a coat of silver deposited outside at each end, and exhausted to a pressure of 2 m.m. The outline of the tube is shown in Fig. 17. I pass a current and, as you see, the stratifications, though faint, are perfectly formed.

The next tube, seen in outline in Fig. 18, shows the dark space. Like the first it is a closed cylinder of glass, with a central indentation forming a kind of hanging pocket, and almost dividing the tube into two compartments. This pocket, silvered on the air side, forms a hollow glass diaphragm that can be connected electrically from the outside, forming the negative pole, A; the two ends of the tube, also outwardly silvered, form the positive poles, B, B. I pass the current and you all see the dark space distinctly visible. The pressure here is 0·076 m.m., or 100 M.

The next stage, dealing with more rarefied matter, is

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[*] "The thickness of the dark space surrounding the negative pole is the measure of the mean length of the path of the gaseous molecules between successive collisions. The electrified molecules are projected from the negative pole with enormous velocity, varying however with the degree of exhaustion and intensity of the induction current."—(*Phil. Trans.*, Part i., 1879, par. 530).

"The extra velocity with which the molecules rebound from the excited negative pole keeps back the more slowly moving molecules which are advancing towards the pole. The conflict occurs at the boundary of the dark space, where the luminous margin bears witness tothe energy of the discharge."—(*Phil. Trans.*, Part i., 1879, par. 507).

"Here, then, we see the induction spark actually illuminating the lines of molecular pressure caused by the excitement of the negative pole."—(R. I. Lecture, Friday, April 4th, 1879).

"The electrically excited negative pole supplies the *force majeure* which entirely, or partially, changes into a rectilinear action the irregular vibration in all directions."—(*Proc. Roy. Soc.*, 1880, page 472).

"It is also probable that the absolute velocity of the molecules is increased so as to make the mean velocity with which they leave the negative pole greater than that of ordinary gaseous molecules."—(*Phil. Trans.*, Part ii., 1881, par. 719).

[†] "It has been suggested that the extent of the dark space represents the mean free path of the molecules. . . It has been pointed out by others that the extent of the dark space is really considerably greater than the mean free path of the molecules, calculated according to the ordinary way. My measurements make it nearly twenty times as great. This, however, is not in itself a fatal objection; for, as we have seen, the mean free path of an ion may be different from that of a molecule moving among others.—Schuster, *Proc. Roy. Soc.*, xlvii., pp. 556-7.

[‡] "Physical Memoirs," Part ii., vol. 1, page 244. The paragraph is italicised in the original.

[§] *Loc cit.* p. 242.

[*] In a valuable paper read before the Royal Society, November 20th, 1890, by Professors Liveing and Dewar, on finely-divided metallic dust thrown off the surface of various electrodes in vacuum tubes, they find not only that dust, however fine, suspended in a gas will not act like gaseous matter in becoming luminous with its characteristic spectrum in an electric discharge, but that it is driven with extraordinary rapidity out of the course of the discharge.

that of phosphorescence. Here is an egg-shaped bulb, shown in Fig. 19, containing some pure yttria, and a few rough rubies. The positive electrode, B, is on the bottom of the tube under the phosphorescent material; the negative, A, is on the upper part of the tube. See how well the rubies and yttria phosphoresce under molecular bombardment, at an internal pressure of 0·00068 m.m., or 0·9 M.

A shadow of an object inside a bulb can also be projected on to the opposite wall of the bulb by means of an outside pole. A mica cross is supported in the middle of the bulb (Fig. 20), and on connecting a small silvered patch, A, on one side of the bulb with the negative pole of the induction coil, and putting the positive pole to another patch of silver, B, at the top, the opposite side of the bulb glows with a phosphorescent light, on which the black shadow of the cross seems sharply cut out. Here the internal pressure is 0·00068 m.m., or 0·9 M.

Passing to the next phenomenon, I proceed to show the production of mechanical energy in a tube without internal poles. It is shown in Fig. 21 (P. = 0·001 m.m., or 1 3 M.). It contains a light wheel of aluminium, carrying vanes of transparent mica, the poles, A, B, being in such a position outside that the molecular focus falls upon the vanes on one side only. The bulb is placed in the lantern, and the image is projected on the screen; if I now pass the current you see the wheel rotates rapidly, reversing in direction as I reverse the current.

Here is an apparatus, Fig. 22, which shows that the residual gaseous molecules when brought to a focus produce heat. It consists of a glass tube with a bulb blown at one end and a small bundle of carbon wool, C, fixed in the centre, and exhausted to pressure of 0·000076 m.m., or 0·1 M. The negative electrode, A, is formed by coating part of the outside of the bulb with silver, and it is in such a position that the focus of rays falls upon the carbon wool. The positive electrode, B, is an outer coating at the other end of the tube. I pass the current, and those who are close may see the bright sparks of carbon raised to incandescence by the impact of the molecular stream.

You thus have seen that all the old "radiant matter" effects can be produced in tubes containing no metallic electrodes to volatilise. It may be suggested that the sides of the tube in contact with the outside poles become electrodes in this case, and that particles of the glass itself may be torn off and projected across and so produce the effects. This is a strong argument, which fortunately can be tested by experiment. In the case of this tube (Fig. 23, P. = 0·00068 m.m., or 0·9 M.) the bulb is made of lead glass phosphorescing blue under molecular bombardment. Inside the bulb, completely covering the part that would form the negative pole, A, I have painted a substantial coat of yttria, so as to interpose a layer of this earth between the glass and the inside of the tube. The negative and positive poles are silver disks on the outside of the bulb, A being the negative and B the positive pole. If, therefore, particles are torn off and projected across the tube to cause phosphorescence, these particles will not be particles of glass but of yttria, and the spot of phosphorescent light, C, on the opposite side of the bulb will not be the dull blue of lead glass, but the golden yellow of yttria. You see there is no such indication; the glass phosphoresces with its usual blue glow, and there is no evidence that a single particle of yttria is striking it.

Witnessing these effects I think you will agree I am justified in adhering to my original theory that the phenomena are caused by the Radiant Matter of the residual gaseous molecules, and certainly not by the torn off particles of the negative electrode.

(To be continued).

Bleaching Wool and Silk with Hydrosulphite.—Gaston Dommergue.—This method is pronounced preferable to others on account of its simplicity and the low price of the materials.—*Moniteur Scientifique*, iv., Part 2.

A NEW METHOD FOR STANDARDISING THE SOLUTIONS USED IN ALKALIMETRY AND ACIDIMETRY.

By EDWARD HART and STUART CROASDALE.

Several substances have been proposed and used as materials for determining the strength of the standard acid and alkaline solutions used in volumetric saturation analysis, among them sodium carbonate, oxalic acid, and acid potassium oxalate. All of these substances have disadvantages, especially where a great degree of exactness is necessary. Sodium carbonate, which, following Mohr's recommendation, has been most commonly used, is, as found in commerce, seldom quite pure. This was long ago pointed out by Stas. It has the further disadvantage that it must be ignited gently and weighed quickly after cooling, as it takes up moisture from the air quite rapidly. Another disadvantage is that the solution when titrated against an acid must be boiled to drive off carbon dioxide before the titration can be finished. All these things require time. As the volumetric method is especially designed to save time, these disadvantages are serious ones. The difficulty of getting oxalic acid of proper purity, and of protecting it from loss of water of crystallisation, is so well known that it need not be considered further. The same thing holds true, to some extent at least, of acid potassium oxalate. Any crystalline salt is sure to be subjected to more or less suspicion from the impossibility of so preparing it that no water shall be included between the crystals, or that no hygroscopic moisture shall be left adhering to the crystals, or that some of the water of crystallisation may have been driven off by too sharp drying. We have therefore devised a method which avoids all these sources of error, and which for exactness leaves nothing to be desired, and is extremely convenient and easy of execution.

The electrolytic assay of copper has long been known to yield very accurate results when properly carried out, but has recently been subjected to some criticism by English chemists. In order to test the matter, a very large number of analyses have been made in this laboratory, which will soon be ready for publication. The result of this investigation has convinced us that with proper precautions the assay is one of the most accurate known. In ordinary cases, where from 0·1 to 0·2 grm. copper are to be thrown down, the differences in duplicate assays never exceed 0·0002 grm., and generally do not exceed 0·0001 grm.

When normal copper sulphate is subjected to electrolysis, for every 63 parts copper thrown down 98 parts sulphuric acid are set free; and, if we use pure copper sulphate, at the end of the operation we shall have all the copper adhering to the dish, and a corresponding amount of pure sulphuric acid in solution. The copper is weighed as accurately as possible, and a simple calculation shows at once the amount of sulphuric acid in solution, which has thus virtually been weighed, and may be at once used for standardising caustic soda or other alkaline solution with which in turn standard acids can be compared.

A solution of pure copper sulphate when as dilute as this is not a very good conductor, and it is best, therefore, to add a small quantity of neutral potassium or sodium sulphate solution before the electrolysis is started.

The following examples illustrate the method, and show what accuracy can be attained when working in the ordinary rapid way.

Two roughly weighed samples of commercial C. P. copper sulphate were electrolysed, and gave—

$$\begin{array}{lcl} & \text{Cu} = & \text{H}_2\text{SO}_4 \\ (1) & 0·1015 = & 0·15789 \\ (2) & 0·1079 = & 0·16784 \\ \hline & 0·2094 = & 0·32573 \end{array}$$

The acid resulting was then used to standardise a caustic soda solution, which it was intended to dilute to decinormal strength. Phenolphthalein was used as indicator.

(1) required 3·4 c.c. of the caustic soda solution.
(2) ,, 3·6 ,, ,, ,, ,,

$$\begin{array}{l} 3{\cdot}4 \\ \underline{3{\cdot}6} \\ 7{\cdot}0 \end{array}$$

$$\frac{4{\cdot}900}{0{\cdot}32573}=15{\cdot}043;\ 15{\cdot}043\times7=105{\cdot}30$$

In the above calculation, the atomic weight used for copper was 63, and the molecular weight of sulphuric acid was taken as 98. The decinormal solution was then made up, using 105·3 c.c. per litre of the strong solution.

A more careful calculation, using the atomic weight 63·18 for copper, and the molecular weight 97·82 for sulphuric acid, showed that the amount used was too small.

(1) 0·1015 Cu = 0·15715 H_2SO_4 = 3·4 c.c.
(2) 0·1079 ,, = 0·16706 ,, = 3·6 ,,

$$\frac{4{\cdot}891}{0{\cdot}15715}\times3{\cdot}4=105{\cdot}808$$

$$\frac{4{\cdot}891}{0{\cdot}16706}\times3{\cdot}6=\underline{105{\cdot}39}$$

$$\begin{array}{r} 2)\underline{211{\cdot}198} \\ 105{\cdot}599 \end{array}$$

The decinormal solution will therefore turn out to be too weak. This decinormal solution was then titrated against sulphuric acid obtained in the same way, as follows—

Decinorma soda, c.c.

(3) 0·1062 Cu = 0·16442 H_2SO_4 = 34·15
(4) 0·1065 ,, = 0·16495 ,, = 34·35
(5) 0·1049 ,, = 0·16241 ,, = 33·9
(6) 0·1060 ,, = 0·16412 ,, = 34·2

$$1\text{ c.c. will therefore equal}\left\{\begin{array}{ll}(3)\ 0{\cdot}004814 & H_2SO_4. \\ (4)\ 0{\cdot}004802 & ,, \\ (5)\ 0{\cdot}004791 & ,, \\ (6)\ 0{\cdot}004799 & ,, \end{array}\right\}\text{Mean, }0{\cdot}0048015$$

The behaviour of the solution at the point, when neutralisation was nearly reached, led us to suspect that the copper sulphate was not quite pure, for the solution became light pink, and this colour slowly faded. If another drop was added the same process was repeated, and this continued until four or five drops had been added, when the solution took a permanent pink tint.

We therefore prepared a new lot of copper sulphate by heating electrolytic copper with pure concentrated sulphuric acid, and re-crystallising the product eight times. Three determinations with this product gave the following results:—

(7) 0·1021 Cu = 0·1581 H_2SO_4 = 32·8 decinormal soda.
(8) 0·1041 ,, = 0·1612 ,, = 33·5 ,, ,,
(9) 0·1050 ,, = 0·1626 ,, = 34·1 ,, ,,

$$\begin{array}{c}1\text{ c.c. will} \\ \text{therefore equal}\end{array}\left\{\begin{array}{ll}(7)\ 0{\cdot}0048194 & H_2SO_4 \\ (8)\ 0{\cdot}0048112 & ,, \\ (9)\ 0{\cdot}0047674 & ,, \end{array}\right\}\text{Mean}=0{\cdot}0047993.$$

Mean of 7 determinations, 0·0048006.

In (7) (8) and (9) the same fading of the pink tint occurred as in the first lot. This was traced to a little carbonate in the caustic soda, for when the solution, which had lost colour, was boiled, the pink tint reappeared. We have no doubt that with a burette with very fine point, still closer results can be obtained; but for any ordinary work the above are sufficiently accurate.—*Journal of Analytical Chemistry*, Vol. iv., Part 4.

NOTICES OF BOOKS.

Elementary Systematic Chemistry. For the Use of Schools and Colleges. By W. Ramsay, Ph.D., F.R.S., Professor of Chemistry in University College, London. London: J. and A. Churchill.

This manual is in several respects superior to the bulk of its rivals in this very crowded field of literature. It is not arranged "to meet the requirements" of any particular examination. It is not fitted up with an appendix of questions which have been put on any occasions, and which possibly may recur. Above all, its teachings are really systematic. Those elements and compounds are described which may serve as types of classes. The information given, *e.g.*, the atomic weights, is correct according to the most recent determinations. The insertion, at the beginning of the work, of a few brief chapters on chemical physics, is a return to a useful custom which has been too generally abandoned.

The remark, in "Lesson I.," that we do not know matter apart from energy, is suggestive. Did it occur, should we recognise it as matter?

The date assigned to the discovery of the periodic arrangement of the elements by Newlands is here given as 1866-68. This is surely a slip of the pen, as the earliest communications of Mr. Newlands appeared in the Chemical News in 1863-64. The author, very justly, does not accept the classification of the elements as metals and non-metals.

The index is exceedingly complete, and the work is one that we can recommend in preference to at least three-fourths of the existing elementary manuals of chemistry.

Recovery of Hydrochloric Acid from Waste Products. (Turner's Patent). London: W. J. Fraser and Co.

The waste products here referred to seem to be the spent "pickle" used in certain departments of the iron trades. At the same time, the process here described would be applicable to other liquid wastes. The refuse in question is considerable in quantity, and has already tasked the ingenuity of chemists. It can no longer, as of old, be simply run into the nearest stream. Its neutralisation with limestone is unremunerative, whilst the motive for its recovery is strengthened by the certainty that the price of hydrochloric acid must ultimately rise.

The Turner process is exceedingly simple and inexpensive, and appears to be quite successful. The waste pickle, an impure solution of ferrous chloride along with a certain quantity of free acid, is run continuously into a furnace of peculiar construction. Here it is decomposed, as we learn, into hydrochloric acid and ferric oxide. The latter product is raked out of the furnace as it accumulates, and is used for "fettling" in the puddling process. The acid is condensed in a series of cooling pipes and serves over again in the galvanising process, being of the same strength as that originally used for pickling. The economical features of the process are most satisfactory; only 4 cwts. of fuel are used for every ton of the waste liquor treated. The plant is not costly, and, as it works at a low temperature, the wear and tear are small. No skilled labour is employed, one labourer being sufficient to attend to a plant of the largest size. According to the actual experience of a firm who have worked the process since July, 1889, the recovery of one ton of acid of a quality fit for use in pickling costs eight shillings.

Few processes for utilising waste products can show such good results.

Biographisch-litterarisches Handwörterbuch der Wissenschaftlich bedeutenden Chemiker. ("Biographical-Literary Dictionary of Chemists who are Scientifically of Importance.") Herausgegebon von Dr. Carl Schaedler. Berlin: R. Friedlaender and Sohn.

It sometimes happens that we feel uncertain as to the time and place when some chemist "flourished," as to his researches and discoveries, the works he wrote, or the positions he filled. Dr. Schaedler's compact little work meets this want in a very convenient manner. The notices of the various chemists here mentioned are necessarily brief, but they are almost without exception accurate. The work is characterised of a spirit of fairness and impartiality. There is no tendency to unduly exalt German *savants* at the cost of their French or English contemporaries. A similar impartiality is observed as between the different tendencies which spring up within the field of chemical science. We notice with pleasure that the author pronounces Baumé's hydrometer "erratical." Chemists who read German will find this work exceedingly useful.

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

Sir,—*Post hoc ergo propter hoc* is but a *prima facie* argument, and surely not one upon which agitators may be allowed to claim that *they* have brought about a so-called reform.—I am, &c.,

Nemo.

THE JUBILEE OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

Sir,—I venture to suggest that the Jubilee of the Chemical Society be in part celebrated by the foundation of a Benevolent Fund for the relief of distressed Fellows and others, and of their widows and orphans; to be administered by the Society, alone or in conjunction with the Institute of Chemistry and the Society of Chemical Industry.

I will gladly give £50 if nineteen other subscribers will each contribute a like sum. The few wealthy chemists amongst us would probably promise much larger amounts.

The Fund once started, doubtless many chemists would contribute a guinea annually.—I am, &c.,

John Attfield.

Watford, Feb. 17, 1891.

STARCH-PAPER TEST FOR IODINE.

To the Editor of the Chemical News.

Sir,—While analysing qualitatively a mixture containing iodides and bromides the other day, it occurred to me, as my starched paper (prepared according to the careful directions of the text-books) was done, and I was disinclined to break off my work to make more, that I might find an efficient substitute in ordinary white writing-paper. I tried this after moistening with water, and found to my delight that it did as well as the best starch-paper that ever was prepared; and why not, seeing that in the process of manufacture, writing or, indeed, any common paper is finished with size which contains a notable quantity of starch?

As I had never before heard of this simple and ready substitute, I thought the notice of it might be welcome to other analysts, to whom, like everyone else worthy of existence, time is money.—I am, &c.,

Alex. Johnstone.

Mineralogical Laboratory,
University of Edinburgh.
Feb. 14, 1891.

AMERICAN COPYRIGHT.

To the Editor of the Chemical News.

Sir,—In view of the several favourable criticisms of my "Manual of Assaying," which have appeared in the Chem. News from time to time, I trust you will insert this protest against the "reprint" noticed in the issue for Dec. 5, 1890. This "copy" is issued entirely without the authority of my publishers or myself, and could not possibly have been put forward had there been any International Copyright Law. The fact that many American publishers have "pirated" English publications could hardly be tendered as an apology for this re-issue. The reprint is backed as "Brown and Griffiths." The actual contribution of Prof. Griffiths is *one* chapter on "Fuels," and, presumably, the slight revision, consisting of the elimination of the personal "I" in favour of the editorial "we," and the substitution of English financial values for American ones.

While we may not expect the utmost ideas of honour from publishers, certainly we do expect the highest order of action from scientists; and it was therefore with feelings the most mingled, of surprise, sorrow, and indignation, that I saw the name of so distinguished a man as Prof. Griffiths attached to the book I protest against.—I am, &c.,

W. Lee Brown.
Author of Brown's "Manual of Assaying."

Office of North-western Gas-Light
and Coke Co., Evanston, Ill.
Jan. 27, 1891.

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. cxii., January 26, 1891.

Contributions to the History of the Nitrogenous Principles Contained in Vegetable Soils.—M. Berthelot and G. André.—The author studies the action of acid and alkaline solvents upon the organic nitrogen (previously insoluble) contained in vegetable soils. By the prolonged action of alkalies we may render soluble, in 26 hours' treatment in the water-bath, 93·6 per cent of the organic nitrogen of soils. By the successive action of alkalies and acids we may extract 95·5 per cent. If we begin with dilute hydrochloric acid, 71 per cent of the nitrogen are rendered soluble by 13 hours' treatment in the water-bath, and the subsequent action of dilute potassa brings the total thus made soluble up to 91 per cent. These experiments show how the insoluble nitrogen contained in the humic compounds is gradually rendered soluble and capable of assimilation. The action of plants is certainly not comparable to that of the alkalies and acids used in the author's experiments; but the natural agents compensate for their smaller energy by their prolonged action.

New Observations on the Volatile Nitrogenous Compounds given off by Vegetable Mould.—M. Berthelot.—The exhalation of nitrogenous products proceeds as long as the earth is humid. If it is dry the phenomenon in question is beyond comparison slower, though it still goes on. The nitrogen contained in the volatile organic compounds given off by sandy clays is always much greater in quantity than that escaping as ammonia. From a true vegetable soil the quantities are equal.

Experiment on the Synthesis of Proteic Compounds.—P. Schutzenberger.—This memoir will b inserted in full.

On the Application of the Measure of the Rotatory Power to the Determination of the Compounds Formed by Aqueous Solutions of Malic Acid with the White Alkaline Phosphomolybdates.—D. Gernez.—This memoir is not adapted for useful abstraction.

The Conductivity of Isomeric Organic Acids and of their Salts.—Prof. Ostwald.—The author contests the novelty or originality of the results signalised in a communication by D. Berthelot (*Comptes Rendus*, January 5th, 1891, p. 46).

Reply to Professor Ostwald.—D. Berthelot.—The author contests the reclamation of Prof. Ostwald.

The Mordants used in Dyeing and the Theory of Mendeleeff.—M. Prud'homme.—This memoir will be inserted in full.

Note on Diabetes.—H. Arnaud.—This paper is more physiological than chemical in its character.

Revue Générale des Sciences Pures et Appliquées.
Vol. ii., No. 1, January 15, 1891.

The Artificial Reproduction of the Ruby.—A. Verneuil.—M. Frémy, in conjunction with the author, has improved his process. He has obtained not only the ruby but the sapphire, and even the oriental emerald, by modifying the quantity of chrome employed. The most suitable temperature for the reaction appears to be about 1350°. The largest stones obtained weigh a little more than 75 m.grms., or one-third of a carat; but he hopes, by working on a larger scale, to produce specimens of one or two carats.

Revue Universelle des Mines et de la Metallurgie.
Vol. xii., No. 2.

This issue contains no chemical matter.

MEETINGS FOR THE WEEK.

Monday, 23rd.—Medical, 8.30.
—— Society of Arts, 8. "The Electric Transmission of Power," by Gisbert Kapp.
Tuesday, 24th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S.
—— Royal Medical and Chirurgical, 8.30.
Wednesday, 25th.—Society of Arts, 8. "Colonisation and its Limitations," by E. J. Ravenstein.
—— Geological, 8.
Thursday, 26th.—Royal, 4.30.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "The Position of Lulli, Purcell, and Scarlatti in the History of the Opera," by Professor C. Hubert H. Parry.
—— Society of Arts, 4.30. "Ths Economic Development of Siam," by Robert Gordon.
Friday, 27th.—Royal Institution, 9. "The Art of Acting," by Percy Fitzgerald.
—— Society of Arts, 4.30. "The Science of Colour," by Captain Abney.
—— Physical, 5. (1) "Proof of the Generality of Certain Formulæ Published for a Special Case by Mr. Blakesley; Tests of a Transformer," by Prof. W. E. Ayrton and Mr. J. F. Taylor. (2) "Further Contributions to Dynamometry," by Mr. T. H. Blakesley. (3) Note on Electrostatic Wattmeters," by Mr. Swinburne. (4) "Interference with Alternating Currents," by Prof. W. E. Ayrton and Mr. Sumpner.
Saturday, 21th.—Royal Institution, 3. "The Forces of Cohesion," by The Right Hon. Lord Rayleigh.

THE CHEMICAL NEWS.

Vol. LXIII., No. 1631.

PHOTO - CHEMICAL RESEARCHES.*

By Professor V. SCHUMANN.

I have unfortunately not been able to continue my spectroscopic photographs on account of the severe weather; but I have been able to carry on the photochemical part of my investigations, and not without some results. I have studied the absorption spectrum of AgBr at higher temperatures, and have found that melted AgBr has a very dense absorption band near "D," and if heated still more strongly it absorbs almost all the rays of the visible spectrum. In presence of AgI all the maxima of AgBr are displaced towards the red. This displacement is not the same in all maxima, but increases with their wave-length. This refers also to the maximum of illumination, which appears at the wave-length 630. The circumstance that the dark rays effect the absorption of the luminous rays, whereby probably the photographic sensitiveness is increased, will help me to photograph the infra-red. I purpose observing this region with the aid of my fluorite train. I expect a good result from the use of fluor-spar, because it possesses a distinguished diathermance as regards refraction and dispersion, and is therefore less affected by heat than any other optical medium. I renounce rock-salt because its transparence, as its refractive planes become dim, is not sufficiently constant, and does not suffice for permanent insolation, whatever its diathermance may be when freshly polished.

AgBr displays very peculiar structures. I have latterly been able to obtain it in the shape of the fig cactus (*Opuntia*), certainly only in a tender microscopic form. I can distinguish these structures only with apochromatic object-glasses, and with the rays of the illuminating lens falling at right angles to the objective axis. All my apochromatic lenses have been obtained from the workshops of Carl Zeiss, of Jena.

H. W. Vogel, in opposition to Abney, maintains that there exist two modifications of AgBr photographically distinct. One of them, if previously dried and if it had been precipitated in alcohol, can not be suspended in gelatin. The other, it is alleged, which has been precipitated from watery solutions, can, on the contrary, not be diffused in collodion. Extended experiments have convinced me that no such difference exists. It may easily happen that the phenomenon observed by Herr Vogel is manifested, especially if too high a temperature has been used in drying the precipitate. AgBr always becomes incapable of suspension if dried in hot air. This is the case whether it has been precipitated from alcohol or from water. If one precipitate has been treated at a much higher temperature than another, the phenomenon reported by Herr Vogel may easily have been manifested.

This, in fact, happened to me in the outset of my experiments on this subject; but on going to work more cautiously, and drying both precipitates quite equally, at the respective temperatures of 15°, 80° and 160°, I arrived at opposite results.

At 15° the aqueous and the alcoholic AgBr were found capable of suspension in collodion and in gelatin. At 60° the capability of suspension of both is much reduced, and at 160° I attempted in vain to emulsify AgBr. I cannot, therefore, admit the statements of Vogel, the less as, on the other hand, his allegation that gelatin is only a feeble sensitiser in my recent series of experiments, encounters still stronger contradictions. I shall at an early date demonstrate that gelatin is absolutely a powerful sensitiser.

I have likewise been unable to detect a spectral difference of the two precipitates when they are suspended in gelatin. In all proofs there appeared the same spectrum which the ordinary silver-bromide gelatins display. The slight displacements which occur in my spectrograms are solely due to atmospheric fluctuations. I have not yet succeeded in a simultaneous and contiguous illumination of both emulsions, and it might hence be inferred that the photographic action of the sunlight in my proofs had varied exceptionally, and thus occasioned the difference from the observations of Herr Vogel. But however justifiable such an argument might seem, its validity is at once enfeebled by the circumstance that the spectral proofs from both emulsions were taken in rapid succession. Hence so considerable a displacement as Vogel calls is exceedingly improbable. On the other hand, it is not conceivable that my instrument can have occasioned the discrepancy. I have in these operations used only the most accurate and sensitive spectrographic apparatus which my cabinet includes.

A SIMPLE ELECTRICAL SAW.

By H. N. WARREN, Research Analyst.

Whenever a powerful electrical circuit is closed by a platinum wire of suitable dimensions, the well-known heating effect of the same is at once manifested; yet no one seems to have been struck with the idea that the simple heated wire may be employed as a most effective disintegrator of the hardest organic compounds. A similar but more convenient article may be constructed as follows. It consists of two upright pieces of very stout brass or copper wire, connected at the lower extremities by a non-conducting medium, while across the top is secured a piece of moderately thin platinum wire. On thus connecting the apparatus by means of side binding screws to the terminals of about four Bunsen batteries, the platinum wire at once becomes heated to bright redness, and will be found to cleave the hardest wood with great facility, insomuch that a large number of useful appliances may be thus manufactured in a short space of time. Owing, however, to the platinum wire frequently breaking, probably on account of its intimate contact with the carbon, whilst at an elevated temperature, the author has devised and used with advantage a modified wire, formed by depositing metallic platinum upon fine steel wire, by exposing that substance to the action of a slow electrical current, in contact with an ethereal solution of platinic chloride.

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

Appointment.—The Professor of Agriculture at the Royal Agricultural College, Cirencester, Professor James Muir, M.R.A.C., F.C.S., has been promoted to the newly endowed Chair of Agriculture at the Yorkshire College, Leeds. Mr. Muir has had a distinguished career both as student and lecturer, and the Leeds College is to be congratulated at having secured his services.

International Congress of Geologists.—We learn that the 5th meeting of the Congress will be held at Washington, on August 26th next. Persons wishing to be present are requested to announce their intention to the Secretary's Office, 1330 F. St., Washington, D.C. The fee is 2½ dollars. Special reduced rates will be charged by the steamship lines from Europe, and by the railway companies on occasion of the geological excursions.

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* Extracts from a letter to the Editor.

ELECTRICITY *IN TRANSITU:* FROM PLENUM TO VACUUM.*

By WILLIAM CROOKES, F.R.S.,
President of the Institution of Electrical Engineers.

(Continued from p. 93).

Phosphorescence in High Vacua.

I have already pointed out that the molecular motions rendered visible in a vacuum tube are not the motions of molecules under ordinary condition, but are compounded of these ordinary or kinetic motions and the extra motion due to the electrical impetus.

Experiments show that in such tubes a few molecules may traverse more than a hundred times the *mean* free path, with a correspondingly increased velocity, until they are arrested by collisions. Indeed, the molecular free path may vary in one and the same tube, and at one and the same degree of exhaustion.

Very many bodies, such as ruby, diamond, emerald, alumina, yttria, samaria, and a large class of earthy oxides and sulphides, phosphoresce in vacuum tubes when placed in the path of the stream of electrified molecules proceeding from the negative pole. The composition of the gaseous residue present does not affect phosphorescence; thus, the earth yttria phosphoresces well in the residual vacua of atmospheric air, of oxygen, nitrogen, carbonic anhydride, hydrogen, iodine, sulphur, and mercury.

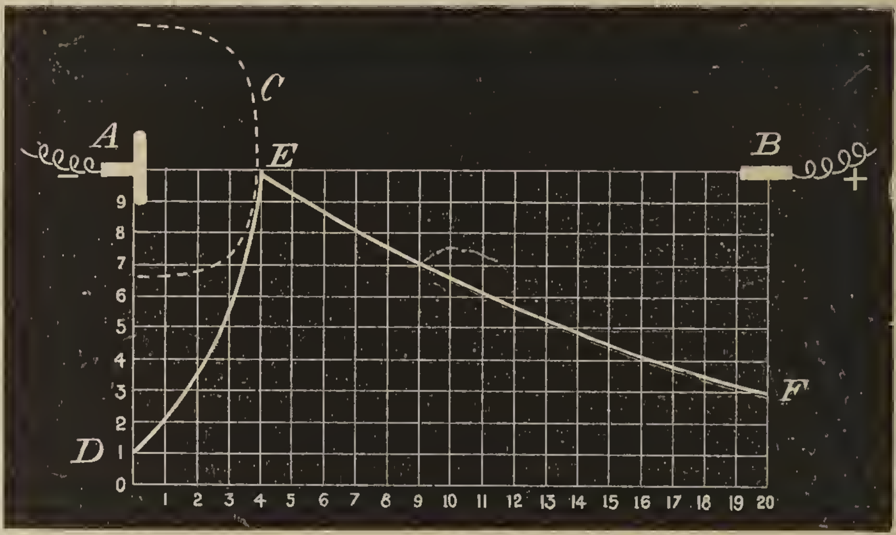

Fig. 24.—P. = 0·25 m.m., or 330 M.

With yttria in a vacuum tube the point of maximum phosphorescence, as I have already pointed out, lies on the margin of the dark space. The diagram (Fig. 24) shows approximately the degree of phosphorescence in different parts of a tube at an internal pressure of 0·25 m.m., or 330 M. On the top you see the positive and negative poles, A and B, the latter having the outline of the dark space shown by a dotted line, C. The curve D, E, F, shows the relative intensities of the phosphorescence at different distances from the negative pole, and the position inside the dark space at which phosphorescence does not occur. The height of the curve represents the degree of phosphorescence. The most decisive effects of phosphorescence are reached by making the tube so large that the walls are outside the dark space, whilst the material submitted to experiment is placed just at the edge of the dark space.

Hitherto I have spoken only of phosphorescence of substances placed under the negative pole. But from numerous experiments I find that bodies will phosphoresce in actual contact with the negative pole.

This is only a temporary phenomenon, and ceases entirely when the exhaustion is pushed to a very high point. The experiment is one scarcely possible to exhibit to an audience, so I must content myself with describing it. A U-tube, shown in Fig. 25, has a flat aluminium pole, in the form of a disk, at each end, both coated with a paint of phosphorescent yttria. As the rarefaction approaches about 0·5 m.m. the surface of the negative pole A becomes faintly phosphorescent. On continuing the exhaustion this luminosity rapidly diminishes, not only in intensity, but in extent, contracting more and more from the edge of the disk, until ultimately it is visible only as a bright spot in the centre. This fact does not prop a recent theory, that as the exhaustion gets higher the discharge leaves the centre of the pole, and takes place only between the edge and the walls of the tube.

If the exhaustion is further pushed, then at the point where the surface of the negative pole ceases to be luminous, the material on the positive pole, B, commences to phosphoresce, increasing in intensity until the tube refuses to conduct, its greatest brilliancy being just short of this degree of exhaustion. The probable explanation is that the vagrant molecules I introduce in the next experiment, happening to come within the sphere of influence of the positive pole, rush violently to it and excite phosphorescence in the yttria, whilst losing their negative charge.

Loose and Erratic Molecules.

In the brief time left to me this evening I cannot touch upon the mass of experiments made to render this result clear, so I will at once show you a piece of apparatus that clearly illustrates the cause of phosphorescence at the positive pole. A drawing of this tube is shown at Fig. 26, but let me first explain the effect I expect to obtain, and then endeavour to show the actual experiment.

A C B is a U-shaped tube with terminals, A and B, at each end; D and E are two mica screens covered with a phosphorescent powder, having at F and G other screens with a small slit in front, so as to allow only a narrow beam of charged molecules to pass through. At first the tube is exhausted to a pressure of 0·076 m.m., or 100 M., and you see how sharp and slightly divergent is the luminous image on screen D, whilst not a trace of phosphorescence is to be seen on the screen E in the other limb of the tube. Now I push the exhaustion to the highest point short of non conduction (0·000076 m.m , or 0·1 M.), and the phenomena change. The initial line of light on D becomes wider and unsteady, whilst at the gate, G, a decided phosphorescence is observable entering the second

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* Inaugural Address delivered January 15th, 1891.

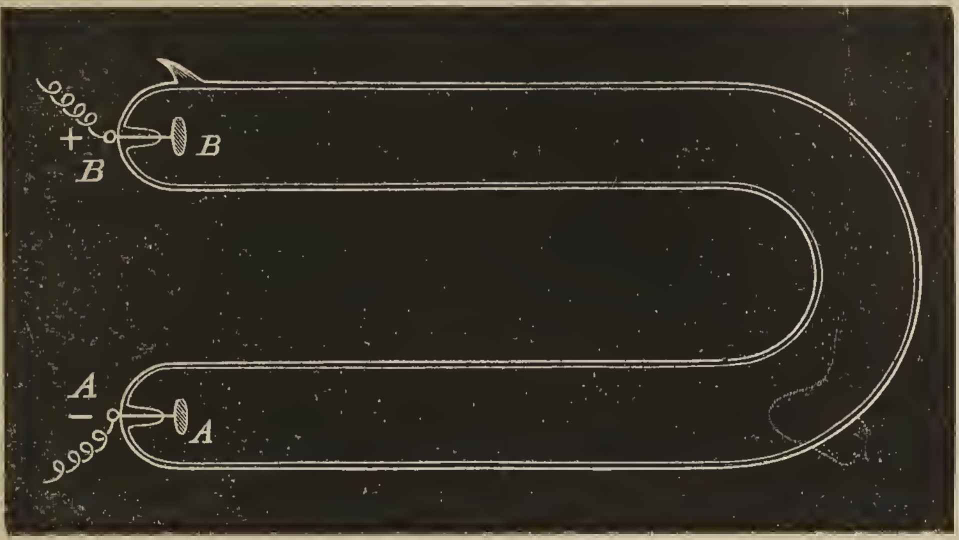
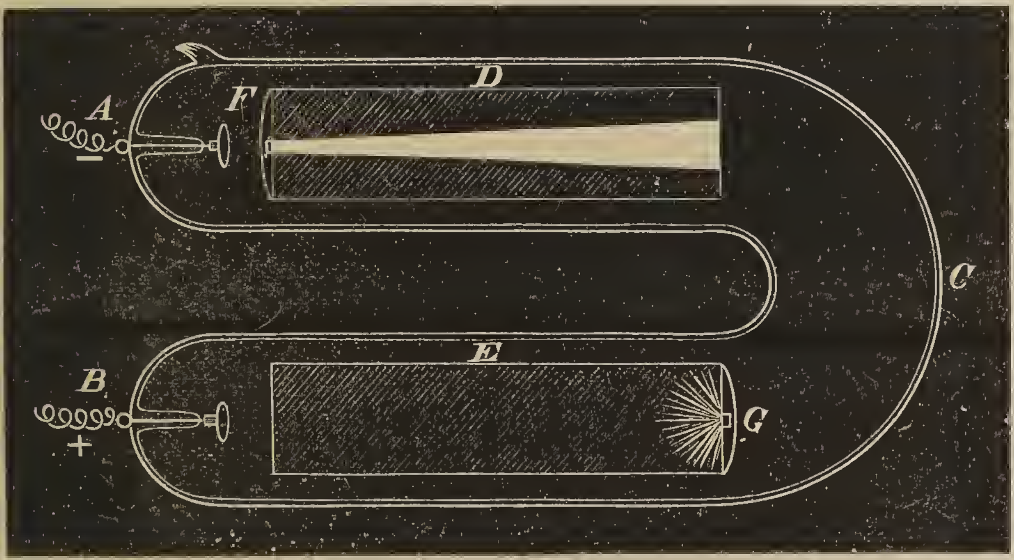


Fig. 25.



P. = 0·076 m.m., or 100 M.

P. = 0·000076 m.m., or 0·1 M.

Fig. 26.

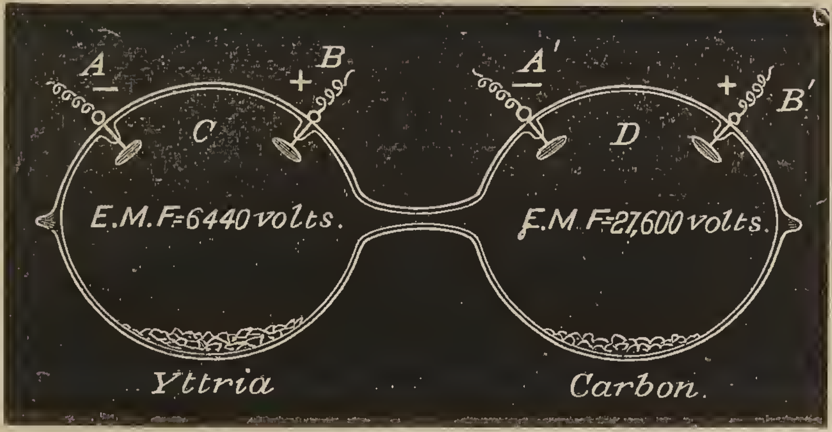


Fig. 27.—P. = 0·02 m.m., or 26 M.

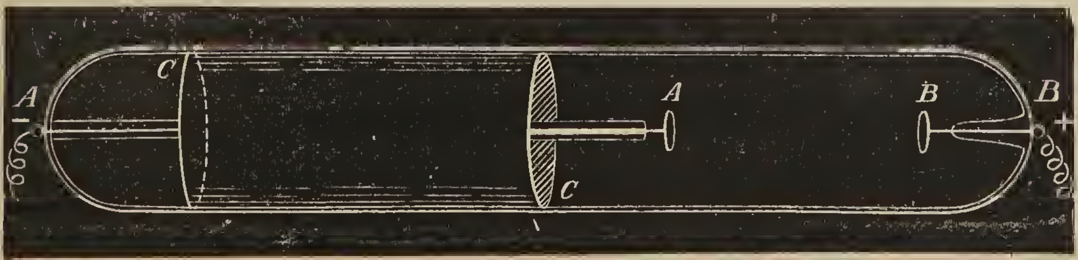


Fig. 28.—P. = 0·00068 m.m., or 0·9 M.

screen, E. This luminosity diverges to a considerable extent, much more than did the stream of charged molecules observed in the first limb of the tube at the lower exhaustion. This is only to be expected, inasmuch as those sparse molecules which have run the gauntlet of the crowd and have been hunted and buffetted round the corner will have little or no lateral support, but wander to the furthest end of the tube, and altogether behave differently to the orderly procession of molecules at more moderate exhaustion.

The Resistance of High Vacua.

I must only lightly touch this phenomenon to-night; it is a subject of deep interest, and one to which I have lately devoted much time. Shortly I hope to publish a full account of results recently obtained.

The passage of an induction current at a high vacuum through a tube depends much upon the material of the tube or the substance enclosed within it. Given the same degree of exhaustion, and the same distance between the terminals inside the tube, the E.M.F. necessary to force the current through may vary from 3000 volts to 20,000 volts, according to the particular material used.

Here is a very striking example that will serve to illustrate this phenomenon. Fig. 27 is a double tube joined by a narrow open channel and therefore in the same state of exhaustion throughout (P.=0·02 m.m., or 26 M.). Each tube is furnished with a pair of poles, A, B, and A′, B′. One tube contains the phosphorescent earth yttria, the other contains finely divided carbon. I first connect the yttria tube, C, to the coil, and place in parallel circuit with it a spark gauge. To begin with, this gauge is set to a gap of 1 m.m. (An E.M.F. of 920 volts is necessary to strike across 1 m.m. of air; therefore the difference of potential at the terminals inside the yttria tube is 920 volts, and this you perceive is not sufficient to force the current through the tube). I now gradually open the gauge until the potential of the inner terminals has risen to a point high enough to allow the spark to pass through the tube, making the yttria phosphorescent.

The gap is at 7 m.m. equal to an E.M.F. of 6440 volts. I next attach the coil wires to the tube D containing the carbon, and the exhaustion in the tubes being the same as before, I repeat the experiment; you now see that the gap has to be opened to 30 m.m., equivalent to an E.M.F. of 27,600 volts, before the current will pass through the tube. The fact of whether the vacuum tube contains yttria or carbon makes a difference of 21,160 volts in the E.M.F. required to cause a discharge between the terminals.

One other experiment I would like to show in further illustration of this resistance. The idea suggested itself that possibly differences in the material or conductivity of the particular bulbs might influence the results you have just seen. Here (Fig. 28) is a long cylindrical tube of phosphorescent Bohemian glass containing a pair of terminals, A, B; it also contains a shorter cylinder of glass, C, C, brighly silvered inside. The internal pressure is 0·00068 m.m., or 0·9 M. The silver cylinder is now at one end of the tube out of the way of the terminals, which therefore have phosphorescent glass around them. I turn on the coil and find that the E.M.F. necessary to force the current through, now that the terminals are in a phosphorescent chamber, is 1380 volts. I slide the cylinder down to the end of the tube so as to inclose the terminals in a metallic silver chamber, and you see the E.M.F. necessary to pass the current rises to 6440 volts. Metallic silver does not phosphoresce, whilst Bohemian glass phosphoresces very well. It appears that the greater the phosphorescing power of the substance surrounding the poles so much the easier does the induction spark pass. Surround the poles with Bohemian glass or yttria—two phosphorescent non-conductors of electricity—and the induction spark passes easily; immediately I surround the terminals with a non-phosphorescent conductor the current refuses to pass.

(To be continued).

DETERMINATION OF WATER IN SUPERPHOSPHATES.

By JULIUS STOKLASA.

The author's extensive experiments both with chemically pure monophosphates and with such as are mixed with free phosphoric acid show to what transformations the hygroscopic water and that in chemical combination are exposed. An accurate study of all the chemical processes taking place with the joint action of sulphates and tri- and di-phosphates is required to lead to an accurate method of determination.

1. *Influence of Temperature upon Monocalcium Phosphate.*

As the experiments of Birnbaum upon the influence of temperature upon monocalcium phosphate are in some repeat unexplained and incomplete, the author resolved to repeat them. The experiments were carried out with the chemically pure preparation of the following composition:—

CaO	22·36 per cent.
P_2O_5	56·67 ,,
H_2O	21·53 ,,

containing 0·014 per cent of free phosphoric acid. In the first place, 3·59 grms. of the compound were dried at 100°.

The loss of water in	10	hours was	1·83
,, ,,	20	,,	2·46
,, ,,	30	,,	5·21
,, ,,	40	,,	6·32
,, ,,	50	,,	6·43

This loss of water, 6·43 per cent, remained constant, for no further decrease of weight was observed below 100°. This quantity of water corresponds to 1 molecule. $CaH_4(PO_4)_2.H_2O$ therefore loses its crystalline water at 100°, but only in 50 hours. The calcium phosphate thus obtained forms opaque crystals, not hygroscopic, which were found to contain 24·02 per cent CaO, 60·74 P_2O_5, and 15·00 per cent H_2O.

It dissolves in water very slowly and without decomposition in the proportion 1 : 200. The temperature in drying may reach 105° without any perceptible change in the monocalcium phosphate. But if dried at 105° for longer than 20 hours it undergoes a further decomposition, though to a slight extent. The decomposition is promoted if the temperature is gradually raised to 200°, according to the following scheme:—

$$4CaH_4(PO_4)_2 = Ca_2P_2O_7 + Ca(PO_3)_2 + CaH_2P_2O_7 + \\ +2H_3PO_4 + 4H_2O.$$

If water acts upon such dried calcium phosphate (in the proportion 1 : 200) the undecomposed monocalcium phosphate by the monocalcium pyrophosphate and the phosphoric acid dissolve, whilst the pyro- and meta-calcium phosphate remain undissolved.

The experiment in question was carried out as follows:—The monocalcium phosphate was dried in a platinum capsule at 105°—200°, and in a very thin layer, so that the temperature might be uniform. The loss of water was determined at fixed intervals, and the dried monocalcium phosphate was afterwards dissolved in water at 15° in the proportion of 1 : 200. In the filtrate the free phosphoric acid and the total orthophosphoric acid were determined in part directly by means of uranium acetate, and in part with molybdic mixture after the solution had been boiled with nitric acid. Lastly, the calcium oxide was determined. The part insoluble in water was collected on the filter, and in it the phosphoric acid and the calcium oxide were determined.

5·0 grms. monocalcium phosphate were dried for an hour at 200°. The loss of water was 7·20 per cent. Therefore, according to the equation given above, 50·4 per cent of monocalcium phosphate had been decomposed. The dried substance was mixed with a litre of water. The undissolved residue of pyro- and meta-phosphate, after being shaken for an hour, was filtered through a weighed filter, washed, dried at 120°, and weighed. The dried substance was dissolved in *aqua regia*, the excess of acid evaporated off, and the solution diluted to ¼ litre.

The analysis showed:—

CaO	36·81 per cent.
P_2O_5	62·20 ,,

or by calculation:—

CaO	37·12 per cent.
P_2O_5	62·88 ,,

The analysis showed 23·15 per cent pyro- and meta-calcium phosphate (by calculation 22·42 per cent), and these have been separated out:—

$Ca_2P_2O_7$	12·6 per cent.
$Ca(PO_3)_2$	9·82 ,,

In all experiments the author found in the amorphous matter thus separated out 62—63 per cent P_2O_5, and 36—37 per cent CaO if the original monocalcium phosphate had been dried at 110—190°.

During drying there is separated out neither pure pyrophosphate, as Birnbaum conjectured, nor meta-phosphate, as Joulie and Millot maintain.

In the aqueous solution of the dried monocalcium phosphate there was first determined the free phosphoric acid by titration with decinormal potassa, with methyl orange as indicator. There was found 6·66 per cent P_2O_5, corresponding to 9·2 H_3PO_4, or by calculation, 9·72 per cent H_3PO_4.

If the total orthophosphoric acid in the solution is determined by titration by means of uranium acetate, the results will always be lower than when the molybdenum method is used. The difference is occasioned by the phosphoric acid which is contained in the solution as monocalcium pyro-phosphate. This compound may be converted into monocalcium orthophosphate by boiling with a few drops of nitric acid.

Whilst the titration of the solution showed 35·8—36·0 per cent phosphoric acid after heating with nitric acid (0·55 grm. HNO_3 to 25 c.c. of solution and boiling for thirty minutes), there were found by the molybdenum method 42·70—42·90 per cent phosphoric acid.—*Zeitschrift Anal. Chemie.*

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 5th, 1891.

Dr. W. J. Russell, F.R.S., in the Chair.

Certificates were read for the first time in favour of Messrs. Albert Edward Bell, Sherborne School, Sherborne, Dorset; Rhys Pendrill Charles, Plas Newydd, Neath; Gilbert John Fowler, Dalton Hall, Victoria Park, Manchester; Berington H. Gibbins, Ocala, Florida, U.S.A.; J. A. R. Greaves, Old Rectory, Grappenhall, Cheshire; William Beaumont Hart, Gransmoor Avenue, Fairfield, near Manchester; Rev. Edgar Norman Langham, M.A., St. John's College, Cambridge; James Leicester, 3, Queen's Parade, Brandon Hill, Bristol; William Macdonald, 109, Crofton Road, Peckham, S.E.; Frederick Johnson Merrils, 65, Roe Lane, Pitsmoor, Sheffield; George R. Morrison, Richmond House, Plaistow; Lewis Ough, 15, Upper King Street, Leicester; James Ashburner Storey, Moorside, Lancaster; Albert Searl, The Caxtons, Miskin Road, Dartford.

It was announced that the following changes in the Council list were proposed by the Council:—

As *President*, Professor Crum Brown, *vice* Dr. Russell.

As *Vice-Presidents*, Mr. J. Pattinson and Professor Tilden, *vice* Professors Crum Brown and Mallet.

As *Foreign Secretary*, Professor Meldola, *vice* Professor Japp.

As *Members of Council*, Dr. Atkinson, Mr. Boverton Redwood, Professor Perkin, and Dr. J. Voelcker, *vice* Mr. Cross, Professor Dunstan, Professor Meldola, and Dr. Plimpton.

The following papers were read:—

5. "*The Formation of an Explosive Substance from Ether.*" By Professor P. T. Cleve.

The author, in the course of a letter to the Secretary, describes a remarkable explosion occasioned by impurities in commercial ether. On distilling about 250 c.c. of the ether, it was noticed that a viscid residue remained; after drying on the water-bath, this formed a transparent amorphous mass, estimated to weigh about 0·75 grm. Prof. Cleve states that, having poured a little water on to the substance, he proceeded to stir it gently with a rounded glass rod; this occasioned a most violent explosion. A number of the pieces of glass which were projected about perforated the windows just as if they had been revolver bullets. The explosive substance was probably ethyl peroxide, as it gave the well-known perchromic colouration, besides liberating iodine and discharging oxygen from silver oxide; it was at once destroyed by reducing agents; it exploded with as much violence as if it had been chloride of nitrogen or fulminate.

Discussion.

Professor Dunstan remarked that several cases had been recorded of explosions during the distillation of impure ether, one a few years ago by Schaer in the *Archiv. der Pharmacie* for 1877.

6. "*Does Magnesium form Compounds with Hydrocarbon Radicles?*" By Orme Masson, M.A., D.Sc., and U. T. M. Wilsmore, B.Sc., University of Melbourne.

According to Hallwachs and Schafarik (*Annalen*, cix., 206), magnesium in the form of filings and ethyl iodide commence to interact at ordinary temperatures, and the interaction is complete at 180°; they state that the metal becomes converted into a white mass, the liquid disappearing, much gas being generated. On heating the white mass, a colourless volatile liquid distilled over, which fumed strongly in the air, but did not inflame; this liquid, it was believed, consisted of hydrocarbons mixed with traces of magnesium ethide, but, as the residue decomposed water with explosive violence, it was thought that it contained a considerable amount of magnesium ethide combined with magnesium iodide.

Cahours (*Annales de Chimie et de Physique* [5], xviii., 17) also found that much heat was evolved on adding methyl or ethyl iodide to magnesium filings. Having digested a mixture of the metal and ethyl iodide at 130° till the liquid had disappeared, he heated the resulting white mass in an atmosphere of hydrogen, and obtained a liquid distillate which took fire in the air and acted strongly on water. Carbon and hydrogen were estimated in two fractions of this liquid, but the results were far from agreeing with the theoretical values; the discrepancies were attributed to insufficient purification. No evidence of the presence of magnesium in the product was adduced by Cahours.

Wanklyn heated sodium zinc ethide with mercury and magnesium wire, and obtained a white, spontaneously inflammable, solid product. This contained magnesium and zinc, but only traces of sodium; it was believed to be magnesium zinc ethide.

The authors state that they have in vain endeavoured to prepare magnesium ethide (1) from magnesium and ethyl iodide; (2) from magnesium copper couples and ethyl iodide; (3) from an alloy of magnesium and sodium and ethyl iodide; (4) from magnesium and zinc ethide; (5) from magnesium and mercury ethide; and (6) from anhydrous magnesium iodide and zinc ethide.

An alloy formed by heating magnesium and sodium together in a hard glass flask in an atmosphere of hydrogen acted very slowly on ethyl iodide at 100°, and no signs of the formation of magnesium ethide were observed. On heating together magnesium and zinc or mercury ethide in sealed tubes, no action occurred till the temperature rose sufficiently high to decompose the ethide; large quantities of gas were then formed, zinc or mercury separating, but no magnesium ethide. Similarly, magnesium iodide and zinc ethide appeared not to interact, the ethide being decomposed simply by the heat.

There appeared to be little or no advantage in using magnesium copper couples, the action being in all respects similar to that of magnesium alone, although occasionally somewhat quicker. Magnesium iodide and gaseous hydrocarbons were the sole products.

Several experiments on the action of ethyl iodide on magnesium were tried under varied conditions and using the two substances in different proportions; sometimes a crystal of iodine was added as recommended by Frankland for the preparation of zinc chloride. In most cases the materials were heated together in a flask connected to a reflux condenser, from which the air was displaced at the outset by hydrogen or carbon dioxide. The magnesium used was prepared by fusing commercial ribbon in an iron crucible under a flux of ammonium, magnesium, and potassium chlorides, and subsequently filing down the lump; it was practically free from impurities except traces of iron. The results obtained were uniformly negative, and although previous observers have stated that interaction occurs at ordinary temperatures, the authors have never perceived the slightest sign of action till after the iodide and metal had been heated together for some time. Thus, in an experiment in which 30 grms. of specially dried ethyl iodide was added to 5 grms. of magnesium, and the temperature of the bath containing the flask was maintained a little below 100°, no action seemed to take place for a time, but after a while gas was given off and a white powder was seen to slowly form on the metal; after thirty hours' continuous heating, ethyl iodide ceased to run back, and the evolution of gas —which had been continuous—came to an end. On heating the residue to 270°, no distillate except a little unused iodide was obtained; the residue proved on analysis to be simply magnesium iodide. It no case was a trace of distillate obtained showing any tendency to fume in the air. The authors point out that magnesium iodide is very hygroscopic, and is so violently acted on by water that they are inclined to think that Hallwachs and Schafarik may possibly have been led to suppose that magnesium ethide in combination was present when really there was only magnesium iodide. Magnesium iodide forms a crystalline compound with ether which apparently has the composition $MgI_2 \cdot 2Et_2O$.

The authors are hence inclined to conclude that previous experimenters have used magnesium containing some impurity which facilitated its action on the iodide; but they do not see reason for assuming that the result was the production of magnesium ethide. They also suggest that possibly the magnesium previously used may have contained zinc, and that small quantities of zinc ethide mixed with hydrocarbons may have been mistaken for magnesium ethide.

The results, however, raise a question of no slight interest. Of the elements of the second natural group, zinc and mercury very readily form compounds with hydrocarbon radicles; cadmium appears to be capable of forming them, though much less readily; and beryllium propide and ethide have been described by Cahours. Calcium, strontium, and barium, on the other hand, presumably do not form such compounds. In which subgroup must magnesium be placed according to this test? Again, aluminium, which follows magnesium in series, forms well-defined compounds with hydrocarbon radicles, while sodium, which precedes it, forms only an unstable double compound with zinc and ethyl. Which does magnesium resemble, if either? Or has it an intermediate character. It is exceptional for elements on the descending portions of the curve of atomic volumes to unite with hydrocarbon radicles, and a glance at the curve shows that beryllium and magnesium are the only elements undoubtedly occupying such a position that are believed to do so. As to beryllium, it may be pointed out that Cahours (*Comp. Rend.*, lxxvi., 1383) worked with very small quantities and apparently based his conclusions on purely qualitative observations. With regard to magnesium, the authors think that the extremely slight character of the older evidence, and the fact that their own experiments have led to directly contrary conclusions to those of Cahours, justify them in denying its power to form free compounds of the kind discussed. It is, however, just possible that, as indicated by Wanklyn's qualitative experiment, magnesium may form an unstable double ethide with zinc, thus resembling sodium, which immediately precedes it in the natural classification.

DISCUSSION.

Dr. ARMSTRONG said that Messrs. Masson and Wilsmore's paper had been despatched from Melbourne on December 29th; meanwhile the question which they had put, and to which they inclined to give a negative reply, had been answered in the affirmative by Löhr in one of the latest numbers of *Liebig's Annalen* (cclxi., 72). Löhr, like the authors, had found that methyl and ethyl iodides had no action at ordinary temperatures either on magnesium alone or on magnesium associated with copper or sodium; and that the action was very sluggish at high temperatures. The presence of a little ethylic acetate served, however, to cause an interaction to set in vigorously in the cold, which was completed within forty to fifty hours at 110°; but the product gave no liquid distillate even at 330°, and Löhr had established the interesting fact that magnesium methide and ethide were solid, non-volatile compounds.

These observations, taken in conjunction with those of the earlier workers in the same field, afforded further evidence that in the formation of organo-metallic compounds, as in so many other cases, it was necessary that some third substance should be present to condition interaction.

Referring to the authors' suggestion, that the magnesium used by previous workers contained zinc, Professor THORPE said that he had had occasion when at the Owens College to analyse a large number of samples of magnesium from Mr. Sonstadt, who, in those days, was the sole maker of the metal, and these never contained zinc, so that he could not agree with the authors in their explanation.

7. "*Compounds of the Oxides of Phosphorus with Sulphuric Anhydride.*" By R. H. ADIE, B.A.

The author has endeavoured to prepare compounds of phosphorus similar to those which the other elements of the group form with sulphuric anhydride.

Employing a preparation obtained from Messrs. Harrington, of Cork, approximately consisting of H_3PO_3, he obtained, by the action of sulphuric anhydride, a product very nearly of the composition corresponding to the formula $H_3PO_4 \cdot 3SO_3 = (SO_3H)_3PO_4$, in the form of a viscid liquid which was decomposed by water, but without violence, yielding sulphuric and orthophosphoric, and but traces of meta- and pyro-phosphoric acids. Sulphuric anhydride and phosphorus were found to interact violently; the author represents the product by the formula $3P_2O_4 \cdot 2SO_3$. The compound slowly decomposes into phosphoric and sulphurous anhydrides; it is instantly decomposed by water, but the phosphorus containing part dissolves only very slowly.

DISCUSSION.

Professor RAMSAY, after referring to the interest attaching to the investigation of compounds such as were described by the author, expressed the opinion that they were legitimately regarded as salts, and that the existence of such salts must serve to break down the distinction which was usually made between metals and non-metals based on the formation of salts.

Professor Thorpe dissented from this view. He also took occasion to correct the statement made by Mr. Tutton and himself, that the oxide P_4O_6 becomes red on exposure to light; this change, they had since discovered, was due to the presence of a small quantity of phosphorus.

8. "*Combustion of Magnesium in Water-Vapour.*" By G. T. Moody, D.Sc.

The author points out that the combustion of magnesium in water-vapour, which is very difficult to conduct in the manner commonly described (*cf.* Kessler, *Ber.* ii., 369), may be conveniently demonstrated, as a lecture experiment, by carrying out the operation in a piece of hard glass tube, of about 10 m.m. in diameter, and 250 m.m. in length, bent at an angle of 120° so as to leave one arm nearly twice as long as the other. The shorter arm is inserted through a cork closing the mouth of a "tin can" or other convenient vessel, in which steam can be generated; and the longer arm, which contains a few strips of magnesium ribbon, is connected by a fairly wide delivery tube with the pneumatic trough, at which the liberated hydrogen may be collected. When the air in the apparatus has been displaced by a slow current of steam, the arm in the tube containing the magnesium is cautiously heated by means of a Bunsen burner until the temperature of the tube is considerably higher than that at which water-vapour condenses; the Bunsen burner is then replaced by a blowpipe flame, which is moved about in such a way that the whole of the arm becomes very hot, and on allowing the flame to impinge for a few seconds on a portion of the tube against which the magnesium rests, the metal takes fire and burns with great brilliancy.

The success of this experiment is only assured when there is a *very slow* current of steam passing through the apparatus, and when the tube containing the magnesium is carefully heated, as in the manner above described. Under such circumstances, the metal burns with great regularity, fracture of the tube being usually avoided, and the whole of the hydrogen evolved may be collected.

CHEMICAL SOCIETY'S JUBILEE—1891.

February 24th.

An afternoon meeting took place in the Theatre of the London University, between 3 to 5 o'clock p.m.

The programme included—(1) Introductory speech by the President, Dr. Russell; (2) Address by the Rt. Hon. Sir Wm. Grove, and Address by the Rt. Hon. Sir Lyon Playfair (Original Fellows of the Society); (4) Presentation, by Mr. R. Warington, of album containing portraits of original Fellows and letters relating to the formation of the Society; (5) Address by Professor Odling on the Development of Chemical Theory since the foundation of the Society; (6) Presentation of addresses from the Royal Society, Pharmaceutical Society, *Société Chimique de Paris*, *Deutsche Chemische Gesellschaft*, and the Russian Physico-Chemical Society; (7) Letters from foreign members.

It is our intention to give a full report of the above proceedings in an early number.

In the evening the Fellows, their friends, and invited guests, to the number of over 1000, were present at a *soirée* at the Goldsmith's Hall, where the following apparatus, specimens, and objects of interest were exhibited.

William Gilbert, M.D.,

Author of "De Magnete," founder of the Science of Electricity. Physician to Queen Elizabeth. Born at Colchester, 1540; died, 1603.

This portrait-medallion was executed in clay from the engraved portrait of Dr. Gilbert, in the studios of the City and Guilds' Technical College, Finsbury, by E. Dunkerley, student, and was electrotyped in copper in the electrical laboratory of the College, by E. Rousseau. Upon the surface of the copper medallion, a layer of metallic cobalt was then deposited by the process invented by Prof. Silvanus P. Thompson.

(Exhibited by Professor Silvanus Thompson).

Ambrose Godfrey Hanckwitz (a.d. 1660—1741).

Phosphorus.—This specimen was prepared about the year 1680 by the alchemist, Ambrose Godfrey Hanckwitz, F.R.S., in Robert Boyle's laboratory in Southampton Street, Covent Garden, and is reputed to be a part of the first specimen prepared in this country. For nearly two centuries it remained in the possesion of the firm of Messrs. Godfrey and Cooke, which Hanckwitz founded, and in 1876 was presented by them to the Museum of the Pharmaceutical Society.

At the time when this phosphorus was prepared, Hanckwitz was Boyle's assistant, and he obtained it from urine by the method described in Boyle's posthumously published paper (*Phil. Trans.*, 1693). For many years, subsequently, Hanckwitz was the only manufacturer of the substance in Europe. He claims to have been the first to obtain the element in a solid "glacial" form (*phosphorus glacialis urinæ*). In the account (*Phil. Trans.*, 1733), which he gave of his method to the Royal Society in 1733, it is stated "An operator that is not well versed in the degrees of fire, and does not know how and when to take away these oils apart, will have nothing but a volatile salt and fetid oil, and get at least only a little unctuous opaque phosphorus, such as the famous Kunckel, Dr. Krafft, and Brandt did, as they acknowledge in their writings, but not our hard transparent phosphorus."

Engravings.—Two engraved portraits of Hanckwitz, dated 1718 and 1738 respectively.

Three engravings of Robert Boyle's laboratory in Southampton Street, Covent Garden, where Hanckwitz worked. One of these shows the furnaces and retorts used in the preparation of phosphorus. After Boyle's death this laboratory passed into the possession of Hanckwitz, and until the year 1862 was occupied by Messrs. Godfrey and Cooke, who constantly used the original furnaces. The Roman Catholic Church in Maiden Lane, Covent Garden, now stands on the site of the laboratory. These engraving are kindly lent by Joseph Ince, Esq.

(Exhibited by Professor Dunstan).

Sir Isaac Newton.

Cupellation furnace, said to have been used by Sir Isaac Newton when Master of the Mint.

(Exhibited by the Science and Art Department, South Kensington).

E. W. Scheele (1742—1786).

Balance in a pocket-case, which belonged to Scheele, who gave it to his pupil Orfila.

(Exhibited by Professor W. H. Corfield).

Henry Cavendish.

Balance used by Cavendish in his chemical and physical investigations.

(Exhibited by the Council of the Royal Institution).

Sir Humphry Davy.

Balance used by Davy and Young at the Royal Institution.

Galvanic battery used by Davy in the discovery of potassium and sodium.

Specimens which illustrate the experimental development of the miners' safety lamp, as left by Davy at the Royal Institution.

(Exhibited by the Council of the Royal Institution).

Thomas Young.

Slide rule for Chemical equivalents, constructed for Young.

(Exhibited by the Council of the Royal Institution).

John Dalton.

Apparatus employed by John Dalton in his researches.

The apparatus employed by John Dalton in his classical researches, whether physical or chemical, was of the simplest and even of the rudest character. Most of it was made with his own hands, and that which is exhibited has been chosen as illustrating this fact, and as indicating the genius which, with so insignificant and incomplete an experimental equipment, was able to produce such great results.

Manuscript book containing an account of some of his experiments, in his own handwriting.

Two home-made barometers used by Dalton, consisting of simple syphon tubes with bulbs. One has probably been used for tension experiments.

Graduated glass tube attached to a bottle of india-rubber, probably used in his researches on the absorption of gases in water.

Two phials containing iodine.

Eudiometer.

Gas receiver.

Graduated funnel used probably as gas receiver.

(The Council of the Literary and Philosophical Society Manchester).

Sir John Herschel.

First known photographs on glass taken on precipitated silver chloride, by Sir J. Herschel (Slough, 1839).

"Having precipitated muriate of silver in a very delicately divided state from water very slightly muriated, it was allowed to settle on a glass plate; after forty-eight hours it had formed a film thin enough to bear drawing off the water very slowly by a siphon and drying. Having dried it, I found that it was very little affected by light; but by washing with weak nitrate of silver and drying, it became highly sensible. In this state I took a camera-picture of the telescope on it. Hyposulphite of soda then poured cautiously down washes away the muriate of silver and leaves a beautiful delicate film of silver representing the picture. If, then, the other side of the glass be smoked and black varnished, the effect is much resembling daguerreotype, being dark on white as in nature, and also right and left as in nature, and as if on polished silver."—(Sir J. Herschel; MS. Journal of Chemical Experiments).

(Exhibited by Prof. A. S. Herschel).

Frame of early specimens of the cyanotype and other photographic processes.

(Exhibited by the Science and Art Department, South Kensington).

Photograph of the solar spectrum taken by Dr. Draper, given by him to Sir John Herschel.

(Exhibited by W. Crookes).

J. J. Berzelius.

Medallion of Berzelius in selenium. (From the Museum of the Pharmaceutical Society). This was given by Heinrich Rose, of Berlin, to Dr. Theophilus Redwood, then Professor of Chemistry to the Pharmaceutical Society, and one of the early Secretaries of the Chemical Society.

(Exhibited by Professor Dunstan).

A portion of the identical seleniferous deposit in which Berzelius discovered selenium.

(Exhibited by W. Crookes).

Michael Faraday.

Solutions of gold illustrating the various effects arising from the visibility of gold in a chemical state of division.

Apparatus used by Faraday in the earliest experiments on the liquefaction of gases.

Bar of heavy glass, made and used by Faraday in the discovery of the rotation of the plane of polarisation in the magnetic field.

Specimen of benzole.

Specimen of carbon tetrachloride.

(Exhibited by the Council of the Royal Institution).

Thomas Graham,
First President of the Society, 1841.

Apparatus employed by Thomas Graham, F.R.S., Professor of Chemistry in University College, and afterwards Master of the Mint, in his principal researches between the years 1834 and 1866.

This series is interesting as showing the simplicity of the appliances with which he discovered laws and facts that have proved of such great importance.

Tubes with discs of graphite and of hydrophane employed by Graham in experiments on the diffusion of gases.

The apparatus employed for ascertaining the diffusion rates of liquids (Bakerian Lecture, 1849).

Osmometers, or apparatus employed in Graham's researches on "Osmotic Force."

Apparatus employed in experiments on liquid diffusion applied to analysis and dialysis.

Apparatus by which Graham studied capillary liquid transpiration in relation to chemical composition.

Tube atmolyser, or instrument for the separation of gases by diffusion.

Barometrical diffusiometer, used for the investigation of the molecular mobility of gases.

Apparatus employed in experiments on absorption and dialytic separation of gases by colloid septa of metal or of india-rubber.

The penetration of metals by gases was studied by the aid of metallic tubes, of which the palladium tube shown is an original one.

(Exhibited by Professor Roberts-Austen, C.B., F.R.S.).

Palladium medal struck by Graham at the Royal Mint, and charged by him with hydrogen. Presented by Graham to the late Dr. Matthiessen.

(Exhibited by the President of the Society).

Sir B. C. Brodie, Bart.,
Secretary to the Chemical Society, 1850—1854;
President of the Chemical Society, 1859—61;
Waynflete Professor of Chemistry, Oxford University, 1855—1872.

Apparatus used in researches on ozone, and the action of electricity on gases, 1860—1872.

Induction tube for producing ozone.

Gas holder for preserving electrised gas over concentrated sulphuric acid.

Measuring pipette. Vol. 290·8 c.c. To deliver a constant volume of electrised gas.

Absorption bulb and aspirator for measuring residual gas after absorption of ozone (calibrated at each of the glass points).

(Exhibited by Dr. W. Odling, Waynflete Professor of Chemistry, Oxford).

Dr. Gladstone, F.R.S.,
President, 1877—1879.

Hydrate of turpentine, re-crystallised from water. 1846.

Cotton xyloidin. 1847.

Hydrosulphate of menthol. 1865.

Coeruleine, a blue substance found in many essential oils.

Dr. Gladstone and the late Mr. Tribe.

Aluminium ethylate, an alcohol substitution product capable of distillation.

$C_{13}H_{10}O$, phenyl ketone produced by heating phenylate of aluminium.

$C_{15}H_{12}O_2$, from a ketone obtained from paracresylate of aluminium.

$C_{15}H_{14}O$, cresyl ketone produced by heating paracresylate of aluminium.
$C_{15}H_{14}O$, ketone produced by heating thymolate of aluminium.
$C_{15}H_{14}O$, the above sublimed.
$C_{20}H_{14}O$, naphthyl ether, obtained from naphthylate of aluminium.
Isodinaphthyl from α naphthylate of aluminium.
Chryseudiene from β-naphthylate of aluminium.
α-Benzylene obtained from benzyl bromide.
β-Benzylene obtained from benzyl bromide.
The original copper-zinc couple.
The dry copper-zinc couple and its constituents.
The original air battery.
Early form of the air battery.

Dr. Gladstone and Mr. Hibbert.

Para caoutchouc obtained by precipitation.
Penang caoutchouc obtained by precipitation.
$C_{10}H_{15}Br_5$, action of bromine on caoutchouc.
(Exhibited by Dr. Gladstone).

Warren de la Rue, D.C.L., F.R.S., President, 1867—1869 and 1879—1880.

Photographs of the Moon. One of the earliest applications of photography to celestial physics.

Specimen cells of the great battery of 15,000 cells, used by De la Rue and Müller in their researches on the electrical discharge in gases.

Spark micrometer, for measuring the relation of potential and striking distance.

Tubes used in the study of the electrical discharge in rarefied media.

Voltameter used in connection with the great battery.

(From the De la Rue Collection in the Royal Institution. Exhibited by the Council of the Royal Institution).

Tyrosine from cochineal.
Carminic acid.
Nitrococcusic acid.
(Exhibited by Dr. Hugo Müller).

(To be continued).

PHYSICAL SOCIETY.

Annual General Meeting, February 13th, 1891.

Prof. A. W. Reinold, F.R.S., Past President, in the Chair.

The reports of the Council and Treasurer were read and approved. From the former it appears that there has been a satisfactory increase in the number of members and in the average attendance at the meetings.

During the year a translation of Prof. Van der Waal's memoir on "The Continuity of the Liquid and Gaseous States of Matter" has been issued to members, and it is hoped that the translation of Volta's works, now in hand, will be published before the next General Meeting.

The Council regret the loss by death of Mr. W. H. Snell and Mr. W. Lant Carpenter, and obituary notices of these late members accompany the report.

The Treasurer's statement shows that the financial condition of the Society is very satisfactory, and that the sales of the Society's publications have increased considerably.

A vote of thanks, proposed by Mr. Whipple and seconded by Dr. Gladstone, was unanimously accorded to the Lords of the Committee of Council on Education for the use of the room and apparatus.

Dr. Atkinson proposed a vote of thanks to the auditors, Prof. Fuller and Dr. Fison, which was seconded by Dr. Thompson, and passed unanimously. The proposer, in referring to the satisfactory nature of the accounts, recommended that the publications of the Society should be brought before physicists and other students of physical science, and Prof. Thompson heartily concurred in this recommendation.

A third unanimous vote of thanks was accorded to the President and Officers for their services during the past year, the proposer and seconder being Dr. Waller and Prof. Minchin.

The following gentlemen were declared duly elected to form the new Council:—

President—Prof. W. E. Ayrton, F.R.S.

Vice-Presidents—Dr. E. Atkinson; Walter Baily, M.A.; Prof. O. J. Lodge, D.Sc., F.R.S.; Prof. S. P. Thompson, D.Sc.

Secretaries—Prof. J. Perry, F.R.S.; T. H. Blakesley M.A., M.Inst.C.E.

Treasurer—Prof. A. W. Rücker, M.A., F.R.S.

Demonstrator—C. V. Boys, F.R.S.

Other Members of Council—Shelford Bidwell, M.A. LL.B., F.R.S.; W. H. Coffin; Maj.-Gen. E. R. Festing, R.E., F.R.S.; Prof. G. F. Fitzgerald, M.A., F.R.S.; Prof. J. V. Jones, M.A.; Rev. F. J. Smith, M.A.; Prof. W. Stroud, D.Sc.; H. Tomlinson, B.A., F.RS.; G. M. Whipple, D.Sc.; James Wimshurst.

The meeting was resolved into an Ordinary Science Meeting, and Messrs W. Thorp, B.Sc., G. W. Yule, and S. Joyce were elected members of the Society.

A paper on the "*Change in the Absorption Spectrum of Cobalt Glass produced by Heat*," by Sir John Conroy, Bart., M.A., was read by Mr. Blakesley.

The absorption spectrum of cobalt glass, when cold, consists of three dark bands in the red, yellow, and green, with a considerable amount of absorption between the first two. When a piece is heated to nearly red heat, the absorption between the first two dark bands diminishes, and the band in the red moves towards the least refrangible end of the spectrum, whilst those in the yellow and green retain their position, but become less distinct. During the heating of the glass the intensity of its colour diminishes, and as the glass cools its original colour and absorption spectrum returns. Diagrams and numbers, showing the character and positions of the bands in hot and cold glass, accompany the paper, together with the numbers obtained by Dr. W. J. Russell (*Proc. Roy. Soc.*, xxxii., p. 258) for cold cobalt glass.

In conclusion, the author says that these observations, and those of Feussner on solutions, show that the absorption spectra of some substances vary with temperature. In solutions, this may be due to formation of different hydrates or to partial dissociation, but in a solid, like cobalt glass, an actual change in its chemical constitution at a temperature considerably below its fusing point does not seem probable.

Dr. Gladstone said that it was generally known that heat affects the colouring power of substances, and that in solutions absorption is greater the higher the temperature. Different solvents sometimes produce effects analogous to heat; for cobalt salt dissolved in water and in alcohol give pink and blue solutions respectively, and rise of temperature makes the aqueous solution more blue. He concurred with the author as to the causes of the phenomena in liquids, and that the same explanation would not apply to glass.

Prof. S. P. Thompson thought Sir John Conroy's results agreed with the experiments which Mr. Ackroyd showed before the Society some years ago, when he demonstrated that the colours reflected by opaque bodies, such as porcelain, &c., when heated, tend towards red.

Prof. Minchin showed some experiments in illustration of his paper on "*Photo-Electricity*," read at the previous meeting.

In one of these, a seleno-aluminium battery, illuminated by the light of a taper, deflected an electrometer needle, thereby actuating a relay and ringing a bell. He afterwards exhibited one of his "impulsion cells" in action, and showed the change from the insensitive to the sensitive state produced by a Hertz oscillator at a distance.

In the discussion, Mr. Tunzelmann said Kalischer and von Uljanin had worked on the same subject, the former being the first to make experiments on a photo-E.M.F. in selenium. His cells were made by winding brass wire on glass tubes and coating them with selenium, which was subsequently annealed. These cells lost their power after some time, and would not respond to feeble lights. By using two wires of different metals he obtained better results. Fritts, in 1883, used brass and gold plates coated with selenium, and Uljanin employed platinum plates deposited so thin as to be transparent. The latter experimenter found that the E.M.F. was proportional to the square root of the intensity of the light. He also observed that the orange-yellow of the prismatic spectrum produced the greatest effect, whereas the yellow-green and the green rays of the diffraction spectrum gave the maximum E.M.F. Comparing these results with Langley's observations on the distribution of energy in the spectrum, it would appear that the E.M.F. bears no relation to the maximum energy falling on the surfaces. Speaking of the cause of the phenomena, he said the electrolytic idea of von Uljanin seems inapplicable to Prof. Minchin's results, and he enquired whether a mixture of selenium and aluminium would undergo a gradual change by exposure to light.

Dr. Gladstone said such a change, if it occurred, would be very slow, for nearly all difficult chemical reactions take time to complete. The fading of colours was adduced as an instance of slow chemical change produced by light.

Dr. Waller thought the subject might throw light on the changes occurring in the retina, and asked if it was possible to separate thermo-electric and photo-chemical effects.

Dr. Burton said he had suggested that the action of light on the retina was a photo-chemical one, some time ago. But hitherto it had been difficult to obtain substances sensitive to any but the blue and violet rays, whereas the eye was most sensitive to green and yellow light. In the photo-electric batteries, however, the E.M.F. may generate a current, and, therefore, energy, and the important question seemed to be—Where does this energy come from? Is it a chemical change precipitated by the action of light, or does a direct conversion of light into electrical energy occur?

Prof. Minchin, in his reply, said he thought his cells really transformed the incident energy. They were usually kept on open circuit, and there appeared to be no deterioration with time, the only change being a sluggishness in developing their maximum E.M.F.

CORRESPONDENCE.

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To the Editor of the Chemical News.

Sir,—I notice in your last issue (Chem. News, vol. lxiii., p. 95), a letter from Mr. W. L. Brown, concerning his "Manual of Assaying," and in reply I may say that I was assured (in writing) by the English publisher that he had made the necessary arrangements with the American publishers of the book.

If this had not been so, I can assure Mr. Brown that I would not have edited the book, which I was asked to do by the publisher.—I am, &c.,

A. B. Griffiths.

Constitution of Bone-Meal.—Julius Stoklasa (*Chem. Zeitung*).—Analyses and practical trials made with fine and coarse meals, and with samples rich or poor in grease. Fine meals not containing more than 0·6—1 per cent of grease form a better manure not merely than basic slags, but even than precipitated phosphate.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 2.

On Beer Yeast. Results of the most Recent Researches and their Industrial Application.—H. Bungener.—This paper requires the numerous accompanying cuts.

Notes on Dyeing.—M. Grandmougin.—These notes comprise an account of the modern method of black dyeing on woollens (*Faerberzeitung*), on the use of the so-called "patent colours" of Croissant and Bretonnière which are useless on woollens; on patent fustine, on dyeing mixed tissues in different colours, on dyeing wool with indulines and on piece-dyeing—all these processes being taken from the *Faerberzeitung*.

Bleaching Wool and Silk with Hydrosulphite.—Gaston Dommergue.

Means of Distinguishing the Resin Oils of the First and Second Distillation.—A. Chenevier.—The author has studied the proportion of acids present in these oils, and makes use of two methods—the gravimetric and the volumetric. He prefers the latter, making use of the process of Burstynn:— To 50 grms. of the oil in a ½ litre flask he adds 100 c.c. of alcohol (at 90° or 95°) and ten drops of an alcoholic solution of rosolic acid at 1 per cent, or five drops of an alcoholic solution of phenolphthaleine at 25 per cent. Then, whilst agitating strongly, he adds with a burette a normal soda, until a permanent red colour is produced. The acidity of the rectified oils rarely reaches 4 per cent, whilst the oils of the first distillation vary from 4 to 10 per cent.

New Practical Method for Detecting Colouring Matters Fraudulently added to Wines.—J. Weirich.—A practical and expeditious method within the reach of all has long been sought for the recognition of wines artificially coloured. The author's method is founded upon the action of air and light upon the colouring matters of wine spread out in an extremely thin layer. The wine is applied with a brush upon a piece of paper of good quality which is not pervious. It is kept for an instant in contact with the paper, which is then drained off and let dry. The colouring matters of wine give the paper a tone quite different from those of the colouring matters—vegetable, animal, or artificial—which serve for the sophistication of wines; the difference is categorical. The natural colours of wine and vegetable colours are transformed upon paper, each according to its nature. The artificial colours are either transformed very slightly or not at all.

New Process for Detecting the Presence of Colouring Matters in Wines.—A. Pagnoul.—The process depends on the property of soap-lyes to destroy the natural colouring matter of wines without giving them the greenish tint communicated by other alkaline solutions, and without affecting strange colours.

Another Process for Detecting Foreign Colouring Matters in Wine.—L. Sostigni (*Chem. Central Blatt*).—Foreign colouring-matters which are not decomposed by alkalies at an ordinary temperature (*e.g.*, safranine, eosine, &c.), or which they turn to a violet (*e.g.*, the tropeolines and cochineal), may be easily detected as follows. The wine is treated with 1-10th of its volume of a solution of potassa at 10 per cent, shaken up for five minutes, and the liquid poured into a filter of parchment paper, in contact externally with water. After some hours a yellow liquid containing the oxidation products of the tannin is diffused. This result is complete in twenty-four hours, or in forty-eight hours in case of wines very rich in tannin. The colouring matters foreign to wine are fixed upon the parchment paper with their own colours. Natural wines colour the paper yellow.

Analyses of Concentrated Superphosphates.—J. Hughes (*Chemiker Zeitung*).—Iron and aluminium phosphates are insoluble in water, but soluble in a strong solution of super phosphate. When we extract the soluble phosphoric acid from superphosphates, it is of the greatest importance to use a sufficient quantity of water for the first extraction. Otherwise, the quantity of soluble phosphoric acid may be found too high by 1 to 2 per cent.

Manufacture of Ammoniacal Manures.—Gahn and Burte (German Patent, No. 47601), pass ammoniacal vapours into troughs containing acid phosphates. The ammonia is obtained from gas-liquor by means of lime.

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.

Detection of Sulphites in Presence of Thiosulphates and Sulphides.—Will any reader of the Chemical News inform writer where details of this test—mentioned in Fresenius's "Qualitative," 8th English Edition, pp. 174-175, and there attributed to Bödeker—are to be found. Reference to original publication containing details of reaction of sulphides with sodic nitroprusside would assist writer.—Theion.

MEETINGS FOR THE WEEK.

Monday, Mar. 2nd.—Medical, 8.30. (Annual Meeting).
—— Royal Institution, 5. General Monthly Meeting.
—— Royal Medical and Chirurgical, 8.30. (Anniversary).
—— Society of Arts, 8. "The Electric Transmission of Power," by Gisbert Kapp.
—— Society of Chemical Industry, 8. "The Chemical Changes between Nitric Acid and Metals," by V. H. Veley. "Further Researches on the Butter of the Cow," by J. A. Wanklyn.
Tuesday, 3rd.—Institute of Civil Engineers, 8.
—— Pathological, 8.30
—— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S.
Wednesday, 4th.—Society of Arts, 8. "Modern Flour Milling," by J. Harrison Carter.
Thursday, 5th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Chemical, 8.
—— Royal Institution, 3. "Modern Chemistry in Relation to Sanitation," by Professor C. Meymott Tidy.
Friday, 6th.—Royal Institution, 9. "Electromagnetic Repulsion," by Prof. J. A. Fleming.
—— Society of Arts, 4.30. "The Science of Colour," by Captain Abney.
—— Geologists' Association, 8.
—— Quekett, 8.
—— Physical, 5.
Saturday, 7th.—Royal Institution, 3. "The Forces of Cohesion," by The Right Hon. Lord Rayleigh, F.R.S.
—— Medical, 8.30. (Annual Dinner).

TO CORRESPONDENTS.

Spectroscope.—Paper washed with a weak solution of chloride of cobalt changes colour according to the dryness or humidity of the atmosphere.

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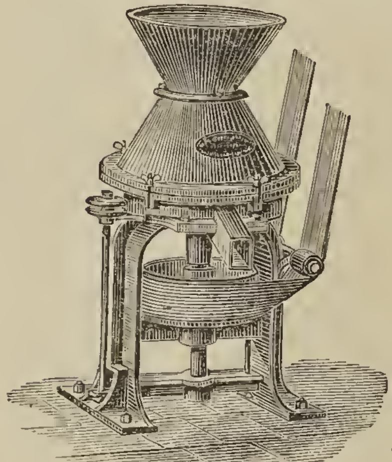

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THE CHEMICAL NEWS.
Vol. LXIII., No. 1632.

ON THE
TRANSITION OF CERTAIN PRECIPITATES FROM THE AMORPHOUS TO THE CRYSTALLINE STATE.

By GEORGE WATSON, F.C.S.

A NUMBER of precipitates are known which, when newly thrown down from a solution, are amorphous, but which, on standing in contact with the liquid in which they have been formed, pass more or less rapidly into the crystalline state.

Thus, for example, antimonious chloride, when added to water, gives at first a bulky amorphous precipitate of basic antimonious chloride. On standing, however, and especially if well stirred, this precipitate changes into a heavy crystalline powder. So also calcic carbonate, when formed from a watery solution of calcic chloride, by the addition thereto of an alkaline carbonate, is, when newly formed, amorphous and somewhat bulky, but soon changes, at temperatures below 30° C., into crystals of calc spar. If, on the contrary, the liquid containing the amorphous precipitate be heated to the boiling-point, crystals of "arragonite" are said to be produced. Several other cases of a similar nature might be instanced.

On considering such cases the questions naturally arise in the mind, why does this change take place? and what is the method of working according to which it proceeds? Hence, having examined a few of them, and having obtained what seemed to me to be satisfactory answers to the above questions, I thought my results might be of sufficient interest to place on record.

Consider first the case of basic antimonious chloride. If some antimonious chloride solution be added to water there is obtained the well-known bulky precipitate of basic antimonious chloride, which changes, on standing, into a heavy crystalline powder. If, while it is still amorphous, a number of scratches be made on the surface of the glass in contact with the precipitate, these scratches will be found to be covered with attached crystalline precipitate after the change from the amorphous to the crystalline state has taken place. If the scratches be washed with hydric chloride and again put in contact with a new quantity of amorphous precipitate, no fixation is now found to have occurred after the transition has happened. But if, on the other hand, scratches with adhering crystalline precipitate be again placed in contact with a new quantity of the amorphous form, the deposit is found to increase in amount. This latter result shows that the crystalline modification influences favourably this change from the amorphous to the crystalline state. In other words, the change, in one respect at least, is an accelerating one. This may be seen by forming a quantity of the amorphous precipitate in admixture with a pre-formed quantity of the crystalline one, and comparing the speed with which the change now proceeds with that of a parallel experiment to which no pre-formed crystalline precipitate has been added. It will be found that the former rapidly settles to the bottom of the glass, while the latter still remains suspended in the amorphous form.

These facts were recorded in a paper which I published in the CHEMICAL NEWS, vol. lxi., p. 207. At that time I thought that this fixation of precipitate on the abrasions took place directly from the amorphous precipitate lying contiguous to them; but since then I have examined the matter more minutely, and now find that it occurs from the acid liquid in which the precipitate is suspended, and that the way in which the change from the amorphous to the crystalline state takes place is as follows:—

The precipitation of basic antimonious chloride by water occurs in two stages. In the first stage, the bulk of the antimony is thrown down as amorphous, basic, antimonious chloride. A small quantity, however, remains in solution, constituting, as it were, a saturated solution of amorphous basic antimonious chloride, but a supersaturated one if regarded as a solution of the crystalline basic salt. In the second stage this small quantity of basic chloride is deposited in the crystalline state, and attaches itself to any scratches which may be made on the glass. But simultaneously with this deposition a new quantity of the amorphous precipitate has again gone into solution, the amorphous precipitate being more soluble in hydric chloride than is the crystalline form. Supersaturation is therefore maintained, and the previously deposited crystals now act on this solution and hasten the formation of the next quantity of crystal. The process of alternate re-solution and re-precipitation thus proceeds until the change is complete.

The following are the experiments on which this explanation is based:—

A solution of antimonious chloride was made by dissolving 2 ounces of crystallised antimonious chloride in 50 c.c. of water and 25 c.c. strong hydric chloride (1·160).

1. To 100 c.c. water were then added 5 c.c. of this solution, the mixture stirred well, and 20 c.c. at once filtered off. On diluting this 20 c.c. with water and gassing with hydric sulphide, a considerable precipitate, comparatively speaking, of antimonious sulphide was obtained. The basic antimony chloride precipitate was then allowed to change into the crystalline state and other 20 c.c. of the supernatant filtered off and gassed with hydric sulphide, when a mere trace only of antimonious sulphide was obtained.

2. To 200 c.c. water were added 10 c.c. antimony solution, the whole stirred up, and the liquid at once filtered into a clean, dry test-glass. The filtrate, on standing twenty-four hours, deposited a precipitate of crystalline basic antimonious chloride.

3. 100 c.c. water and 5 c.c. antimony solution were mixed, and 21 c.c. strong hydric chloride run in from a burette with continuous stirring. The precipitate slowly dissolved and gave a milky solution, which, on filtration, yielded a clear liquid. On stirring this clear liquid vigorously, a precipitate came down which increased greatly on standing. The addition of even 24 c.c. of hydric chloride to a similar liquid in which the precipitate had become crystalline failed to effect complete solution in two days' time.

That this change takes place as described is also supported by the fact that if the amorphous precipitate be rapidly separated from the liquid, and all water removed by washing with ether, it may be obtained in that form and preserved indefinitely. (See Roscoe and Schorlemmer's "Treatise on Chemistry," vol ii., Part 2, p. 317).

But it follows from what has been said that until the small quantity of antimony in the supernatant has crystallised out, the change of the already formed amorphous precipitate into the crystalline state cannot take place, a conclusion which shows us how this substance could be used as a substitute for tartar emetic in fixing coal-tar colours on cotton. For, if a piece of cotton impregnated with tannin were immersed in the emulsion, the small quantity of antimony in solution would be withdrawn and fixed as tannate on the fabric. A new quantity of antimony would then go into solution, only to be withdrawn and fixed on the cotton, and, theoretically, this process could go on until all the antimony had become redissolved, withdrawn from solution, and fixed as tannate on the cotton fibres. This substance, therefore, should form a very cheap substitute for tartar emetic and the other antimony salts used for this purpose—a conclusion supported by a statement in the *Journal of the Society of Chemical Industry* for 1885, vol. iv., p. 644.

Another antimonious precipitate which also undergoes a change from the amorphous to the crystalline state in the way already described for the basic chloride is sodic antimoniate. This precipitate, when at first formed in solutions strong enough to give an immediate precipitation, is somewhat bulky and amorphous, but on standing changes comparatively quickly into the crystalline state. In this case also the precipitation takes place in two stages, depending on the greater solubility of the amorphous form as compared with the crystalline one.

In the first stage the bulk of the precipitate is thrown down in the amorphous condition, while in the second the small remainder comes down, but in the crystalline form. If the solution be sufficiently dilute, however, the first stage is eliminated and all the precipitate slowly appears in the crystalline state. In the case of this precipitate also, when formed in strong solutions, the phenomena of attaching itself to abrasions and of acceleration in the rate of change are exhibited, both of which are indications that we are dealing with a solution having the properties of a supersaturated one. In my experiments with this substance I used solutions consisting of 10 c.c. of saturated solution of sodic chloride mixed with 100 c.c. of water, to which were added 25 c.c. of a boiling saturated solution of potassic antimoniate.

Another precipitate which changes from the amorphous to the crystalline state by the process of alternate re-solution and re-precipitation is monocalcic orthophosphate ($CaHPO_4$)—the precipitate obtained by mixing solutions of calcic chloride and disodic phosphate. Thus, if 50 c.c. water, 25 c.c. of a cold saturated solution of disodic phosphate, and 15 c.c. of a 5 per cent solution of calcic chloride be mixed, a white gelatinous precipitate of monocalcic phosphate is obtained. On scratching the glass in contact with the precipitate with a pointed glass rod, such scratches are found to be coated with crystalline precipitate after the change has taken place. Also, if the supernatant be at once filtered off it deposits a further small quantity of precipitate in the crystalline state, and if the amorphous form be produced in admixture with a pre formed quantity of the crystalline modification, the change from the one form to the other, as evidenced by the rapidity with which the precipitate settles, is found to take place much more rapidly.

Yet another instance of change from the amorphous to the crystalline state, by the process of alternate re-solution and re-precipitation, is seen in the case of calcic carbonate. This substance when at first precipitated from a cold solution of calcic chloride by means of an alkaline carbonate is amorphous, but changes on standing at ordinary temperatures into crystals of calc spar. On heating the liquid containing the amorphous precipitate it is said to be transformed into crystals of "arragonite."

The following are my experiments with this precipitate:—

To 60 c.c. of a 5 per cent solution of pure calcic chloride were added 20 c.c. of a 10 per cent solution of sodic carbonate, and the glass in contact with the precipitate abraded with a pointed glass rod. After the change into the crystalline form had taken place, the abrasions were found to be heavily laden with precipitate —a criterion that we are dealing with a supersaturated solution, and therefore that this precipitation also occurs in two stages. In the first, the bulk of the precipitate is thrown down amorphous, while in the second the small remainder crystallises out as "calc spar" or "arragonite," according as the temperature of the solution is low or high.

In this case also, by forming the amorphous modification in admixture with a pre-formed quantity of the "calc spar" form, the fact of acceleration in the rate of change is seen, as evidenced by the rapidity with which the precipitate settles as compared with a parallel precipitate unmixed with pre-formed "calc spar."

Experiments to ascertain if this greater solubility of the amorphous modification were due to dissolved carbon dioxide in the solution, showed that the change took place equally in ammoniacal and in boiled solutions. The change, in this case at any rate, is therefore due to the greater solubility of the amorphous calcic carbonate in solutions of sodic chloride. The solubility of this substance has also been observed by Sterry Hunt (Chemical News, vol. lxii., p. 319).

This change from the amorphous to the crystalline state in the case of calcic carbonate is the cause of the hardening or setting of ordinary mortar, in so far as this is due to the absorption of carbon dioxide. A quantity of calc spar crystals are thus formed which, interlacing with the sand, bind it into a mass of some tenacity, in the same way that a moist powdered salt, such as sodic chloride, when dried gives a cake of more or less coherency, due to the formation of interstitial crystals which interlace with the rest of the salt and bind it together.

It may be of interest to notice here also two other cases which have been examined by other chemists. The first is the transformation of arsenious oxide from the vitreous to the crystalline state, observed when a mass of the former variety is kept for some time exposed to the air. This change has been investigated by C. Winkler (*Journ. Prakt. Chem.* [2] vol. xxxi., p. 247, abst. in *Chem. Soc. Journ.*, 1885, p. 871), who found that the crystalline variety formed from the vitreous form by keeping always contained a small quantity of water, and who, therefore, surmised that the change was caused by this water and was owing to the greater solubility of the vitreous form—a conclusion which he verified by experiment. The other instance is the change of calcic sulphate from the amorphous anhydrous to the crystalline hydrated condition, a change which constitutes the phenomenon known as the "setting" of plaster-of-Paris. This change has been examined by H. Le Chatelier (*Comptes Rendus*, vol. xcvi., p. 715—718, abst. *Chem. Soc. Jour.*, 1883, vol. xliv, p. 712), according to whom the setting of plaster-of-Paris is due to the formation of an agglomerate of interlacing crystals of hydrated calcic sulphate, produced from the amorphous sulphate by a process of solution and crystallisation and conditioned by the greater solubility of the amorphous form as compared with the crystalline one. But from what has already been said it is evident that this change also must proceed at an accelerating rate, so far as the withdrawal of the hydrated calcic sulphate from solution is concerned, although this does not seem to have been noticed by Le Chatelier. This may be seen in the following way. Take 10 grms. of plaster-of-Paris, mix it with 10 c.c. of water, and allow some of the resulting liquid to run out of a pipette on a slab of "set" plaster. Each drop as it falls on the slab at once congeals into the solid state. Or, take a drop on the end of a glass rod and touch the slab with it, when it will congeal and adhere to the slab. On touching this congealed drop with a fresh one, the latter also congeals and adheres to the former, and by continuing this process it is possible to build up a little cone of congealed plaster, while the rest of the mixture still remains liquid.

In conclusion there is one other point to which I would refer. Inasmuch as calcic carbonate is dimorphous, one would conjecture that it should be possible to cause the gelatinous amorphous form of this substance to turn into the form of arragonite crystals at ordinary temperatures (below 30° C.), by introducing a quantity of these crystals into the liquid. In order to see if this were so, three samples of calcic carbonate were prepared; (*a*) by precipitating 2 litres of lime water at the boiling-point by a stream of carbon dioxide; (*b*) same as above, but precipitated in the cold (8° C.); (*c*) by precipitating 1 litre at the boiling-point, cooling, pouring off the liquid, and adding the arragonite crystals thus obtained to another litre of lime water, which was then precipitated in the cold by carbon dioxide. The resulting precipitates were then washed, dried, and their specific gravities taken, with the following results :—

A	2·642	water at 8° C.
B	2·676	,,
C	2·646	,,

As these figures are practically identical, and are, in fact, the same as the specific gravity of calc spar, it is impossible to draw any definite conclusion from them. I am therefore now engaged in further experiments to examine this point more minutely, and likewise to determine to what extent, and at what rate, "arragonite" crystals revert to the form of "calc spar" on standing in contact with water.

ESTIMATION OF GLYCERIN BY ALKALINE PERMANGANATE.

By WILLIAM JOHNSTONE, D.Sc.

On the 16th inst. I had the honour to read a paper before the Society of Chemical Industry upon the above subject.

The experiments were undertaken owing to Professor Wanklyn having expressed to me a doubt as to whether butyric acid could not be converted into oxalic acid by boiling with alkaline permanganate. Known quantities of butyric acid were therefore taken and boiled with alkaline permanganate, and to my great astonishment, and contrary to the statements of Benedict and Zsigmondy, I obtained 94 per cent of the butyric acid originally taken, calculating it from the oxalic acid found.

The following equation apparently represents the reaction :—$C_4H_6O_2+O_6=2C_2H_2O_4+H_4$. The acid used has been boiled with dilute sulphuric acid and bichromate of potash for six hours without any alteration ; consequently the sample was free from any iso acid, which might have interfered with the accuracy of the results obtained.

Mr. Allen's improved method of Benedict and Zsigmondy's process (*Jour. Chem. Soc. Ind.*, vol. v., p. 70), is therefore utterly inapplicable for the estimation of glycerin in oils and fats containing butyric acid.

A GENERAL METHOD FOR THE ANALYSIS OF THE BRANDIES AND ALCOHOLS OF COMMERCE.

By M. ED. MOHLER.

In the spirits of commerce we have already methods for determining extract, alcohol, acids, and furfurol. The method now described renders it possible in half-litre samples to determine also the ethers, the aldehyds, the higher alcohols, and the nitrogenous products. These determinations have to be made on the distilled liquid brought to the standard of 50°, except as regards the nitrogenous products, which are determined in the sample itself.

Determination of Ethers.—The author boils 100 c.c. of the distilled alcohol for an hour along with 20 c.c. of decinormal potassa, the flask being fitted with an ascending condenser. The quantity of potassa absorbed is calculated by taking account of the acidity of the alcohol, and the results are calculated as ethyl acetate.

Aldehyds.—The intensity of the violet colour developed by the action of rosaniline bisulphite upon alcohols containing aldehyds is not proportional to the quantity in solution. To apply this reagent to the determination of the aldehyds it must be caused to act upon a solution of known strength, and to bring the alcohol to be analysed by dilution to contain a quantity of aldehyd equal to that of the standard.

To 10 c.c. of a solution of ethylic aldehyd at $\frac{1}{10000}$ and to 10 c.c. of the alcohol under analysis (both at 50° of alcoholometric strength) we add at the same time 4 c.c. of rosaniline bisulphite. The tints are allowed to develop for twenty minutes, and their intensity is then compared by means of the Dubosc colorimeter. The operation is re-commenced by diluting the alcohol in question until the colours have the same intensity. If *m* represents this dilution, the weight of ethylic aldehyd per litre will be $M \times 0·050$.

Higher Alcohols.—Sulphuric acid in the conditions in which it is employed acts only on the aldehyds and the higher alcohols. The aldehyds are kept back by means of aldehyd phosphate.

To 100 c.c. of the distilled sample we add 1 c.c. of aniline and 1 c.c. of phosphoric acid at 45° B. The liquid is boiled for an hour with an ascending condenser, and is then distilled to dryness in a salt-bath.

The distillate is treated with sulphuric acid at 66° according to the known method, and the tint observed is examined comparatively in the colorimeter with that given by an alcoholic solution containing 0·250 isobutylic alcohol per litre.

We operate, as in the case of the alcohols, by diluting the alcohol until the tints are equalised.

Nitrogenous Products.—We have determined the weight of ammonia corresponding on the one hand to the amides and to saline ammonia, and on the other to the pyridic bases and the alkaloids, by submitting the alcohol in question first to the action of sodium carbonate and then to that of alkaline permanganate, titrating the small quantities of ammonia produced in each operation with Nessler's reagent.

To 100 c.c. of the sample not distilled we add 2 c.c. of phosphoric acid at 45° B., and expel all the alcohol by boiling. The phosphoric solution of the bases is diluted with about 1 litre distilled water ; 10 grms. of pure sodium carbonate are added, and the mixture is distilled until no more ammonia passes over. The permanganate and the potassa are then introduced, and the distillation is continued, the ammoniacal water being collected in another receiver. The ammonia obtained from each operation is determined with Nessler's reagent comparatively with a solution containing 0·00001 grm. ammonium hydrochlorate per c.c.

The method just described permits us to analyse in samples of 500 c c. alcohol containing not more than 1-200,000th of acids, 1,200,000th of ethers, 1-1,000,000th of ethers, 1-1,000,000th of furfurol, 1-20,000th of higher alcohols, and 1-100,000th on operating with alcohol at 90°, 1-1,000,000th of ammonia corresponding to saline ammonia and amides, and 1-10,000,000th of ammonia corresponding to the alkaloids and to pyridic traces.—*Comptes Rendus.*

Observations by M. Edm. Becquerel on M. Lippmann's Communication concerning the Photographic Reproduction of Colours.—The author points out the distinction existing between the purely physical process which M. Lippmann has just expounded for the photographic reproduction of the colours of light and the photo-chemical process which the speaker discovered in 1848 for obtaining the coloured images of the luminous spectrum as well as the images of objects with their own colours, that is by means of one and the same chemical substance, argentous chloride. This matter possesses the curious attribute, when properly prepared, of being not merely sensitive to the action of the coloured rays from the red to the violet, but also of receiving an impression which seems sensibly proportional to the intensity of the corresponding luminous impressions upon the retina.—*Comptes Rendus*, Vol. cxii., No. 5.

ELECTRICITY *IN TRANSITU*: FROM PLENUM TO VACUUM.[*]

By WILLIAM CROOKES, F.R.S.,
President of the Institution of Electrical Engineers.

(Concluded from p. 100).

What Occasions Phosphorescencc ?

I SHOULD like to interest you in a question that has exercised my mind for some time past. What is it that occasions the phosphorescence of yttria and other bodies in vacuo under molecular bombardment?

So far I have found this phosphorescence to be an attribute of non-conductors only. We know that in the act of phosphorescence the molecules of yttria are in a state of intense vibration. Each molecule may be viewed as the radiating centre of the entire bundle of rays, which, when decomposed by the prism, displays a discontinuous spectrum. We may also suppose that the residual atoms of gas charged with negative electricity give off their electricity on coming in collision with a phosphorescent body, and on their return take up a fresh charge.

The Electrolysis Hypothesis.

There is a certain amount of evidence in favour of an electrolytic hypothesis of the passage of electricity through rarefied gases. This has been ably advocated by Professor Schuster in the Bakerian Lecture before the Royal Society, March 20th, 1890.[†]

A molecule of hydrogen gas, for instance, may be made up of one group of atoms of hydrogen having an equivalent of negative electricity inherent in it, and one group of atoms having an equivalent of positive electricity bound up with it. These atoms are also charged with *additional* equivalents of positive or negative electricity, which they carry about as a ship carries its cargo. We are not concerned with the inherent electricity—of which we are ignorant—but with the extra or "cargo" charge. Let us imagine a molecule of hydrogen near the face of the negative pole in a vacuum tube. I turn on the current, and the atoms of the hydrogen molecule are dragged apart. The positive atom is attracted to the negative pole, where the violence of impact, or the discharge of electricity, renders it apparent with evolution of light. The internal luminous layer, which is closely adjacent to the negative electrode, is due, therefore, to the positive atoms rushing to the negative pole, and not, like the glow round the edge of the dark space, to the negative atoms projected from it. The negative atom, on the other hand, is driven violently from the negative pole, in virtue of the mutual repulsion existing between any two bodies similarly electrified, with a velocity varying with the intensity of the electrification and the degree of the vacuum; the more perfect the vacuum the greater the velocity, the atoms flying outwards in straight lines until they meet with an obstacle. Such an obstacle may be a procession of positively charged atoms from the positive pole; in this case the two kinds of atoms mutually discharge each other's cargos with a display of light. This phenomenon occurs at the margin of the dark space when the vacuum is only moderate. Or the obstacle may be produced by the vacuum being so high that the atoms of gas present are too few to form a continuous procession. (*Why* a high vacuum should be non-conductive does not clearly appear, but the fact itself is beyond doubt; it is probably connected with the inability of electrified atoms to leave the poles.) Or again, the obstacle may be a phosphorescent body like yttria. In this case the negatively charged atoms deliver up their charge of electricity to the yttria, which is so constituted—perhaps after the manner of a Hertz resonator—that its atoms charge and discharge, vibrating about 550 billion times in a second, and producing waves in the ether of the length, approximately, of 5·74 ten-millionths of a millimetre, and occasioning in the eye the effect of citron light.

We are not under the necessity of supposing that this number of hydrogen atoms are driven against the yttria in the second, although even at a high vacuum there are quite enough atoms left in the bulb to keep up such a supply. All that is needed is that a succession of shocks, not necessarily rhythmical, may strike the yttria at frequencies which will set up such a number of vibrations, just as a series of slow impacts on a gong causes it to emit sound waves of much greater frequency.

In a low vacuum only very few atoms can run the gauntlet among the crowd of inrushing atoms, and those few which succeed in reaching the yttria arrive with much reduced velocity, and so faint is the phosphorescence they set up that it is completely obscured[*] by the brighter phosphorescence of the residual gas. As the vacuum becomes higher, more and more atoms find their way across, and their speed being at the same time accelerated, the phosphorescence becomes intensified.

At a good vacuum most of the atoms hit the yttria, their velocity is increased, and the rhythmical excitation reaches its maximum.

The Dark Space in Mercury Vapour.

In applying the electrolytic hypothesis, I have used for illustration's sake the gaseous residue of hydrogen, which is known as a diatomic gas. I have found, however, the phenomena of the dark space, &c., to occur in the vapour of mercury, which is a monatomic gas. This important result induced me to patiently investigate this subject, and the result of one experiment is before you (Fig. 29). The tube is furnished with aluminium terminals, and is so arranged that the induction spark can be kept passing during exhaustion to drive off occluded gases. When at the highest attainable vacuum, the tube is filled with pure mercury by simply raising a reservoir. On applying heat the entire contents of the tube are boiled away and pass down the fall tubes of the pump, exhaustion going on at the same time. When the whole of the mercury has thus been boiled away *in vacuo*, except a little condensed at the upper part of the tube, the results on passing the spark are as followed:—When the tube is cold the induction current refuses to pass; on gently heating with a gas-burner the current passes and the dark space is distinctly visible. Continuing the heat so as to volatilise the drops of mercury condensed on the sides, the whole tube becomes filled with a green phosphorescent light, the dark space gets smaller and smaller, and ultimately the negative pole becomes covered with a luminous glow. On allowing the tube to cool the same phenomena ensue in inverse order. The luminous halo expands, showing the dark space between it and the pole, and this dark space gradually grows larger as the tube becomes cooler. The mercury again condenses on the side of the tube, the green phosphorescence grows paler and paler, until at last the induction spark from the large coil refuses to pass.

At first sight this result appears fatal to the electrolytic hypothesis, for if the molecule of mercury contains only one atom how can we talk of its separation into positive and negative atoms by the electric stress? It must be remembered, however, that we are as yet ignorant of the absolute mass of the atom of any element. All that can be said is that a molecule of free hydrogen becomes halved in combining chemically with certain other elements, whilst a molecule of free mercury does not suffer division on yielding any known compound of mercury: the physical atoms in the one behave as two separate groups, and those in the other as one undivided group. It has been agreed by chemists, for simplicity's sake and for facili-

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[*] Inaugural Address delivered January 15th, 1891.

[†] *Roy. Soc. Proc.*, xlvii., 526.

[*] This faint phosphorescence at a low vacuum can be rendered visible by the electrical phosphoroscope described in my lecture at the Royal Institution in 1887.

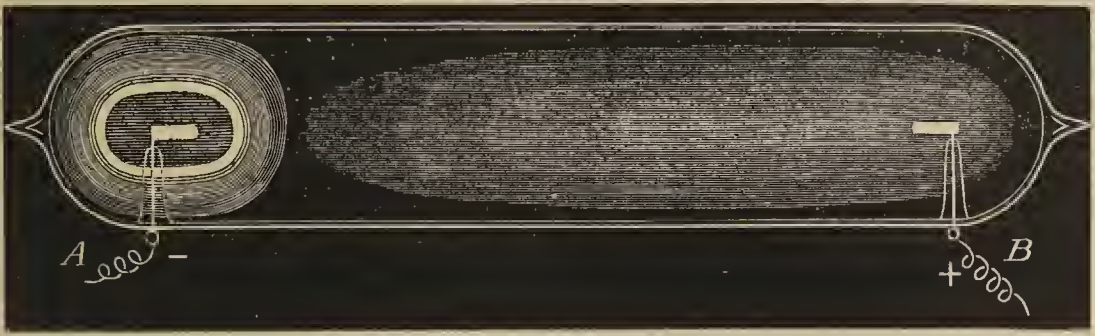
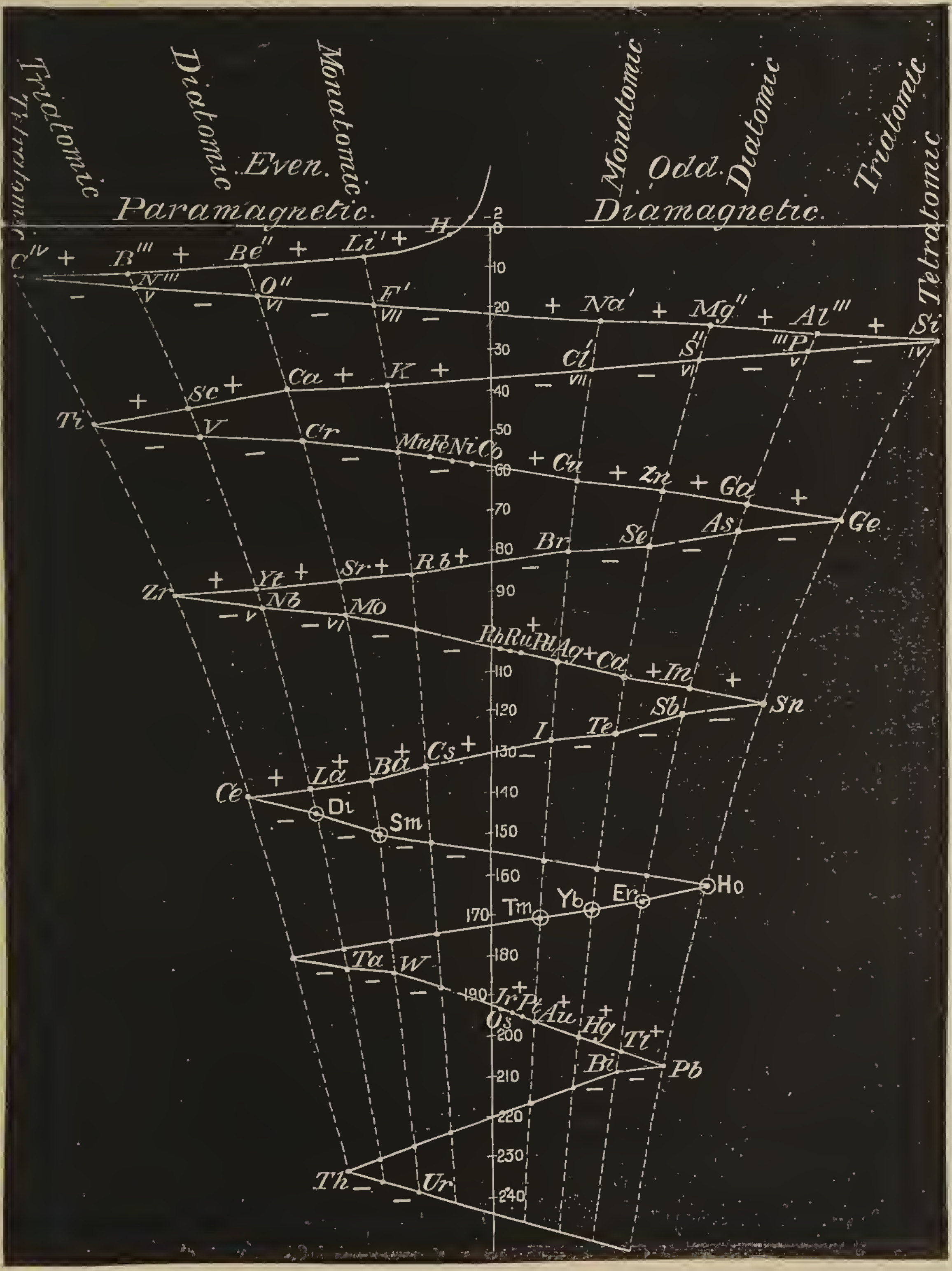

A
−
B
+

Fig. 29.


Tetratomic
Triatomic
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Even.
Monatomic
Paramagnetic.
Monatomic
Odd.
Diatomic
Triatomic
Diamagnetic.
Tetratomic
H
Li'
Be''
B'''
C^IV
N'''
O''
F'
Na'
Mg''
Al'''
Si
P
S
Cl
K
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Cr
Mn Fe Ni Co
Cu
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W
Os
Ir
Pt
Au
Hg
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30
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50
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70
80
90
110
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130
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160
170
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190
200
210
220
230
240

Fig. 30.

tating chemical calculations, to reduce the units to the lowest term, consistent with the avoidance of fractions; we therefore say that the atoms in a molecule of free hydrogen act in chemistry as two separate groups, each of a minimum relative weight of 1, whilst those in a molecule of free mercury act as one undivided group of the relative weight 200. But to what number of atoms the 1 and 200 correspond respectively no chemist knows.

To show how intimately chemistry and electricity interlock, I may here remark that one of the latest theories in chemistry renders such a division of the molecule into groups of electro-positive and electro-negative atoms necessary for a consistent explanation of the genesis of the elements. This is so important that I may be excused for digressing a little into this development of theoretical chemistry.

Genesis of the Elements.

It is now generally acknowledged that there are several ranks in the elemental hierarchy, and that besides the well-defined groups of chemical elements, there are underlying sub-groups. To these sub-groups has been given the name of meta-elements. The original genesis of atoms assumes the action of two forms of energy working in time and space—one operating uniformly in accordance with a continuous fall of temperature, and the other having periodic cycles of ebb and swell, and intimately connected with the energy of electricity (Fig. 30). The centre of this creative force in its journey through space scattered seeds or sub-atoms that ultimately coalesced into the groupings known as chemical elements. At this genetic stage the new born particles vibrating in all directions and with all velocities, the faster moving ones would still overtake the laggards, the slower would obstruct the quicker, and we should have groups formed in different parts of space. The constituents of each group whose form of energy governing atomic weight was not in accord with the mean rate of the bulk of the components of that group, would work to the outside and be thrown off to find other groups with which they were more in harmony. In time a condition of stability would be established, and we should have our present series of chemical elements each with a definite atomic weight—definite on account of its being the average weight of an enormous number of sub-atoms or meta-elements, each very near to the mean. The atomic weight of mercury, for instance, is called 200, but the atom of mercury, as we know it, is assumed to be made up of an enormous number of sub-atoms, each of which may vary slightly round the mean number 200 as a centre.

We are sometimes asked why, if the elements have been evolved, we never see one of them transformed, or in process of transformation, into another? The question is as futile as the cavil that in the organic world we never see a horse metamorphosed into a cow. Before copper, *e.g.*, can be transmuted into gold it would have to be carried back to a simpler and more primitive state of matter, and then, so to speak, shunted on to the track which leads to gold.

This atomic scheme postulates a to and fro motion of a form of energy governing the electrical state of the atom. It is found that those elements generated as they approach the central position are electro-positive, and those on the retreat from this position are electro-negative. Moreover the degree of positiveness or negativeness depends on the distance of the element from the central line; hence calling the atom in the mean position electrically neutral, those sub-atoms which are on one side of the mean will be charged with positive electricity, and those on the other side of the mean position will be charged with negative electricity, the whole atom being neutral.

This is not a mere hypothesis, but may take the rank of a theory. It has been experimentally verified as far as possible with so baffling an enigma. Long-continued research in the laboratory has shown that in matter which has responded to every test of an element, there are minute shades of difference which have admitted of selection and resolution into meta-elements, having exactly the properties required by theory. The earth yttria, which has been of such value in these electrical researches as a test of negatively excited atoms, is of no less interest in chemistry, having been the first body in which the existence of this sub-group of meta-elements was demonstrated.

Conclusion.

I frankly admit I have by no means exhausted the subject which daily and nightly fills my thoughts. I have ardently sought for facts on which to base my theory. I have struggled with problems which must be conquered before we can arrive at exact conclusions—conclusions which, so far as inorganic Nature is concerned, can only be reached by the harmonious interfusion—not confusion—of our present twin sciences, electricity and chemistry. Of this interfusion I have just endeavoured to give you a foretaste. In elaborating the higher physics, the study of electrical phenomena must take a large, perhaps the largest, share.

We have invaded regions once unknown, but a formidable amount of hard work remains to be completed. As we proceed we may look to electricity not only to aid, as it already does, our sense of hearing, but to sharpen and develop other powers of perception.

Science has emerged from its childish days. It has shed many delusions and impostures. It has discarded magic, alchemy, and astrology. And certain pseudo-applications of electricity, with which the present Institution is little concerned, in their turn will pass into oblivion.

There is no occasion to be disheartened at the apparent slow pace of elemental discovery. The desponding declare that if Roger Bacon could re-visit "the glimpses of the moon" he would shake his head to think we have got no further, that we are still in a haze as to the evolution of atoms. As for myself I hold the firm conviction that unflagging research will be rewarded by an insight into natural mysteries such as now can scarcely be conceived. Difficulties, said a keen old statesman, are things to be overcome, and to my thinking Science should disdain the notion of Finality. There is no stopping half way, and we are resistlessly driven to ceaseless inquiry by the spirit "that impels all thinking things, all objects of all thought, and rolls through all things."

DETERMINATION OF WATER IN SUPERPHOSPHATES.*

By JULIUS STOKLASA.

(Continued from p. 101).

If the phosphoric anhydride corresponding to the free phosphoric acid is deducted from the 35·8 per cent P_2O_5 found, we have 29·2 per cent P_2O_5 corresponding to the 51·8 per cent of the undecomposed monocalcium phosphate.

In this case the determination of the free phosphoric acid and the monocalcium phosphate by titration with uranium acetate are not accurate, and the results are only approximations, as, by boiling the acid liquid (the solution of uranium acetate used having been as usual acidulated), a small part of the pyrophosphate is converted into orthophosphate.

According to theory the phosphoric acid is present in the solution in the following form :—

	Per cent P_2O_5.	Found. Per cent P_2O_5.
$CaH_4(PO_4)_2 \cdot H_2O$	28·3	29·20
H_3PO_4	7·0	6·60
$3CaH_2P_2O_7 \cdot 2H_2O$	7·03	6·94
Sum	42·33	42·74

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* From the *Zeitschrift Anal. Chemie.*

By the decomposition of half the original monocalcium phosphate during the drying there have been formed :—

	Per cent.	
$Ca_2P_2O_7$	12·60	Insoluble part.
$Ca(PO_3)_2$	9·82	
$CaH_2P_2O_7$	10·71	Soluble part.
H_3PO_4	9·72	
	42·85	
H_2O	7·15	
	50·00	

The results above indicated give an interesting explanation of the processes during the desiccation of monocalcium phosphate in a quite new direction. Birnbaum certainly recognised the normal calcium pyrophosphate and free phosphoric acid, but he nowhere mentions having found metaphosphate and monocalcium pyrophosphate. He considers that the decomposition takes place as follows :—

$$2[CaH_4(PO_4)_2+H_2O]=Ca_2P_2O_7+2H_3PO_4+3H_2O.$$

The decomposition cannot take place in this manner, since by the continued action of the temperature monocalcium pyrophosphate is formed from pyrophosphate and free phosphoric acid.

S. Drewsen, who examined the transformations of superphosphates at higher temperatures, does not mention the formation of normal calcium pyrophosphate and metaphosphate. He merely observed that a considerable quantity of monocalcium pyrophosphate is formed even at 100°. But this phenomenon, as I will show below, is occasioned by other factors, and not merely by temperature. He suggests, therefore, that the aqueous solution of superphosphates on analysis should be boiled with nitric acid, as we cannot know if the superphosphate in question has been artificially dried at a high temperature. From the tabular conspectus in which he summarises the results of his experiments, it is seen that the quantity of the phosphoric acid soluble in water remained unaltered even in drying the superphosphates at 300°, for if the aqueous solution of such a dried superphosphate was boiled in nitric acid, the same quantity of phosphoric was found as in the original sample. Drewsen does not, indeed, mention the composition of the superphosphates which he examined, but it is evident from his memoir that he means the soluble phosphoric acid which appears in superphosphates as monocalcium phosphate. He is thus in a serious error, for his results cannot be applied to superphosphates, which contain the soluble phosphoric acid chiefly in the state of monocalcium phosphate.

The author repeated the experiments with superphosphates which contained 18 per cent of soluble phosphoric acid (17 per cent as monocalcium phosphate and 1 per cent as free phosphoric acid), and on drying for four hours at 120°, he observed great losses of soluble phosphoric acid. Slightly different results are reached if free phosphoric acid is found in the superphosphates in addition to monocalcium phosphate. Drewsen's results may be explained on the supposition that he operated upon superphosphates containing at least 80 per cent soluble phosphoric acid in the state of free acid. At high temperatures the free phosphoric acid, or that liberated by decomposition, reacts upon the normal calcium pyrophosphate so as to form monocalcium pyrophosphate :—

$$Ca_2P_2O_7+2H_3PO_4=2CaH_2P_2O_7+H_2O.$$

The author has proved this reaction. Chemically pure calcium pyrophosphate ($Ca_2P_2O_7+4H_2O$) was prepared from calcium chloride and sodium pyrophosphate.

The analysis showed :—

		(Calculated).
P_2O_5	42·85 per cent.	43·56 per cent.
CaO	34·92 ,,	34·35 ,,
H_2O	21·26 ,,	22·09 ,,
	99·03 ,,	100·00 ,,

A mixture of 2 grms. pyrophosphate and 1·202 grms. phosphoric acid was dried for ten hours in a platinum capsule at 200°. The monocalcium pyrophosphate formed was placed in a litre flask which was filled with water up to the mark. After shaking for an hour, the solution became slightly turbid, and contained free phosphoric acid only in traces. There was found in the solution monocalcium pyrophosphate (without heating with nitric acid) and 4 per cent of phosphoric acid; after the solution had been heated with nitric acid, there were found 56·08 per cent of phosphoric acid by the molybdenum method. In our case there was first formed monocalcium phosphate, which afterwards loses water and passes into monocalcium pyrophosphate.

If we dry monocalcium phosphate at 150° for longer than an hour, we do not find the quantity of free phosphoric acid which corresponds to the monocalcium phosphate taken. This phenomenon led to the thought that the decomposition is different. On examining the aqueous solution, there was found a large quantity of monocalcium pyrophosphate. The author proved by a number of experiments that not merely the temperature reached, but the time during which the desiccation is prolonged at 150°, a higher has great influence on the formation of monocalcium pyrophosphate.

(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 January 31st, 1891.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford ;
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

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

London, February 7th, 1891.

Sir,—We submit herewith the results of our analyses of the 142 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

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

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

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

Of the 142 samples examined, 131 were found to be clear, bright, and well filtered, 1 being recorded as "very slightly turbid," and 10 as "slightly turbid."

As a consequence of the impracticability, during the prolongation of the frost, of obtaining samples of water from some of the standpipes, the record of analytical results included in this Report is more defective than in any that we have hitherto made. Samples of water were occasionally still met with manifesting the evanescent smoky taste spoken of and considered in our previous Report for December; but the analytical results obtained during the first three weeks of the month of January, and ecorded in our present Report, continued to be, except for two instances occurring of slight turbidity, entirely satisfactory. With the breaking up of the long frost, however, a distinct deterioration became noticeable in the character of the water supplied by several of the Thames companies; but only in a single sample, taken on January 30th, was the organic matter present—and that inferred to be of a non-animal origin—at all excessive.

Owing to the almost complete want of samples of the Southwark and Vauxhall Company's water during the early part of the month, the mean results of the examination of this Company's supply recorded in the Tables are, in fact, rather means for the least satisfactory week of the month than for the entire month; whereby they are exposed, in some particulars, to an unduly unfavourable comparison with the mean results recorded in the case of the other Thames companies' supplies.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY'S JUBILEE—1891.

February 24th.

(Continued from p. 105).

Edward Frankland, D.C.L., LL.D., F.R.S., President, 1871—1873.

1. *Eudiometer and Calibration Table.*—In this eudiometer ethyl was first analysed.—*Journ. Chem. Soc.*, 1850, p. 263.

(Exhibited by the Science and Art Department, South Kensington).

2. *Isolation of the Organic Radicles, and Conception of their Hydrides as a Class.*—Ethyl butane; ethylic hydride ethane.—*Journ. Chem. Soc.*, 1850, p. 263.

3. *Digester* used in the production of organo-metallic compounds, and for chemical reactions under heat and pressure.—*Journ. Chem. Soc.*, 1850, p. 297.

4. *Organo-metallic Compounds.*—Zinc ethyl, $ZnEt_2$; stannic ethodimethide, $SnEt_2Me_2$.

5. *The First Regenerative Gas Burner.*—An intermediate glass (broken) caused the air to pass close to the innermost glass before it reached the flame.—"Ure's Dictionary," vol. ii., p. 562, 1854.

6. *Artificial Human Milk.*—Prepared by the partial removal of casein from, and addition of, milk-sugar to cow's milk.—*Manchester Guardian*, Dec., 1854.

7. *Substitution of* $'N_2''$ *for* C^{IV} *in Organic Compounds.*—Cupric dinitroethylate—

$$2\,\begin{matrix}'N_2''EtO\\ 'N_2''EtO\end{matrix}\,(CuO_2),\ OH_2.$$

—*Phil. Trans.*, 1856, p. 59.

8. *Influence of Atmospheric Pressure on the Rate and Light of Combustion.*—The six candles burnt for one hour on the summit of Mont Blanc.—*Journ. Chem. Soc.*, 1861, p. 168.

9. *Organo boron Compounds.*—Boric ethide, BEt_3.—*Journ. Chem. Soc.*, 1862, p. 363.

10. *Source of Muscular Power.*—Thompson's apparatus used in the determination of the potential energy in various articles of food.—*Phil. Mag.*, 1866, Series 4, vol. xxii., p. 182.

(Exhibited by the Science and Art Department, South Kensington).

11. *Simple Apparatus for Gas Analysis.*—*Journ. Chem. Soc.*, 1868, p. 109.

12. *Apparatus Used for the Combustion of Hydrogen and Carbonic Oxide under Great Pressure.*—*Proc. Roy. Soc.*, 1868, p. 419.

13. *Thermometric Observations in the Alps.*—Black box in which water was boiled by the unconcentrated sun's rays at Davos, Dec. 22nd, 1873. The plain thermometer in the box rose to 221° F.—*Proc. Roy. Soc.*, 1874, p. 317.

14. *Self-registering Maximum Solar Thermometer.*—This is essentially a differential air thermometer, one bulb of which is blackened and exposed in vacuo to the solar rays upon a white ground, the other bulb is freely exposed to the air beneath the shade of a white arch. The difference in temperature is read off upon an arbitrary scale attached to the capillary limb of the inverted syphon, the maximum height attained by the mercury in this limb being registered in the usual manner.—*Proc. Roy. Soc.*, 1882, p. 331.

Dr. Frankland and Dr. Kolbe.

15. *Transformation of Cyanogen* (CN) *into Oxatyl* (COHo).—Caproic acid from AyCy.—"Mem. Chem. Soc.," iii., 1847, p. 386.

16. *Polymerisation of Ethylic Cyanide.*—Kyanethine $N_3(CEt)_3$.—*Journ. Chem. Soc.*, 1848, p. 69.

Dr. Frankland and Mr. Duppa.

17. *Organo-mercury Compounds.*—Mercuric amylide, $HgAy_2$.—*Journ. Chem. Soc.*, 1863, p. 420.

18. *Transformation of the Acetic into the Acrylic Series of Acids.*—

$$\text{Ethylcrotonic acid}\left\{\begin{matrix}CEt''Et\\ COHo\end{matrix}\right.$$

$$\text{Cupric ethylcrotonate}\left\{\begin{matrix}CEt''Et\\ \begin{matrix}CO\\ CO\end{matrix}\,(CuO_2)\\ CEt''Et\end{matrix}\right.$$

—*Journ. Chem. Soc.*, 1865, p. 133.

19. *Synthesis of Esters.*—

$$\text{Ethylic diethacetoacetate}\left\{\begin{matrix}COMe\\ CEt_2\\ COEto\end{matrix}\right.$$

$$\text{Ethylic diethacetate}\left\{\begin{matrix}CE_2H\\ COEto\end{matrix}\right.$$

—*Journ. Chem. Soc.*, 1865, p. 395.

20. *Synthesis of Ketones.*—

$$\text{Diethylated acetone}\left\{\begin{matrix}CE_2H\\ COMe\end{matrix}\right.$$

—*Journ. Chem. Soc.*, 1865, p. 401.

21. *Synthesis of Acids of the Acetic Series.*—

$$\text{Ethacetic (butyric) acid}\left\{\begin{matrix}CEtH_2\\ COHo\end{matrix}\right.$$

obtained by the successive action of sodium and ethylic iodide on ethylic acetate.—*Journ. Chem. Soc.*, 1865, p. 395.

22. *Synthesis of Acids of the Lactic Series.*—

$$\text{Ethylic diethoxalate}\left\{\begin{matrix}CEt_2Ho\\ COEto\end{matrix}\right.$$

$$\text{Diamyloxalic acid}\left\{\begin{matrix}CAy_2HO\\ COHo\end{matrix}\right.$$

—*Phil. Trans.*, 1866, p. 37.

Dr. Frankland and Dr. Armstrong.

23. *Eudiometer for the Determination of Nitrogen in Nitrates and Nitrites.*—*Journ. Chem. Soc.*, 1867, p. 102.

24. *Analysis of Potable Water.*—Tube charged for combustion of water-residue.—*Journ. Chem. Soc.*, 1868, p. 77. (Exhibited by Dr. Frankland).

Sir Frederick Abel, K.C.B., D.C.L., D.Sc., F.R.S., President, 1875—1877.

1. Specimen of gun-cotton prepared according to presciption of Schönbein, by F. A. Abel, Aug., 1846, in the Royal College of Chemistry.

2. Specimens illustrating researches on the stability of gun-cotton, 1863—1865.

3. Sample of gun-cotton manufactured by Hall and Son, 1846, buried after explosion at the works, until 1864.

4. Preparations of nitro-glycerin and of gun-cotton (glyoxiline), 1867.

5. Specimens of granulated gun-cotton, 1876.

6. Specimens of compressed gun-cotton, Abel's system.

7. Gun-cotton slab fired through from a Martini-Henry rifle, without being exploded.

8. Gun-cotton slabs perforated by the electric discharge without ignition.

9. Explosion vessel used in researches on gun-cotton, 1865—1868.

10. First explosion vessel used in Abel and Noble's researches on fired gunpowder, &c., 1871—1880.

Note.—Largest powder-charge exploded in the vessel, 2¼lb.; pressure developed, 43 tons per sq. in.; largest gun-cotton charge exploded, 14 oz. In larger vessels of the same model, 22 lbs. of powder have been exploded, and gun-cotton has been detonated with developments of nearly 70 tons pressure per sq. in.

11. Vacuum bomb used in researches on the combustion of gunpowder and gun-cotton in rarefied atmospheres, 1867.

12. Specimens of "cordite," the new smokeless powder.

13. Photographs showing the 6-in. quick-firing gun, fired with black powder and with cordite (smokeless powder).

(Exhibited by Sir F. A. Abel).

Sir Henry Roscoe, M.P., F.R.S.,
President, 1880—1882.

A complete series of specimens of vanadium compounds:—

Vanadium ore. Roasted ore. Ammonium vanadate. Vanadium pentoxide. Vanadium trisulphide, disulphide, and pentasulphide. Silver hypovanadate. Sodium hypovanadate. Hypovanadic tetrachloride and disulphate. Lead hypovanadite. Aqueous solutions of vanadium dioxide, trioxide, tetroxide, pentoxide, dichloride, trichloride, tetrachloride, and vanadyl trichloride. Divanadyl monochloride. Lead metavanadate. Ammonium metavanadate. Vanadium mononitride, trioxide, pentoxide, silicon alloy, and platinum alloy. Vanadous sulphate. Vanadium oxidibromide and trichloride. Vanadyl trichloride. Vanadium tetrachloride (decomposed) and dichloride. Potassium anhydrovanadate and anhydrochromate. Vanadium metal, pentoxide, and nitride. Barium hypovanadate. Vanadic vanadate. Ammonium magnesium phosphate (from Berzelius's vanadium). Metavanadic acid. Sodium anhydrovanadate. Ammonium hypovanadate. Hypovanadic hydrate. Thallium tetravanadate, decakaivanadate, and hexakaivanadate. Silver octakaivanadate. Metavanadic acid. Ammonium vanadate and vanadite. Vanadium sesquioxide. Artificial vanadinite. Ammonium metavanadite. Sodium orthovanadite. Silver orthovanadite. Sodium orthovanadite (fused mass) and pyrovanadate. Pyrovanadate of lead. Sodium octavanadate. Barium pyrovanadate. Silver pyrovanadate. Vanadyl dichloride. Calcium divanadate. Sodium vanadate-vanadite.

(Exhibited by Sir H. E. Roscoe).

J. H. Gilbert, LL.D., F.R.S.,
President 1882—1883.

Dr. Gilbert, having been engaged with Sir J. B. Lawes in the conduct of the Rothamsted Investigations from 1843 up to the present time, sends the following illustrations of some of the lines of inquiry undertaken:—

Apparatus used in an investigation by Messrs. Lawes, Gilbert, and Pugh, in the years 1857, 1858, 1859, and 1860, to determine whether plants assimilate free or uncombined nitrogen. The plants were grown in ignited pumice or soil (with plant-ash added), either with no other supply of combined nitrogen than that contained in the seed sown, or with the addition of known and limited quantities of combined nitrogen; and they were supplied with washed air, and washed carbonic acid. The conditions of growth were, therefore, those of sterilisation; and there was, under such conditions, no gain from free nitrogen, in the growth of either Gramineæ, Leguminosæ, or other plants.

Plate of Gramineous plants grown in 1857 and 1858; and coloured photograph, of coloured scale-drawings, of Leguminous plants grown in 1860.

Three enlarged Photographs, of Leguminous Plants grown in Experiments in 1889, on the Question of the Fixation of Free Nitrogen; in some cases with sterilisation, and in others with microbe-seeding of the soil. With suitable microbe infection of the soil there was abundant formation of the so-called "Leguminous nodules" on the roots of the plants; and there was, coincidently, very considerable fixation of free nitrogen. The evidence at present at command points to the conclusion that the free nitrogen is fixed in the course of the development of the organisms within the nodules, and that the resulting nitrogenous compounds are absorbed and utilised by the higher plant.

Coloured Drawing, by Lady Lawes, of the Rothamsted Rain-gauges. For the purpose of accurate measurement of the rain, and of obtaining sufficient quantities for analysis, a large gauge of one-thousandth of an acre area has been in use since the beginning of 1853; also an ordinary funnel-gauge of 5 inches diameter; and these are represented in the drawing. An 8-inch "Board of Trade" copper-gauge has also been in use since January, 1881. The funnel portion of the large gauge is constructed of wood lined with lead; the upper edge consisting of a vertical rim of plate glass, bevelled outwards. The rain is conducted by a tube into a galvanised iron cylinder underneath, and when this is full it overflows into a second cylinder, and so on into a third and fourth, and finally into an iron tank. Each of the four cylinders holds rain corresponding to half an inch of depth, and the tank an amount equal to 2 inches. Each cylinder has a gauge-tube attached, graduated to read to 0·002 inch, but which can be read to 0·001 inch. Small quantities are transferred to a smaller cylinder with a gauge-tube graduated to 0·001, or one-thousandth of an inch.

Coloured Drawing, by Lady Lawes, of the Rothamsted Drain-guages. The three "drain-gauges," each of one-thousandth of an acre area, for the determination of the quantity and composition of the water percolating respectively through 20 inches, 40 inches, and 60 inches depth of soil (with the subsoil in its natural state of consolidation), have been in use since September, 1870,—that is, for a period of more than twenty years. The gauges were constructed by digging a deep trench along the front, gradually undermining at the depth required, and putting in plates of cast-iron (with perforated holes), to support the mass. The iron plates were then kept in place by iron girders, and the ends of the plates and of the girders supported by brickwork on three sides. Trenches were then dug bit by bit round the block of soil, which was then enclosed on each side by walls of brick laid in cement. Below the perforated iron bottom a zinc funnel, of the same area as the soil, was finally fixed, and the drainage water is collected and measured in galvanised iron cylinders, with gauge-tubes, as in the case of the rain.

Photograph of a case (now in the Science Museum, South Kensington), illustrating the influence of different manures on the botanical composition of the Mixed Herbage of Permanent Grass-land.

A set of bound volumes of Rothamsted Memoirs, &c., published 1847 to 1890, inclusive. Also the annual "Memoranda" for 1890.

Book of Drawings and Plans of the "Lawes Testimonial Laboratory," Rothamsted, Herts.

(Exhibited by Sir J. B. Lawes and Dr. Gilbert.)

W. H. Perkin, Ph.D., F.R.S.,
President, 1883—1885.

Dinaphthylguanidine.

Bromacetic acid. Dibromacetic acid. Dibromacetamide.

Glyoxylic acid (crysd. $C_2H_4O_4$). Calcium glyoxylate.

Diethyl tartrate. Diethyl diacetotartrate. Diethyl benzoyltartrate. Diacetoracemic anhydride. Diethyl diacetoracemate.

Dibromosuccinic acid.

Tartaric acid (inactive, from argentic dibromosuccinate).

α Azoamidonaphthalene.

Mauveine. — The base of the mauve dye; the first of the coal-tar colours; discovered in 1856.

Mauveine hydrochloride. Mauveine hydriodide. Mauveine sulphate. Mauveine acetate. Mauveine carbonate. Nitrate of parasafranine (prepared from Mauveine).

Salicyl aldehyde (salicylol). Salicylaldehyde and acetic anhydride.

Coumarin (from Tonka bean). Coumarin (artificially prepared). Propionic coumarin. Butyric coumarin. Valeric coumarin. Chlorocoumarin. Tetrachlorocoumarin. Bromocoumarin. α Dibromocoumarin. β Dibromocoumarin. Coumarilic acid. Potassium coumarilate. Baric sulphocoumarilate. Bromopropionic coumarin.

Anthracene. Anthraquinone. α Dibromanthraquinone. β Dibromanthraquinone. Barium disulphoanthraquinonate. Monochloranthracene. Dichloranthracene. Monobromanthracene. Dibromanthracene. Dichloranthracene and Picric acid. Sodium disulphodichloranthracenate. Strontium disulphodichloranthracenate. Barium disulphodichloranthracenate.

Anthraflavic acid. Diacetylanthraflavic acid. Barium anthraflavate.

Isoanthraflavic acid. Anthrapurpurine (sublimed). Triacetylanthrapurpurine.

Alizarine (sublimed). Acetylalizarine. Diacetylalizarine. Bromalizarine. α Nitroalizarine. α Amidoalizarine.

Phenylacrylic acid (cinnamic acid). Phenylacryliccrotonic acid. Phenylacrylicangelic acid.

Cumenylacrylic acid. Cumenylacryliccrotonic acid. Cumenylacrylicangelic acid. Sodium cumenylcrotonate.

Methylparoxyphenylacrylic acid. Methylparoxyphenylacrylate of methyl. Methylparoxyphenylcrotonic acid. α Methylorthoxyphenylacrylic acid. β Methylorthoxyphenylacrylic acid. β Methylorthoxyphenylcrotonic acid. β Methylorthoxyphenylangelic acid. Barium β Methylorthoxyphhenylacrylate.

Cinnamonylacrylic acid. Cinnamonylcrotonic acid.

Isobutenylbenzene. Isobutenylbenzene dibromide. Isopropylallylbenzene. Isobutenylvinylbenzene (Iso butenyl cinnamene).

Parallylanisoïl (anisoïl, made artificially). Orthoallylanisoïl. Butenylanisoïl. Iso butenylanisoïl.

Vinylbenzene (cinnamene), polymerised. Vinyl-p-anisoïl, polymerised. Vinyl-o-anisoïl, polymerised. Vinylisopropylbenzene, polymerised.

Orthoisobutenylphenol.

Acetomalic anhydride. Maleic anhydride (obtained by distillation of the above).

Chlorofumaric acid. Amidofumaramide. Potassium chloromaleate. Ethyl chloromaleamate.

Diphenyleneketone oxide.

Nitrophenyldiazobenzeneacetonitrile. Nitrophenyldiazotoluenenitrile.

Tritolylenetriamine. Tolyltriparalolylenetriamine.

Butyrylphenol. Propionylphenol.

(Exhibited by Dr. Perkin.)

Dr. Hugo Müller, F.R.S.,
President, 1885—1887.

Warren de la Rue and Hugo Müller.

Emodin. Chrysophan. Original Resin of *Ficus rubiginosa*, in which the Sycocerylic acetate was discovered. Sycocerylic acetate. Sycocerylic alcohol.

Hugo Müller.

Chlorinated Derivatives obtained by the Iodine process:—

Dichlorbenzene. Quatrichlorbenzene. Hexichlorbenzene. Malonic acid, from Cyanoacetic acid. Methyl-Pyrocatechin, or Guaiacol, from Wood Kreasot. Methyl-Homo-Pyrocatechin, from Wood Kreasot. Homo-Pyrocatechin. Inosite, from Cochineal. Guanine Hydrochlorate, from Cochineal. Quercite, from the leaves of *Chamacrops humilis*. Cocosite, a substance resembling Inosite, from the leaves of several species of Cocoanut Palm.

(Exhibited by Dr. Hugo Müller.)

(To be continued).

CHEMICAL SECTION OF THE FRANKLIN INSTITUTE.

Held at the Institute, Tuesday, January 20, 1891.

Dr. Wm. H. Wahl, President, in the chair.

The annual report of the Treasurer was read and approved.

The report of Mr. H. Pemberton, Jun., as chairman of the committee of conference of the Chemical Section, appointed to confer with a similar committee of the American Chemical Society, was read and accepted. This committee was appointed by the President a few days after the last meeting of the section in December, and in response to a request for such a committee from Mr. A. A. Breneman, chairman of the committee of arrangements of the American Chemical Society.

The object of this conference was to consider, in a preliminary way, the question of forming a general organisation of American chemists, who should thus constitute a national society. A general meeting of eighteen delegates, representing seven different chemical organisations, was held in connection with the general meeting of the American Chemical Society at the University of Pennsylvania, on the 30th of December. On the following day a meeting of the chairmen of the various committees of conference was held at the Manufacturers' Club, in Philadelphia, and, as a result of the two meetings, a set of resolutions was adopted, a copy of which was submitted by Mr. Pemberton as a part of his report to the section.

Inasmuch as another meeting of the various conference committees is provided for in the above-mentioned resolutions, the committee was continued for the performance of such duties as were implied in the resolutions. After Mr. Pemberton's report had been accepted, the President extended the thanks of the section to the committee for its action.

Mr. Lee K. Frankel then read a paper "On the Electrolysis of the Metallic Sulpho-cyanides."

Prof. Geo. A. Koenig followed with a paper, entitled "Is Sulphuric Hydrate Volatile at Ordinary Temperatures?"

Prof. Koenig's observations and experiments tended towards an affirmative answer of the question which formed the title of his paper, and some interesting discussion was evoked.

Dr. Tuttle referred to recorded experiments, in which the absence of change in solutions of barium salts exposed to the possible evaporation of sulphuric acid tended to prove the non-volatility of the acid.

Prof. Smith cited some observations made by himself in connection with electrically deposited mercury, in which a weight of 0·3 grm. of that metal lost in the course of something less than twenty-four hours a weight of 0·002 grm., presumably by evaporation.

The paper by Dr. Hans v. Strombeck "On the Specific Heat of Brines of Different Specific Gravity, and on the Determination of the Specific Heat of a Body Generally," was read by title.

A paper from Mr. J. M. Emanuel, U.S.N., "On the Occurrence of Amberite, Ambrite, or Fossil Gum, in a Coal Seam at Hawakawa Colliery, Bay of Islands, N.Z.," was read by the Secretary.

Prof. Smith then presented a paper "On the Electrolytic Separation of Certain Metals in Phosphate Solutions."

After a number of interesting comments upon Prof. Smith's contribution, the section adjourned.

NOTICES OF BOOKS.

On the Greening of French Vegetables with Sulphate of Copper. Report by Sub-Committee of the Glasgow Corporation.

The industry of preserving fruits and vegetables has, unfortunately, its chief seat in France. "Unfortunately" we are justified in saying, on the faith of Professor Gautier's admission, that "nine-tenths at least of the green preserved vegetables sold in France or abroad are re-greened with sulphate of copper." This salt is added, it seems, in the proportion of 8 to 27 parts per 100,000 of vegetables.

This practice has sprung up in obedience to a mistaken demand on the part of the consumer. The idea of colour is one essentially foreign to the kitchen and the dining-room, where flavour, aroma, and wholesomeness should alone be taken into consideration. This fraudulent addition of copper sulphate is illegal in France, but breaches of the law are winked at.

It is, indeed, urged that no injury to the health of consumers—who are many—has hitherto been detected. But this assertion merely means that no acute and fatal cases have occurred. Knowing that the salts of copper are poisons we are slow to believe that their habitual introduction into the human system, even if in small proportion, can be harmless. One of the French experts who have examined the question (M. Bussy) thinks that the risk to public health should not be run. He asks with what consistency can a Government which interdicts the use of poisonous pigments in the manufacture of children's toys sanction, tacitly at least, the colouring of articles of food with salts of copper.

M. Pasteur very wisely suggests that all peas or other vegetables re-greened with sulphate of copper shall be labelled as containing this salt, at the peril of the maker and the seller.

It has even been recommended that re-greening for exportation should be permitted, *but not for home use!* We find further that cupriferous peas are actually known in the trade as "*petits pois à l'anglaise.*"

We can only recommend that until the Customs are authorised to seize and destroy all coppered vegetable, the local authorities should not be slack in prosecuting the vendors of re-greened vegetables.

Why does not a trade in honest preserved vegetables spring up in Canada, the West Indies, &c.? From every point of view such an attempt should be made and encouraged.

A Series of Chemical Problems, with Key, for Use in Colleges and Schools. By T. E. Thorpe, B.Sc., Ph.D., F.R.S. Revised and enlarged by W. Tate, Assoc.-N.S.S., F.C.S.; with a Preface by Sir H. E. Roscoe, B.A., Ph.D., F.R.S. New edition. London: Macmillan and Co.

The recommendation of this work expressed by Sir H. E. Roscoe in his preface to its first edition in 1870 may still be accepted as well founded. The calculations are exceedingly well chosen, and the solution of the questions necessitates an accurate knowledge of the theoretical phase of chemistry. It is, of course, possible that a student might have a perfect mastery of such calculations, and yet be utterly helpless in the laboratory. But if this work is used in conjunction with sound practical training it will prove invaluable.

CORRESPONDENCE.

EXPLOSION—A WARNING!

To the Editor of the Chemical News.

Sir,—A few drops of strong sulphuric acid were added to a few crystals of potassium permanganate in a clean test-tube kept cool with water, and the production of ozone having been demonstrated, the test-tube containing the mixture was placed in a test-tube stand. Some *ten minutes* afterwards the mixture exploded with great violence, shattering bottles, flasks, &c., and scattering the contents of the tube in all directions. I can find no warning in any text-book as to danger in performing this common experiment, nor have I ever had an explosion with it before. It may prevent a serious accident if I send this note of warning to you for publication.—I am, &c.,

D. B.

P.S.—I know that manganese heptoxide is formed, and that it explodes when heated or in contact with organic matter, but this was *in the cold*, and no organic matter was present to my knowledge.

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. cxii., No. 5, February 2, 1891.

The Photography of Colours.—G. Lippmann.—(See p. 87).

On the Basicity of the Organic Acids, according to their Conductivity. Mono-basic and Bi-basic Acids.—Daniel Berthelot.—The author proposes to characterise the basicity of the organic acids by means of the electric conductivity of mixtures of these acids with potassa made in different proportions. The existence of acid salts in the solutions forms the knot of the problem, and the novelty of his researches consists in the definition by this means of the peculiar characters of the organic acids.

On the Reaction of the Oxyalkyl Derivatives of Dimethylaniline.—Ed. Grimaux.—It appears not merely that the introduction of an OR group into dimethylaniline modifies its reactional aptitudes and affects the nature of the colour formed, but that there is a great difference in the behaviour of the oxyalkylised dimethylanilines according as the group OR occupies an ortho- or a meta-position with respect to the group $N(CH_3)_2$.

On Levosine—A New Proximate Principle of the Cereals.—C. Tanret.—The composition of levosine dried at 110° may be represented by the formulæ $C_{48}H_{40}O_{40}$ or $(C_{12}H_{10}O_{10})_4$. It yields on analysis the same figures as starch and dextrine, and on the application of Raoult's method its molecular weight is found to be 652. The anhydrous product on exposure to the air resumes 11 per cent of its weight of water, which gives for hydrated levosine $(C_{12}H_{10}O_{10}H_2O_2)_4$. Levosine is a white body, amorphous and almost tasteless. It dissolves in water in all proportions, and is readily soluble in weak alcohol, but scarcely in alcohol at 95°. It softens at 145°, but does not melt decidedly until 160°. Its specific gravity is 1·62. It is lævo rotatory:—$[\alpha_D] = -36°$.

On the Enrichment of the Blood in Hæmoglobine according to the Conditions of Existence.—A. Müntz.—From comparative analysis of the blood of rabbits living on the Pic du Midi, and of those living in the plains, it is found that when animals live at a great altitude, that is in a medium where the tension of the oxygen is notably diminished, their blood becomes richer in hæmoglobine, as is shown by the increase of fixed matter, and especially in iron. It thus acquires a greater absorbent power for oxygen, which compensates the effect of the rarefaction of the air. A sojourn of seven years, comprising many generations of rabbits, has therefore sufficed to effect this enrichment of the blood.

The Influence of the Nature of Soils upon Vegetation.—G. Raulin.—A mixture of four soils, sand, clay, lime-stone, and peat-earth, yielded both beets and maize of a weight superior to that of plants grown in any of the earths separately; the beets were also richer in sugar than the average. The results did not by any means follow in the same order; for the weight of the crop of maize clay took the first rank among the unmixed soils, and the sand was decidedly inferior. For the weight of beets, peat took the first rank and sand the lowest. For richness in sugar, clay gave the lowest yield and lime-stone the maximum. All the soils had received no manure for several years, and were very much exhausted.

No. 6, February 9, 1891.

On the Experiment of M. Wiener.—H. Poincaré.—A purely mathematical paper.

On the Communication of M. Poincaré.—M. Berthelot.—The author holds that to his knowledge there does not exist any purely chemical reaction which can, strictly speaking, furnish a measure of luminous energy. It is not necessary to ascribe to the luminous radiations any appreciable expenditure of energy in effecting the chemical phenomena of photography.

Photographic Reproduction of the Solar Spectrum in its Own Colours. — Edmond Becquerel exhibited proofs which he had obtained more than forty years ago, and which have remained unchanged, though they have been on several occasions examined and studied by daylight.

On the Conductivity of Tri-basic Organic Acids—A New Characteristic of Basicity.—Daniel Berthelot.—Electric conductivities yield a new characteristic for the basicity of acids whose atomic weight is known. We may thus determine by purely physical procedures the equivalent and the basicity of an acid, though knowing neither its formula nor even its elementary composition.

The Combinations formed by Ammonia with the Chlorides.—M. Joannis.—Contrary to the opinion of Rose, this author has obtained a compound of sodium chloride of the composition $NaCl+5NH_3$. He has not succeeded in forming the corresponding potassium compound, but he has obtained $BaCl,4NH_3$.

On the Formation of the Isopurpurates.—Raoult Varot.—Silver, mercury, and copper cyanides do not react upon picric acid or the picrates so as to form isopurpurates. Zinc cyanide, on the contrary, reacts, but more slowly than the alkaline cyanides.

On the Manner of Combination of Sulphuric Acid in "Plastered" Wines, and on the Detection of Free Sulphuric Acid.—L. Magnier de la Source.—Wines containing, respectively, 4 and 18 grms. per litre of free sulphuric acid cannot be drunk; with 1 grm. per litre the wine is very acid but good, and with 0·55 grm. it is very agreeable. Below 1 grm. per litre the addition of sulphuric acid cannot be detected by an analysis of the ash.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 2.

Manufacture and Composition of Peat Litter.—P. Kulisch (*Chemiker Zeitung*).—Analyses of peat used as litter in cow-houses, &c.

Assay of Essential Oils by Maumené's Reaction.—Rowland Williams.—From the Chemical News.

Formation of Chloroform. — E. Koefoed. — In the action of a solution of chloride of lime upon alcohol there are formed for 3 mols. hypochlorite, 1 mol. chloroform, 1 mol. calcium carbonate, and ½ mol. calcium hydrate. Hence, Liebig's formula for the production of chloroform is not correct.

Absorption of Iodine by Essential Oils.—From the Chemical News.

Mandragorine.—F. B. Ahrens (*Chemiker Zeitung*).—The author obtains from the root of this plant a base—$C_{17}H_{23}NO_3$—an isomer of atropine.

Presence of Oxygenated Water in Ether.—Brunner (*Pharm. Zeitung*).

Explosive Compounds Contained in Ether.—J. Konig (*Land. Vers.*).—On submitting to fractionated distillation the residue left on rectifying commercial ether, white fumes were given off at about 100°, and a violent explosion took place. This result is due to the presence of hydrogen peroxide.

Musk: Natural and Artificial.—These two compounds are not absolutely identical. Quinine sulphate completely removes the odour of artificial musks, whilst natural musk undergoes no change. The artificial musk also undergoes changes on keeping.

Revue Universelle des Mines et de la Metallurgie.
Vol. xii., No. 3.

This issue does not contain any chemical papers.

MISCELLANEOUS.

The Proposed Benevolent Fund.—We have much pleasure in announcing that Mr. Ludwig Mond has given £500, and Dr. J. H. Gladstone £100 to this fund.

Announcement.—Mr. Albert Fuerst, of the firm of Fuerst Bros., chemical merchants, 17, Philpot Lane, London, E.C., left for New York on Wednesday, the 25th ult., by s.s. *Majestic*, to manage the American branch office of the firm.

Royal Institution.—Professor Victor Horsley, F.R.S., will give a discourse on "Hydrophobia" on Friday, March 20th, in place of Professor W. E. Ayrton, F.R.S., who is unable to give his promised lecture on "Electric Meters, Motors, and Money Matters."

MEETINGS FOR THE WEEK.

Monday, 9th.—Medical, 8.30.
—— Society of Arts, 8. "Photographic Chemistry," by Prof. R. Meldola, F.R.S.
Tuesday, 10th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8
—— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S.
—— Society of Arts, 8. "Enamelling and Damascening," by J. Starkie Gardner.
Wednesday, 11th.—Society of Arts, 8. "Electricity in Relation to the Human Body," by H. Newman Lawrence and Arthur Harries, M.D.
—— Geological, 8.
—— Pharmaceutical, 8.
Thursday, 12th.—Royal, 4.30.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "Modern Chemistry in Relation to Sanitation," by Professor C. Meymott Tidy.
Friday, 13th.—Royal Institution, 9. "The Culture of the Singing Voice," by Felix Semon.
—— Society of Arts, 4 30. "The Science of Colour," by Captain Abney.
—— Astronomical, 8.
Saturday, 14th.—Royal Institution, 3. "The Forces of Cohesion," by The Right Hon. Lord Rayleigh, F.R.S.

THE CHEMICAL NEWS.

Vol. LXIII., No. 1633.

ON THE SYNTHESIS OF PROTEIC SUBSTANCES.

By P. SCHÜTZEN.

THE synthesis of nitrogenous substances, so-called proteic, entering into the constitution of the tissues and the liquids of the living organism, is a problem so complex that we cannot hope to find its complete solution by a single effort, however suitably directed.

The results of the experiments which the author submits seem to him calculated to lead to the object, and to furnish a good clue to the way to be followed. From this point of view they merit notice.

In an extended series of researches which have formed the subject-matter of several memoirs presented to the Academy, the author has made known the terms resulting from the decomposition of the proteic matters, albumenoids, or others, by hydratation, under the influence of bases (baryta). For the better understanding of what is to follow, the author recapitulates and sums up the most important results of his researches.

1. Proteic matter, when it is hydrated in presence of baryta at a temperature higher than 100°, utilises approximately as many molecules of water (H_2O) as it contains atoms of nitrogen.

2. A fraction of the total nitrogen, varying with the nature of the substance employed from ¼ to ⅕, is separated out in the form of ammonia. There is observed at the same time the liberation of oxalic and carbonic acids in such proportion that for 2 molecules $2NH_3$ of free ammonia we find 1 molecule of free bibasic acid (CO_2 and $C_2H_2O_4$).

3. The other terms of the decomposition are all amido-compounds. The elementary composition of their mixture answers exactly to an expression of the form

$$C_aH_{2a}N_2O_4,$$

with a slight excess of oxygen.

4. This mixture is formed of two series of terms: the one, of the form $C_bH_{2b+1}NO_2$ ($n=2, 3, 4, 5, 6$), are amido-derivatives of the fatty acids $C_nH_{2n}O_2$, which may be obtained synthetically by the action of the chlorine derivatives of the fatty acids upon ammonia. The others of the form $C_cH_{2c-1}NO_2(C=4{\cdot}5)$ may be regarded as anhydrides of the amido-oxyacids—

$$C_nH_{2n+1}NO_3.$$

The author has some years ago realised the synthesis of compounds of the form $C_nH_{2n-1}NO_2$ (leuceines), presenting the same characters as those obtained by the hydration of the proteic substances by the action of the ethylenic bromides upon the zinc compounds of the fatty amido-acids $C_nH_{2n+1}NO_2$.

A proteic substance such as albumen may be regarded in broad outline as formed of—

$$\underbrace{C_2H_2O_4}_{\text{Oxalic acid.}}+2NH_3+\underbrace{3(C_mH_{2m+1}NO_2)+3(C_nH_{2n-1}NO_2)-8H_2O}$$

or $C_qH_{2q}N_6O_{12}[q=3(m+n)]=C_{q+2}H_{2q-8}N_8O_8$.

If we put $q=28$, the foregoing formula leads to numbers which approach closely to those obtained by the elementary analysis of albumen. It is distinctly understood that there is here no question of a molecular formula.

After this study of an analytical order, which the author believes he has pushed as far as possible, the inverse problem presents itself. Can we, with the elimination o water, re-combine the above amides and amido-compounds of a relatively simple constitution so as to form complex bodies approaching to the proteic matters by their constitution and the totality of their chemical characters? In other words, can we effect the synthesis of a proteic substance by setting out from the simple products of its decomposition by hydration?

As numerous attempts made in this direction remained fruitless, the author was led to fear that on the decomposition by hydration render the influence of baryta, there may be produced inter-molecular transpositions of the kind which saccharose undergoes when it is split up into lactic acid. If it were thus, the process of the synthesis of the proteic matters would be much less simple, and in place of consisting merely of the reunion of several molecules with the elimination of water (as it happens in the formation of the compound ethers and the neutral fatty matters), it might be complicated by a molecular transposition inverse of that produced by the alkalies—a transposition which chemists are not yet able to realise at their will.

The author's recent experiments tend to remove this cause of complication. He has, in fact, succeeded in forming a nitrogenous compound, which, from its characters, should rank in the class of the proteic compounds. It has been obtained by eliminating water, and combining the ultimate and crystallisable products derived from the decomposition of albumen and fibrine under the influence of baryta.

The mixture of amido-compounds ($C_mH_{2m+1}NO_2$ and $C_nH_{2n-1}NO_2$), along with about 10 per cent of urea, finely ground and dried at 110°, was intimately mixed with 1½ parts by weight of phosphoric anhydride. The whole was heated in a flask in the oil bath.

Below 120° no change was produced, and the mass remains in a state of powder. About 125° the dehydrating action begins and terminates in a few instants. The phosphoric anhydride is rapidly hydrated at the expense of the water, the elements of which are drawn from the amido-compounds. The mass becomes pasty, and solidifies into a compact compound without turning appreciably brown.

After cooling it is dissolved in a small quantity of water and several volumes of alcohol are added to the solution. We obtain thus a copious precipitate which is washed in alcohol and re-dissolved in water. The solution is filtered to eliminate a little insoluble matter. It is then freed from phosphoric acid by means of a slight excess of baryta—an excess which is separated by precipitation with an equivalent dose of sulphuric acid. The liquid is filtered again and concentrated in the water-bath, giving an amorphous product soluble in water, and precipitatable by alcohol in white curdy clots.

The substance thus obtained presents great analogies to the characters of the peptones. Its aqueous solutions are precipitated by tannin, picric acid, mercuric chloride, acid mercuric nitrate, Millon's reagent, potassium di-iodide and iodo-mercurate and phosphotungstic acid in presence of hydrochloric acid, phosphomolybdic acid, lead acetate and sub-acetate. It is not precipitated, at least in the cold, by potassium cyanide in presence of acetic acid.

If mixed with caustic potassa and some drops of solution of copper sulphate, it takes a rose-red colouration. This synthetic pseudo peptone, if heated with nitric acid, after evaporating off the excess of acid, gives a yellow residue which turns orange with ammonia, and which, if heated, is abruptly decomposed with production of a swollen mass of carbon as it happens with gelatin.

If heated upon a sheet of platinum it is carbonised and tumefied, giving off the characteristic odour of burnt animal matter.

It will be interesting to submit to this reaction, one by one, the various amido-derivatives of the proteine compounds, so as to determine which of them play an indispensable and preponderating part in the formation of the proteine molecules.—*Comptes Rendus*, Vol. cxii., No. 4, p. 198.

DETERMINATION OF WATER IN SUPERPHOSPHATES.*

By JULIUS STOKLASA.

(Concluded from p. 115).

The mono-calcium phosphate dried at 205° was treated with water. The solution contained traces of free phosphoric acid, and a considerable quantity of mono-calcium pyrophosphate. When the watery solution had been boiled with nitric acid there were found 16·2 per cent of phosphoric acid, but only 2·3 per cent before boiling. The calcium meta-phosphate eliminated had the following composition:—

P_2O_5 = 70·02 per cent.
CaO = 27·35 ,,

If dried at 210° it lost 21·5 per cent of water. The residual vitreous calcium meta-phosphate is not soluble in water; in the aqueous solution there were found 0·86 per cent soluble phosphoric acid.

The finely pulverised meta phosphate was thoroughly washed and dissolved in *aqua regia* or undiluted sulphuric acid. The analysis gave:—

P_2O_5 .. .. .. 70·53 per cent.
CaO .. .. .. 27·28 ,,

The chemical process is in this case very simple; the mono-calcium pyrophosphate loses 1 mol. of water and becomes metaphosphate, $CaH_2P_2O_7 = Ca(PO_3)_2 + H_2O$.

The vitreous metaphosphate formed adheres so firmly to the sides of the glass or platinum capsules that it is difficult to determine the remaining matter soluble in water.

In all the experiments above mentioned it is necessary to spread out the mono-calcium phosphate uniformly in the capsule in order to obtain concordant results as in this manner the temperature acts uniformly upon the mono-calcium phosphate. The results obtained by drying the mono-calcium phosphate at different temperatures are given in the form of a table. The percentage of mono-calcium phosphate decomposed by exposure for an hour to different temperatures varies from 1·84 at 105° to 48·20 at 200°. These results do not agree with the experiments of Birnbaum and Drewson.

The chemical process on the desiccation of mono-calcium phosphate may thus be represented:—

Influence of temperature at 200° for one hour—

$$8[CaH_4(PO_4)_2)\cdot H_2O] = 4CaH_4(PO_4)_2 + \\ + Ca(PO_3)_2 + Ca_2P_2O_7.$$

Further desiccation at 200° effected the following decomposition:—

$$4CaH_4(PO_4)_2 + Ca(PO_3)_2 + Ca_2P_2O_7 + CaH_2P_2O_7 + \\ + 2H_3PO_4 = 2Ca(PO_3)_2 + 4CaH_2P_2O_7 + Ca_2P_2O_7 + \\ + 2H_3PO_4 + 5H_2O\cdot 2Ca(PO_3)_2 + 4CaH_2P_2O_7 + 2H_3PO_4 = \\ = 6CaPO_3)_2 + 2CaH_2P_2O_7 + 5H_2O.$$

Finally, if the pyrophosphate is completely decomposed at 210° into calcium metaphosphate and water:—

$$6Ca(PO_3)_2 + 2CaH_2P_2O_7 = 8Ca(PO_3)_2 + 2H_2O.$$

All these transformations, on drying at 210°, may be expressed as follows:—

$$8[CaH_4(PO_4)_2\cdot H_2O] = 8Ca(PO_3)_2 + 24H_2O.$$

On Normal Butylamines.—A. Berg.—The author obtains these substances by causing ammonia in a hydro-alcoholic solution to act upon normal butyl chloride.—*Comptes Rendus*, Vol. cxii., No. 8.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

February 19th, 1891.

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

Certificates were read for the first time in favour of Messrs. Walter Johnson Cooper, High Street, Mitcheldean, Gloucester; Charles F. Forshaw, LL.D., D.Sc., Bradford, Yorks; John Alfred Foster, Royal Naval College, Greenwich; Claude Hooper Bater, 4, Westbank Terrace, Gibson Street, Hillhead, Glasgow; William L. Hiepe, Ph.D., 21, Acomb Street, Manchester; F. Stanley Kipping, Ph.D., D.Sc., 7, Milborne Grove, South Kensington; Charles Ainsworth Mitchell, 27, Farnley Road, South Norwood; Percy Morrice Randall, 3, Belsize Park Gardens.

Messrs. Holland Crompton, R. H. Davies, and Bernard Dyer were appointed by the meeting to audit the Treasurer's accounts.

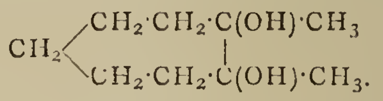
The following were duly elected Fellows of the Society:—Messrs. John Charles Aydans; Henry Austin Appleton; Charles Norrish Adams, M.A.; John Frederick Bloomer; Clayton Beadle; Robert John Brown; Thomas Byrne; Arthur Cole, B.A.; Arthur Colefax, B.A., Ph.D.; Charles Henry Corbett; Hendrie Thomas Donovan; Robert Bond Greaves; Ernest F. Hooper; Frederick William Harrold; Moses William Jones; Henry Charles Jenkins; Frederick Herbert Moore; Reginald Tom Marshall; Edgar J. Millard; William Morley Martin; Arnold Whitaker Oxford; Michael Samuel Pickering; William Jackson Pope; Tom Kirke Rose; R. Stockdale; Matthew Carrington Sykes; Herbert D. Shaw; R. Greig Smith; Kenelm Edward Symes; Howard C. Sucré; A. H. Tapp; Frederick William De Velling, B.A.; David Wilkinson; Thomas M. Wyatt; Stephen Newcombe Wellington; Dr. W. Will.

The following papers were read:—

9. "*The Action of Reducing Agents on αα′-diacetylpentane. Synthesis of dimethyldihydroxyheptamethylene.*" By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, Jun., Ph.D., F.R.S.

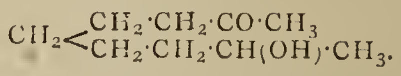
On reducing αα′-diacetylpentane $COMe\cdot[CH_2]_5\cdot COMe$ (*Trans. Chem. Soc.*, vol. lvi., 330), dissolved in moist ether, with sodium, it is converted into a colourless liquid of the composition $C_9H_{18}O_2$. The method of preparation, properties, and some derivatives of this reduction product are described in the paper, and also various experiments made with the object of determining its constitution.

The author's investigations have shown that the reduction product must be regarded as a dimethyldihydroxyheptamethylene of the constitution

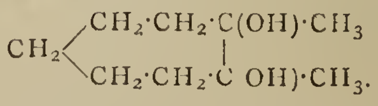


$$CH_2\left\langle\begin{array}{l} CH_2\cdot CH_2\cdot C(OH)\cdot CH_3 \\ \qquad\qquad\quad | \\ CH_2\cdot CH_2\cdot C(OH)\cdot CH_3. \end{array}\right.$$

This conclusion is based on the following considerations:— The reduction product is formed by the addition of two atoms of hydrogen to diacetylpentane, and may, therefore, theoretically have the constitution represented by one of the following formulæ:—

I. 

$$CH_2 < \begin{array}{l} CH_2\cdot CH_2\cdot CO\cdot CH_3 \\ CH_2\cdot CH_2\cdot CH(OH)\cdot CH_3. \end{array}$$

II. 

$$CH_2\left\langle\begin{array}{l} CH_2\cdot CH_2\cdot C(OH)\cdot CH_3 \\ \qquad\qquad\quad | \\ CH_2\cdot CH_2\cdot C(OH)\cdot CH_3. \end{array}\right.$$

As in the one case the compound would be an open-chain ketone alcohol (formula 1), and in the other a dihydroxy-derivative of a closed carbon chain (formula 2), it is comparatively easy to ascertain which of the two

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* From the *Zeitschrift Anal. Chemie.*

formulæ represents the constitution of the compound. 1. The reduction product does not combine with hydroxylamine, or with phenylhydrazine. 2. It yields a diacetyl derivative of the composition $C_{13}H_{22}O_4$ with acetic anhydride. 3. Phosphorus pentabromide converts it into a dibromide of the composition $C_9H_{16}Br_2$. 4. It is not acted on by such reducing agents as zinc and chlorhydric acid, sodium amalgam, or sodium and alcohol. 5. On reduction with hydrogen iodide, it is converted into a hydrocarbon of the composition C_9H_{18}.

These facts, the authors think, are sufficient to warrant the conclusion that the reduction product is a dimethyldihydroxyheptamethylene of the constitution given above.

Dimethyldihydroxyheptamethylene, $C_9H_{18}O_2$, is a thick, colourless liquid, boiling at 201° (180 m.m.); it is only sparingly soluble in cold water, but miscible with alcohol, ether, &c., in all proportions. The *sodium* derivative, $C_9H_{17}O_2Na+H_2O$, is a colourless, semi-crystalline, very deliquescent compound.

Dimethyldibromoheptamethylene, $C_9H_{16}Br_2$, prepared by treating the dihydroxy-compound with phosphorus pentabromide in chloroform solution, is a thick, colourless oil.

Dimethylhydroxyiodoheptamethylene, $C_{19}H_{17}OI$, is formed when the glycol is heated with hydrogen iodide; it is a colourless liquid, with a pleasant, sweetish smell.

Dimethylheptamethylene diacetate, $C_9H_{16}(OAc)_2$, is obtained when the dihydroxy-compound is boiled with acetic anhydride; it boils at 199—202° (65 m.m.) and is readily hydrolysed by dilute soda.

Dimethylheptamethylene, C_9H_{18}, is obtained in the form of a cololourless, mobile oil, when dimethyldihydroxyheptamethylene is heated with hydriodic acid and amorphous phosphorus; it boils at 153—154° and has an odour very like that of light petroleum.

Discussion.

Dr. **Armstrong** and Dr. **Collie** both drew attention to the possible formation of a hexamethylene compound by the reduction of the diketone diacetylpentane, and asked what evidence other than synthetical established the constitution of the reduction product.

Dr. **Kipping**, while admitting that at present there was no such evidence, contended that the formation of a hexamethylene compound was altogether improbable.

10. "*The Osmotic Pressures of Salts in Solution.*" By R. H. **Adie**, M.A.

This paper contains the experimental results of an investigation of the osmotic pressures of salts in solution by direct observation, by the method of Pfeffer. The results are arranged under five headings.

1. *Boyle's Law applied to solutions.* The observations are plotted out with osmotic pressures for ordinates and concentrations (in terms of grm. molecules per litre) for abscissæ. The salts observed were potassium and sodium nitrates, potassium iodide, potassium sulphate, potash alum, potassium ferrocyanide and cobalticyanide, and a few others. The results obtained show that the osmotic pressures do not vary directly as the concentrations, but take a definite curved form, approaching Ostwald's line of no dissociation at two points, and receding from it elsewhere. Potash alum gives the nearest approach to a straight line of the salts examined.

2. *Charles's Law applied to solutions.*—Only one experiment yielded any result, and that was confirmatory of the correctness of applying Charles's Law to solutions.

3. *Influence of bases on osmotic pressures.*—No definite influence can be attributed to the base, except that the salts of some bases, *e.g.*, soda, appear to be more readily dissociated by water than those of others, *e.g.* potash.

4. *Influence of acids on osmotic pressures.*—In the case of inorganic acids, no very definite influence can be detected; though the equivalents of the salts of monobasic acids give in general higher osmotic pressures than those of the salts of dibasic acids. In the case of organic acids an increase in the molecular weight of homologous acids increases the osmotic pressure, and a ring nucleus gives a higher osmotic pressure than an open chain.

5. *Avogadro's Law applied to salts in solution.*—The author examines and compares the differences between the observed results and those calculated on the assumption that Avogadro's Law applies to salts in solution, and suggests that they may be due, as in Crookes's hypothesis, to the existence of simple and complex molecules in solution, as well as to the formation of water compounds in the solution. This hypothesis does not appear to require so large a modification of ordinary chemical ideas as that of Ostwald and Arrhenius.

11. "*A Direct Comparison of the Physical Constants Involved in the Determination of Molecular Weights by Raoult's Method.*" By R. H. **Adie**, M.A.

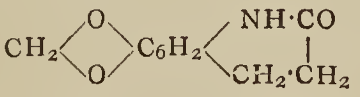
In this paper the author tries to connect the constants of Raoult's method of determining molecular weights of a substance in solution with those ascertained by direct observation of the osmotic pressure of the same solution. Also, by the same method of Raoult, to connect the osmotic pressure with the gaseous pressure of any substance in solution. The substances chosen are potassium iodide and ammonia. The solutions of potassium iodide and ammonia are compared by means of the lowering of the freezing point, and then the osmotic pressures of the same solutions of potassium iodide are given. The author shows that the constants obtained by the two methods do not agree, and suggests an hypothesis to explain the same, which is given above.

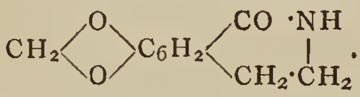
Discussion.

Mr. **Pickering** said that the numerous results brought forward by Mr. Adie could not fail to be of value. They seemed to afford fresh proof of the irregularities almost invariably shown by the properties of solutions, where, according to the physical theory, there should be nothing but regularity and uniformity. It was to be regretted that the determinations had not been pushed further into the region of dilute solutions, for it was here that some of the most surprising irregularities existed, and it was here that the existence of such must tell most strongly against any purely physical theory. Mr. Adie had touched on one of the most fundamental objections to the present physical theory of solution—the existence of osmotic pressure—for this is due to the impermeability of a membrane to the dissolved substance; and how can it be contended that if the molecules of the latter were single, and still more if they were dissociated into ions, they cannot get through holes which the water molecules have no difficulty in threading?

12. "*Derivatives of Piperonyl.*" By **Frederick M. Perkin**.

The author describes the results of experiments made with the object of determining the constitution of the compound $C_{10}H_9NO_3$ obtained by his brother from berberine (*Trans.*, 1890, p. 992), a knowledge of which was essential to the determination of the nature of this alkaloid; two formulæ would account for the properties of the substance, viz.:—



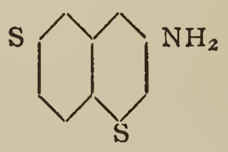


The second of these is found to be applicable to the substance in question. In the present paper, the author describes the preparation of the compound represented by the first formula from piperonal. On heating a mixture of nitropiperonal, acetic anhydride, and sodium acetate, an acid was obtained identical with that formed on nitrating the piperonylacrylic acid of Lorenz. On reduction with ferrous sulphate, this nitro-acid is converted into the corresponding amido-acid, but when zinc or tin and muriatic acid is used, the anhydro-derivative of the amido-acid is obtained.

The action of bromine on piperonylacrylic acid is described, and also the formation of a benzoin-like compound from piperonal and potassium cyanide.

13. "*Studies on the Constitution of Tri-derivatives of Naphthalene, No. 9. Andresen's β-naphthylaminedisulphonic Acid.*" By Henry E. Armstrong and W. P. Wynne.

According to Schultz (*Ber.*, vol. xxiii., page 77), naphthalene-1 : 3'-disulphonic acid on nitration yields a mixture of several nitronaphthalenedisulphonic acids. The chief product on reduction gives the so-called α-naphthylamine-ε-disulphonic acid [NH_2 : SO_3H : SO_3H = 1' : 1 : 3'; *v.* Armstrong and Wynne, *Chem. Soc. Proc.*, 1890, 15] of the German patent 45776. Of the other acids, the production of which has been also noted by Bernthsen (*Ber.*, vol. xxiii., p. 3088, footnote), one yields on reduction, according to Schultz, a β-naphthylaminedisulphonic acid. As this was the first instance in which the formation of a *beta*-nitro acid by the nitration of a naphthalenesulphonic acid has been observed, the attention of the authors was directed to the determination of its constitution, and through the liberality of the Actiengesellschaft für Anilinfabrikation a considerable supply of the material remaining after the separation of the greater part of the ε acid was placed at their disposal for examination. After separation from the associated acids, and comparison with a specimen of the pure Andresen acid received from Dr. Schultz, the amido-acid was analysed by the hydrazine and Sandmeyer methods already described. When reduced by the hydrazine method it gave naphthalene 1 : 3' disulphonic acid, which was characterised by means of its chloride, $C_{10}H_6(SO_2Cl)_2$, melting at 127°, and the derived 1 : 3' dichloronaphthalene melting at 48°. On treatment by the Sandmeyer process it was converted into a chloronaphthalenedisulphonic acid, the chloride of which, $C_{10}H_5Cl(SO_2Cl)_2$, crystallised from benzene in radiate groups of flat needles melting at 174°, and on distillation with PCl_5 yielded 1 : 3 : 3' trichloronaphthalene melting at 80·5°. This acid, consequently, was identical with that obtained by the authors by sulphonating 2 : 2'-β-chloronaphthalenesulphonic with 20 per cent anhydrosulphuric acid (*Chem. Soc. Journ.*, 1890, 133). As a further proof of the identity of the two compounds, the chloronapthalenedisulphonic chloride derived from the Andresen acid was hydrolysed by heating with dilute sulphuric acid at 250—270° for several hours, with the result that β-chloronaphthalene melting at 59·5° was obtained. Combining these results it follows that the Andresen acid *is* a β-naphthylaminedisulphonic acid of the constitution—



The salts of this 2 : 4 : 2' β-naphthylaminedisulphonic acid, and the mode of separation from the other naphthylaminesulphonic acids contained in the mixture, will be described when the examination of the nitration product of naphthalene 1 : 3' disulphonic acid has been completed.

CHEMICAL SOCIETY'S JUBILEE—1891.

February 24th.

(Concluded from p. 118).

W. Crookes, F.R.S.,
President, 1887 — 1889.

The Seleniocyanides. 1851.

1. Original specimen of Seleniocyanide of Potassium.

2. Seleniferous deposit from the Sulphuric Acid Chambers at Tilkerode. From this deposit the Selenium used in the above research was prepared.

3. Residue left on distilling crude Selenium prepared from the above deposit. On examining this residue in the spectroscope a sharp green line was seen, which was afterwards proved to be due to a new element, Thallium.

Thallium and its Compounds. 1861.

4. Thallium, pure metallic, *in vacuo*. Thallium oxide, peroxide, chloride, sesquichloride, bromide, iodide, sulphide, cyanide, sulphocyanide, sulphate, nitrate, carbonate, acetate, oxalate, picrate, chlorate, perchlorate, chromate, bichromate, tartrate, bitartrate, benzoate, and potassium tartrate.

5. A prism of thallium glass, in which thallium replaces lead. Sp. gr. 4·75. Refractive index for the D line 1·751.

6. Crookesite, from Skrikerum, Norway. A selenide of thallium, copper, and silver.

	Per cent.
Thallium	17·25
Copper	45·76
Silver	3·71
Selenium	33·28
	100·00

7. Thalliferous Pyrites, from Millom, Cumberland.

8. Thalliferous Flue Dust, from Sulphuric Acid Works using thalliferous pyrites. (*a*) From Allhusen's Works, Newcastle. (*b*) From the Washington Chemical Works, Durham.

Repulsion resulting from Radiation. 1873.

9. Original Apparatus used in this investigation.

Pith ball balance in air, and *in vacuo*. The balls in air are apparently attracted, and *in vacuo* are repelled if a flame is brought near them.

Pith discs suspended horizontally.

Platinum bar suspended in tube of hard glass. This was heated to a high temperature while exhaustion was proceeding, to show that the repulsion does not depend on the presence of moisture.

Glass rods with mica ends *in vacua*, of various degrees of perfection.

Torsion balance to measure the force with which the blackened disc is repelled when exposed to radiation.

Pith bars with mirrors attached suspended (*a*) in air, (*b*) *in vacuo*. The blackened end of (*a*) is attracted and that of (*b*) repelled when a flame is brought near them.

The Radiometer. 1875.

10. The first Radiometer.

11. Early forms of Radiometers.

12. Lecture form of Radiometer.

13. Radiometers in which the source of heat is a platinum spiral inside the tube which is heated by an electric current.

14. Radiometers with vanes coated with different materials.

15, 16. Radiometers showing a different action according to whether heat or light falls on them. Certain bodies are more affected by luminous radiations than by the heat rays, while others are affected in the inverse order. If pairs of these substances in fine powder, are painted on alternate sides of the vanes of a radiometer, the rotation will be in one direction if the light of a candle is allowed to shine direct on them, and in the opposite direction if the light is first filtered through a plate of alum or a cell of water. One of these radiometers has its vanes coated on alternate sides with persulphocyanogen and copper oxalate, and the other radiometer has its vanes coated with chromic oxide and copper tungstate.

17. Radiometer with vacuum gauge attached.

18. First Radiometer made to investigate the effect of the shape of the vanes. The corners are turned up.

19. Radiometers in which the opposite sides of the vanes are of different shapes or are differently presented to the glass envelope.

Vanes inclined to the arms. Very thin mica vanes. Thicker mica vanes. Cone-shaped vanes. Cylindrical vanes. Cup shaped vanes.

20. Apparatus in which the source of heat is a platinum wire.

21. Radiometers furnished with movable mica or metal screens, which can be jerked into different positions relatively to the vanes.

22. Double Bulb Radiometer to investigate the effect of the dimensions of the bulb. The vanes can be balanced in either bulb.

23. Radiometer to show that, if the vanes are held at rest by means of a magnet attached to them, the bulb, if free to move, will rotate.

24. A Spiral Radiometer of roasted mica blacked on the upper side.

25. A four-armed Metallic Radiometer with deep cups, bright on both sides.

26. A four-armed Radiometer, the vanes consisting of mica cups, bright on both sides.

27. A four armed Radiometer having clear mica vanes. The direction of motion being determined by the angle formed by the mica vanes with the inner surface of the glass bulb.

28. A vertical Radiometer, made with eight discs of mica blacked on one side, and the whole suspended on a horizontal axis which works in two glass cups. The motion of the radiometer is assisted on each side by driving vanes of aluminium blacked on one side.

Application of the Radiometer to Photometry.

29. Apparatus showing variations in the intensity of light on a divided scale.

Otheoscopes or Instruments in which the driving surface is not the glass of the bulb, but an interior disc, or surface which becomes heated.

30. Otheoscope.—A four-armed fly carries roasted mica vanes, and is mounted in an exhausted glass bulb like a radiometer. Fixed to the side of the bulb are three plates of clear mica, equidistant from each other in a vertical plane, but oblique to the axis. A candle brought near the fixed plates generates molecular pressure, which, falling obliquely on the fly, causes it to rotate.

31. Otheoscope.—A large horizontal disc, revolving by the molecular disturbance on the surface of inclined metallic vanes, which are blacked on both sides in order to absorb the maximum amount of radiation.

Molecular Physics in High Vacua. 1878.

Original Apparatus used in this investigation:—

32. Apparatus to show the Dark Space round the Negative Pole. When the spark from an induction coil is passed through an ordinary vacuum tube, a dark space is seen round the negative pole. The shape and size of this dark space do not vary with the distance separating the poles; nor, only very slightly, with alteration of battery power, or with intensity of spark.

33. Apparatus to show the Green Phosphorescent Light of Molecular Impact. At very high exhaustions the dark space becomes so large that it fills the tube, and when German glass is used the sides are beautifully illuminated with a greenish yellow phosphorescent light.

34. Apparatus to show the Conveyance of the Molecular Streams to a Focus. The plate covered with calcium sulphide is furnished with a scale on which the "focal length" of the curved electrode is indicated.

35. Apparatus to show that the Paths of the Molecules are straight lines.

36. Apparatus to show the Projection of Molecular Shadows. The rays exciting green phosphorescence will not turn a corner, but radiate from the negative pole in straight lines, casting strong and sharply defined shadows from objects which happen to be in their path. The best and sharpest shadows are cast by flat discs, and not by narrow pointed poles; no green light is seen in the shadow itself, no matter how thin or whatever may be the substance from which it is thrown.

37. Apparatus to show Shadow of Object which is interposed in the Paths of the Molecules. The molecules which pass the aluminium cross make the glass phosphoresce so that a shadow of the cross appears.

38. Apparatus in which the Negative Pole is a Coin; the device is reproduced on the glass by the phosphorescence excited by the molecular streams.

39. Apparatus to show that the line of phosphorescent light excited by a molecular stream in a plate covered with calcium sulphide is deflected by a magnet, thereby proving that the paths of the molecules are affected by the presence of a magnet.

40. Apparatus to show the Mechanical Action of Projected Molecules. An actual material blow is given by the impinging molecules. A small vaned wheel being used as an indicator, by appropriate means the molecular shadow of an aluminium plate is projected on the vanes. When entirely in the shadow the indicator does not move, but when the molecular stream is deflected so that one half of the wheel is exposed to molecular impact it rotates with extreme velocity.

41. Paddle-wheel which can be rotated in either direction according as the molecular stream is directed to its upper or lower vanes by a magnet.

42. Electrical Radiometers. The vanes revolve when connected with the negative pole of an induction coil. At low exhaustions a velvety violet halo forms over each side of the vanes. On increasing the exhaustion the dark space widens out. On further exhaustion the dark space on the metallic side touches the glass, when positive rotation takes place.

43. Apparatus to show the Focus of Heat of Molecular Impact. Great heat is evolved when the concentrated focus of molecular rays from a nearly hemispherical aluminium cup is allowed to fall on a strip of platinum-foil, the heat sometimes exceeding the melting-point of platinum.

44. A disc is supported by a carbon rod resting on carbon supports which form a microphone. If a telephone be included in the circuit, the movement of the disc produced by the impact of a beam of light can be detected by the sound produced by the microphone.

45. Apparatus with Idle Poles to test the Electrification of Bodies interposed between the poles in the molecular stream.

46. Apparatus to test the effect of the Electrification of a Neighbouring Conductor on the molecular streams.

47. Apparatus to investigate the Shadow of a Vibratory Pendulum.

48. Apparatus with two Negative Poles. When one negative pole only is used lines of light are produced in the phosphorescent plate by the molecular streams. When both are employed simultaneously the lines shift in such a direction as to prove that the molecular streams repel each other.

Radiant Matter. 1879.

Original Apparatus used in this investigation:—

49. Vacuum Tube, with exploring pole, used in investigating the electrical condition of a highly exhausted tube when electrically excited.

50. Apparatus to show the action of the electrified walls of a vacuum tube on the stream of Radiant Matter, projected from the negative pole. In the wide part of the tube the stream of Radiant Matter follows its normal course straight from the negative pole, but in the narrow part of the tube so great is the attraction of the walls that the molecular stream widens out till it covers the whole screen.

51. Apparatus showing that the radiant molecules behave differently at a vacuum just short of non-conducting to what they do in ordinary high vacuum.

52. Apparatus showing the return of the exhausted molecules after having been shot off from the negative pole. The charged molecules pass through a small hole in a glass diaphragm, and turn a mill by their impact.

The returning molecules, passing through another hole, turn a second mill.

Apparatus to show that *Radiant Matter* is not *Radiant Electrode Matter.*

53. Apparatus showing that all the phenomena of Radiant Matter, such as projection of molecular shadows, mechanical energy, production of heat, and phosphorescence, can be produced in tubes without inside electrodes.

54. Apparatus used in experimenting on the Electrical Resistance of High Vacua.

55. Double vacuum tube of different electrical resistance. One side containing carbon, and the other side containing yttria.

56. Apparatus showing that the resistance of vacuum tubes is dependent on the material surrounding the poles.

Phosphorescence in High Vacua. 1879.

57. Apparatus to show the Phosphorogenic Properties of the Molecular Stream. Substances known to be phosphorescent under ordinary circumstances shine with great splendour when subjected to the negative discharge in a high vacuum.

58. Apparatus with cylindrical electrode to show phosphorescence produced in glass.

59. Apparatus with corrugated electrode. The molecular streams from the projections interfere and produce a pattern on the glass.

60. Tubes for the production of phosphorescence by means of the molecular stream on calcium sulphide.

61. Diamonds, various, in vacuum tubes. Under the influence of the induction spark these diamonds phosphoresce of different colours, according to their origin. Thus, Cape diamonds usually phosphoresce blue; Brazilian diamonds phosphoresce red, orange, blue, and yellow; Australian diamonds phosphoresce yellow, blue, and green.

62. Diamonds mounted in enamel. When subjected to the molecular stream they phosphoresce with blue, yellow, green, or apricot-coloured light.

63. Rubies. These stones phosphoresce with a brilliant red light.

64. Mixed stones which phosphoresce with various colours. The collection includes Diamonds, Rubies. Garnet, Topaz, Phenakite, and Spodumene.

65. Topaz.—Phosphoresces blue.

66. Sapphire.—Phosphoresces green.

67. Spinel.—Phosphoresces with a crimson light.

68. Phenakite. — Usually phosphoresces blue. Occasionally a crystal is found which phosphoresces yellow.

69. Pectolite.—Phosphoresces of a straw-colour.

70. Calcite.—Phosphoresces of an orange-colour.

71. Phosphorescent Calcite from Branchville, South Carolina. When heated in air it has the curious property of glowing strongly with a golden yellow light. In the Radiant Matter Tube this phosphorescence is very brilliant.

72. Spodumene. Phosphoresces of a yellow colour. A phosphorescing crystal of Spodumene has all the internal light cut off with a Nicol prism when the long axes of the Nicol and the crystal are parallel.

73. Dolomite.—A granular form from Utah; when scratched with a knife or struck with a pick it emits so strong a phosphorescent red light that the miners call it "Hell-fire Rock." In the Radiant Matter Tube it glows with a fine red light.

74. Zirconium Oxide, Calcined.—Phosphoresces with a bluish white light.

75. Strontium Oxide, Calcined.—Phosphoresces with a fine blue light.

76. Glucinum Oxide, Calcined.—Phosphoresces with a faint blue light.

77. Calcium Sulphide.—Phosphoresces blue, yellow, green, or red, according to the mode of preparation.

78. Zinc Sulphide (Sidot's hexagonal blende).—This is the most brilliantly phosphorescent body yet met with. In the vacuum tube it begins to phosphoresce at an exhaustion of several inches below a vacuum. At first only a green glow can be seen; as the exhaustion gets better a little blue phosphorescence comes round the edges. At a high exhaustion, on passing the current, the green and blue are about equal in brightness, but the blue glow vanishes immediately the current stops, while the green glow lasts for an hour or more. Some parts of a crystalline mass of blende which, under the action of radiant matter, glow of a bright blue colour, give a green residual light when the current ceases; other parts which glow blue become instantly dark on stopping the current.

Electric Lighting by Incandescence. 1881.

79. Structureless cellulose for carbon filaments.

80. Incandescent electric lamps, with structureless carbon filaments.

81. The smallest electric lamp, diameter 3·8 m.m., weight 1·9 grains. 7·4 volts., 0·6 ampère, 1. C.P.

Radiant Matter Spectroscopy. 1883.

Apparatus and Specimens illustrating this investigation:—

82. Alumina in the form of a precipitate or crystallised as the Ruby, phosphoresces of a rich crimson colour, and when the light is examined in the spectroscope it is seen to consist essentially of one sharp line in the red.

83. Yttrium Sulphate.—Phosphoresces with a golden yellow light. Examined with a spectroscope gives a remarkable discontinuous spectrum.

84. Samarium Sulphate.—Phosphoresces with a red light, and gives a spectrum composed of three broad bands.

85. *Specimens of Rare Earths and their Salts:—*

Ceria.
Ceric oxalate.
Decipia.
Didymia.
Didymic oxalate.
Didymic sulphate.
Erbia (rose-coloured).
Gadolinia (Y*a*).
Lanthana.
Lanthanic oxalate.
Thulia (with erbia).
Niobic acid.
Philippic (?) formate.
Tantalic acid.
Terbia.
Thoria.
Thoric oxalate.
Thoric sulphate.
Ytterbia.
Yttria.
Zirconia.

86. Specimens of Yttria from the following minerals:—

Gadolinite.
Samarskite.
Xenotime.
Monazite.
Euxenite.
Hielmite.
Sipylite.
Arrhenite.
Fluocerite,
Clèvite.

Specimens of Minerals containing Rare Earths.

87. Gadolinite. The largest known crystal in the world. It weighs 40 lbs., and contains nearly 50 per cent of Yttria.

88. Samarskite. Various specimens.

89. Allanite. A very large specimen.

90. Thorite and Orangeite in crystals.

91. Eudyalite.

92. Orthite.

93. Alvite.

94. Rhabdophane.

95. Fergusonite.

96. Columbite.

97. Hjelmite.

Genesis of the Elements. 1886.

98. A Model Lemniscate Curve, illustrating the Presidential Address delivered before the Chemical Society, March 28th, 1888.

Elements and Meta-Elements. 1889.

Specimens illustrating the Presidential Address delivered before the Chemical Society, March 21st, 1889.

99. Vacuum tubes containing new earths separated from Yttria by continued fractionation. Under the influence of molecular bombardment these earths phosphoresce brightly, and give spectra consisting essentially of one or two bright lines.

100. The following Table gives the mean wave-length of certain definite absorption-bands or lines in the phosphorescent spectra of presumably new elements which have been separated from the earth yttria by fractional precipitation, repeated many thousand times:—

Position of lines in the spectrum.	Mean wave-length of band or line.	Provisional name.
Absorption-bands in violet and blue ..	443 475	Dα Sβ
Bright lines in		
Deep blue	482	Gα
Green	564	Gγ
Citron	574	Gδ
Yellow	597	Gε
Orange	609	Sδ
Red	619	Gζ
Deep red	647	Gη

(Exhibited by Mr. Crookes.)

GEORGE FOWNES, F.R.S.

A.D. 1815—1849),

One of the early Secretaries of the Society.

Oil of Bran.—This is a portion of the oily liquid obtained by distilling bran with diluted sulphuric acid, from which, in the year 1845, Fownes, the first Professor of Chemistry to the Pharmaceutical Society, isolated a substance which he called "furfurol" (*furfur*, bran, and *oleum*, oil—*Phil. Trans.* 1845).

Furfurine.—This derivative of furfurol, isomeric with furfuramide, was discovered by Fownes, by whom the present specimen was prepared.

Furfurine Nitrate.—Specimen prepared by Fownes.

(Exhibited by Prof. Dunstan.)

EDWARD DANIELL, F.R.S.,

Professor of Chemistry in King's College.

Cell of Daniell's Original Battery.

Daniell's Constant Battery (large cells).

Daniell's Gas Battery.

Daniell's Hypometer on Air-Pump Receiver,

Daniell's Original Pyrometer, with iron case for heating substances in.

(Exhibited by the Council of King's College, London.)

THOMAS THOMSON, F.R.S.

Small Chemical Balance, originally belonging to Prof. Thomas Thomson. F.R.S.

(Exhibited by Prof. J. M. Thomson.)

THOMAS ANDREWS, F.R.S.,

Professor of Chemistry in Queen's College, Belfast.

Collection of Apparatus used by the late Dr. Andrews in his researches:—

1. Six straight Tubes used in experiments on Ozone.
2. Two bent Tubes employed for the same purpose.
3. Two Tubes used in attempts to liquefy the "permanent" gases.
4. A compression Apparatus used in his experiments on the continuity of the liquid and gaseous states.
5. The first Apparatus with which Andrews worked on this subject. (The compression screw and the tube containing carbonic anhydride are not the original ones.)
6. A Tube ready calibrated for the above.
7. A Wooden Curve Model, showing the changes of volume which carbonic anhydride experiences under different conditions of temperature and pressure.
8. A Calorimeter used in determinations of the heat of combination.

(Exhibited by Prof. Letts, Queen's College, Belfast.)

Later and perfected forms of Apparatus used by Andrews in his researches on the critical point of gases and liquids.

(Exhibited by the Science and Art Department, South Kensington.)

JAMES PRESCOTT JOULE, D.C.L., F.R.S.

Model of the Calorimeter used by him in the determination of the Mechanical Equivalent of Heat.

(Exhibited by the Science and Art Department, South Kensington.)

WALTER WELDON, V.P.C.S.

Complete model of a plant for his chlorine process.

(Exhibited by the Science and Art Department, South Kensington.)

DR. EDWARD SCHUNCK, F.R.S.,

Sometime Vice-President of the Society.

Indirubin, crystallised.—The red colouring matter always formed by decomposition of indican along with indigo blue, with which it is isomeric, probably identical with the indigo-red of Berzelius. Dyes red, or rather purple, using the same process as that employed for dyeing blue with indigo-blue.

Chrysammic Acid.—First obtained by the action of nitric acid on aloes in 1841. Is a nitro compound of a di-oxyanthraquinon. Magnesium chrysammate is the most beautiful of its salts.

Magnesium chrysammate.

Anthraruflavic Acid and Iso-anthraflavic Acid.—These are isomerides of alizarin which are formed during the process of the artificial production of the latter. As they are not in the least tinctorial their presence is not desirable, and their formation is prevented as much as possible.

Anthrarufin.—Another isomeride of alizarin formed by the action of sulphuric acid on meta-oxybenzoic acid.

Flavopurpurin.—A trioxyanthraquinon formed by suitable means from anthraflavic acid. It is used in dyeing. The corresponding purpurin from iso-anthraflavic acid is Dr. Perkin's anthrapurpurin.

Tribromflavopurpurin.

Diacetylflavopurpurin.

Phyllotaonin.—Remarkable as being the first derivative of chlorophyll obtained in well-defined measurable crystals. All products previously obtained from chlorophyll were either amorphous or merely crystalline. Ethyl-phyllotaonin and methyl-phyllotaonin are pretty bodies, the solutions of which show a distinct absorption spectrum.

Ethyl-phyllotaonin.

Methyl-phyllotaonin.

(Exhibited by Dr. Schunck.)

WILLIAM FRANCIS, PH.D., F.L.S., F.C.S.

Liebig's Combustion Furnace and Potash Bulbs for organic analysis. The first specimens brought to this country from Giessen, by Dr. Francis, in the year 1842.

Coloured Daguerreotype by Beard. This was one of the first ever taken, and was done at the same time as that of Mr. Robert Warington.

(Exhibited by Dr. Francis.)

ROBERT WARINGTON, F.R.S.

The Jubilee Album, containing the Letters received by Mr. Warington in reply to the circular inviting persons to become Members of the proposed Chemical Society, with various printed papers relating to the formation and early history of the Society and Portraits of 44 of the Original Members.

The Obligation Book of the Chemical Society, containing the signatures of Fellows on joining the Society. On page 1 are the signatures of 53 Original Fellows.

Early Photographs of W. T. Brand, M. Faraday, G. Fownes, T. Graham, W. Gregory, Justus von Liebig, R. Phillips, and R. Warington.

Early Daguerreotype, one of the first taken in London. Portrait of R. Warington.

Berzelius's Filter-Paper. Portion of a parcel sent to Dr. Ed. Turner before 1837.

Dalton's '*Graphic Formulæ*,' published 1835.

(Exhibited by Mr. R. Warington.)

GEORGE MATTHEY, F.R.S.

Platinum Snuff-box. The lid stamped to show the ductility of the metal; made about the year 1816, by the late P. N. Johnson, F.R.S., founder of the firm of Johnson, Matthey, and Co., and used by him until his death in 1864.

Another, made in St. Petersburg about the year 1830.

Platinum Coin or Medal, made in St. Petersburg, 1826.

Nugget of Native Platinum, found in the Ural district very early in the present century Weighs 166 ounces.

Specimen of Jacotinga from the Brazils, in which the greater portion of the palladium was found associated with the gold-dust obtained from it.

Specimens of the six metals of the platinum group, namely, platinum, palladium, rhodium, ruthenium, iridium, and osmium.

(Exhibited by Mr. George Matthey.)

JOHN SPILLER, F.C.S.

Frame of Early Photographs.

(Exhibited by Mr. Spiller.)

Portraits of Past Presidents of the Chemical Society:—

T. Graham (1841—1843, 1845—1847). W. Aikin (1843—1845). W. T. Brande (1847—1849). R. Phillips (1849—1851). C. Daubeny (1851—1853). P. Yorke (1853—1855). W. A. Miller (1855—1857, 1865—1867). L. Playfair (1857—1859). B. C. Brodie (1859—1861). A. W. Van Hofman (1861—1863). A. W. Williamson (1863—1865, 1869—1871). W. De la Rue (1867—1869, 1879—1880). E. Frankland (1871—1873). W. Odling (1873—1875). F. A. Abel (1875—1877). J. H. Gladstone (1877—1879). H. E. Roscoe (1880—1882). J. H. Gilbert 1882—1883) W. H. Perkin (1883—1885). H. Müller (1885—1887). W. Crookes (1887—1889).

Robert Warington, First Secretary of the Society.

Henry Watts, Editor of the Journal, and Librarian of the Society.

G. Longstaff, Founder of the Longstaff Medal.

Justus von Liebig, sometime Foreign Member.

Prof. Mendelejeff, Foreign Member.

PHYSICAL SOCIETY.

February 27th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

PROF. A. GRAY was elected a member of the Society.

THE following communications were read:—

"*Proof of the Generality of Certain Formulæ Published for a Special Case by Mr. Blakesley. Tests of a Transformer.*" By W. E. AYRTON, F.R.S., and Mr. J. F. TAYLOR.

In 1888, Mr. Blakesley published a number of formulæ relating to the measurement of power, &c., in alternating current circuits by means of electro dynometers, one of which had its two coils independent, and placed in different circuits. These formulæ were deduced on certain assumptions, the chief ones being that the currents and magnetisations varied harmonically, and that the magnetic stress in the iron was proportional to the ampère turns. The present paper shows that the above assumptions are not necessary to the truth of the resulting formulæ. To take the case of a transformer:—Let alternating current ammeters be placed in the primary and secondary circuits, and a direct reading "split dynamometer" have a coil in each circuit. Let D_p, D_s, and D_{ps} be the respective readings of these instruments, then, whatever be the law of variation of the currents,—

$$\left.\begin{aligned} D_p &= \sqrt{\frac{1}{T}\int_0^T A_p^2\,dt}, \\ D_s &= \sqrt{\frac{1}{T}\int_0^T A_s^2\,dt}, \\ \text{and}\quad D_{ps} &\sqrt{\frac{1}{T}\int_0^T A_p A_s\,dt}; \end{aligned}\right\}$$

where A_p and A_s are the values of the primary and secondary currents at any instant, and T the time of one complete alternation.

If i be the total induction in the core, P and S the number of turns of wire on the primary and secondary respectively, V_p and V_s the terminal pressures, p the resistance of the primary coil, and s the resistance of the whole secondary circuit, then the following equations hold at any instant:—

$$\left.\begin{aligned} V_p &= pA_p + P\frac{di}{dt} \\ \frac{di}{dt} &= \frac{s}{S}A_s \end{aligned}\right\}$$

Therefore—

$$V_p = pA_p + \frac{P}{S}sA_s;$$

multiplying both sides by A_p we get—

$$A_p V_p = p\,A_p^2 + \frac{P}{S}s\,A_p A_s,$$

and integrating from $t=0$ to $t=T$, and taking the mean,

$$\frac{1}{T}\int_0^T A_p V_p\,dt = \frac{p}{T}\int_0^T A_p^2\,dt + \frac{P}{S}\frac{s}{T}\int_0^T A_p A_s\,dt,$$

or Watts in primary $= pD_p^2 + \frac{P}{S}sD_{ps}$, quite independent of the laws of variation of A and V.

The power lost in heating the iron core was also shown to be—

$$s\left(\frac{P}{S}D_{ps} - D_s^2\right)$$

Other formulæ, such as that given by Mr. Blakesley expressing the primary volts in terms of the dynamometer readings, are shown to be true generally.

On the subject of transformer magnetisations, the authors state that it is desirable not to speak merely of the ampère-turns, but also of the self-induction, for they have reason to believe that the magnetising value of an ampère-turn varies. Defining the self-induction of the secondary by the equation $L_s = \frac{dN}{dA_s}$, N being the total flux through the secondary, they show geometrically (assuming harmonic variations) that if L_s diminishes, the efficiency increases, and, at the same time, the phase angle, θ, between the primary and secondary currents, and the magnetic lag, ϕ, decrease. On comparing this theoretical deduction with the results of experiment, they find a good agreement, as will he seen from the following table:—

Frequency.	Efficiency.	L_s.	θ.	ϕ.
160	96·3%	0·0017	113°	0° 24′
,,	92%	0·0368	169°	18° 24′
,,	85·4%	0·1241	174·6°	45° 36′

The above tests were made on a Mordey transformer, kindly lent by the Brush Electrical Engineering Corporation.

Similar results were obtained in different sets of experiments. It was also noticed that as the secondary current is increased, the efficiency rises to a maximum and then diminishes, whilst L_s, θ, and ϕ diminish and then rise again; the current which gives he maximum efficiency coinciding almost exactly with that which gives the minimum values to L_s, θ, and ϕ.

The methods employed in making the tests are described in the paper, and the formulæ used in working out the results are there demonstrated. Amongst the facts deducible from the experiments are the following:—

1. With constant frequency, the ratios $\frac{V_s}{V_p}$ and $\frac{D_s}{D_p}$ increase as the primary volts rise.
2. With frequency constant, and primary volts constant, $\frac{V_s}{V_p}$ decreases and $\frac{D_s}{D_p}$ increases as the secondary current increases.
3. With constant secondary current, L_s decreases as the primary volts are increased.
4. With small constant secondary currents, the efficiency diminishes as the frequency increases.
5. For large secondary currents the efficiency is approximately independent of the frequency.
6. Shunting the secondary with a condenser increases the efficiency.

"*Further Contributions to Dynamometry.*" By T. H. Blakesley, M.A.

The object of Mr. Blakesley's paper was, in the first place, to show what sort of physical quantities could be advantageously evaluated by using electro-dynamometers of two coils of low resistance in circuits conveying electric currents. The meaning of a dynamometer reading was explained to be the mean value of the product of two currents, either steady or undergoing any periodic variations, with sufficient rapidity. In mathematical language, such an instrument measured—

$$\frac{1}{T}\int_0^T C_1C_2dt\,;$$

where C_1 and C_2 were the instantaneous values of the currents in the two coils, including, of course, the common case where these currents are identical.

Any physical quantity whose value was such a product, C_1C_2, multiplied into something which was independent of the time, and which therefore on integration came outside the integrator, was well adapted to have its mean value given by such instruments. Power was such a quantity, being merely $(\text{Current})^2 \times$ resistance. The square of an E.M.F. was another such quantity, but he did not wish to restrict the method to such evaluations.

It follows that any quantity whose instantaneous value can be expressed by terms each quadratic in current, and whose other factor was independent of time, could have its mean value expressed in dynamometer readings. In addition, the particular place and mode of coupling of the dynamometers was indicated by the instantaneous equation, as well as the factor to be applied to such reading. *Thus the equations are made to indicate the practical arrangement to be adopted, and the use to be made of the observations* in each case.

Examples were given for the cases of transformers in series and parallel, and special applications of the method were suggested in the measurement of the power employed in such diverse apparatus as voltameters subject to direct or variable currents of any sort, welding machines, parallel generators, tuning-fork circuits, vacuum discharges, and imperfect condensers. For parallel generators the power of each could be separately estimated, and in the case of electric welders the power employed in the welding circuit was shown to be measurable without introducing any resistance whatever into that circuit.

Mr. J. Swinburne said the author's assumtion that there is no back or forward E.M.F in the primary and secondary circuits of transformers, except that due to $\frac{di}{dt}$, where i is the total induction in the core, was unwarrantable, for in all real transformers there was a "drop" due to waste field, and this made the split dynamometer method useless. It makes the full load efficiencies too high; and this, he thought, accounted for the extraordinary results obtained by Prof. Ayrton and Mr. Taylor. If a dynamometer be used at all, it should, he said, be used as a wattmeter, the moving coil of one turn being joined in series with a non-inductive resistance and put as a shunt to the primary. The power absorbed by the instrument itself should be then determined, and the power given out by the secondary measured by the same instrument, if the secondary be not non-inductive. Any errors due to self-induction in a wattmeter are, he said, equally present when it is called a split dynamometer, and, in addition to this, the wattmeter as a split dynamometer precludes the possibility of measuring power.

Mr. Mordey said the results obtained by Prof. Ayrton and Mr. Taylor confirmed experiments he had made himself by an entirely different method, for he found that the losses in the iron decreased considerably as the secondary current increased, and this gave increased efficiency. In his experiments he kept the load constant until the transformer attained a steady temperature, and then substituted a direct current for the alternating one, varying its strength until the same steady temperature was maintained. The power thus supplied is a measure of the loss in the transformer under the working condition. A 6-kilowatt transformer tested by this method gave a loss of 110 watts at no load, and at full load 205. Of this 205, 176 was accounted for by the loss in the copper coils, leaving only 29 watts as the iron losses at full load. Figures which he quoted from Prof. Ayrton and Mr. Taylor's paper showed the same general result.

A "Note on Electrostatic Wattmeters," by Mr. J. Swinburne, and a paper on "Interference with Alternating Currents," by Prof. W. E. Ayrton, F.R.S., and Dr. Sumpner, were postponed.

ROYAL INSTITUTION OF GREAT BRITAIN

General Monthly Meeting, March 2, 1891.

William Crookes, F.R.S., Vice-President, in the Chair.

Miss Emily Aston, B.Sc; Henry Daw Ellis, M.A.; Francis Fowke; Augustus William Gadesden, J.P.; Miss Emily Dorah Locock; Signor Alberto Randegger; The Hon. Frederick Hamilton Russell; and John Wilson Walter were elected Members of the Royal Institution.

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

NOTICES OF BOOKS.

Sewage Treatment; or, the Purification of Water Carried Sewage. By H. Leonard Linnell, Ass. Mem. Inst. C.E. Bolton: Tillotson and Son.

From the small bulk of this work the various methods of dealing with sewage cannot be very fully described. The author very properly abstains from recommending any one system as universally applicable. For towns on the seaside—and he might have added, for those on tidal rivers—he justly condemns all devices for impounding the sewage and letting it out during ebb-tide. Concerning inland towns, he ventures on the statement that chemical precipitation processes have hitherto failed to effect the needful degree of purification.

For villages and public buildings he makes no mention either of the pail system or the dry-closet treatment.

In discussing the disposal of the sludge from the treatment of sewage, he mentions without merited condemnation the schemes of burning, first recommended, we believe, by the late General Scott, and that of conveying it out into the sea. Both these methods, as far as the mere waste of plant-food is concerned, are fully on a level with the old system of letting the sewage flow simply into the nearest river, as it was done in London before the construction of the intercepting sewers.

Mr. Linnell is in favour of keeping the storm-water distinct from the sewage properly so called. This system has everything in its favour except the cost of a double system of sewage. The author's proposal to let the top water escape over a weir when the sewage reaches a certain height cannot be recommended, as, especially in a sudden storm after a long duration of dry weather, the overflow water contains a very large share of the suspended impurities.

The proposal to exclude "the refuse from chemical works, tanneries, dye-works, &c.," from the sewers is quite justifiable in theory. But what is to be done with such waste waters? They cannot be permitted to flow into the streams, nor to collect in ponds.

The precipitation processes described are not numerous, and as a rule they find too favourable a judgment. Some few errors in points of fact are met with; but had the author visited all the towns where the processes mentioned are in action and used his eyes and nose in conjunction, we think he would have found good reason to alter his opinion.

The author has certainly compressed into a very brief compass a remarkable quantity of information concerning sewage and its treatment.

Heat as a Form of Energy. By Robert H. Thurston, Director of Sibley College, Cornell University. London: William Heinemann.

The present work is the third volume of "Heinemann's Scientific Handbooks," and reproduces the general preface to which we have already called attention. There is also a special preface, the writer of which speaks of the precincts ascribed "to the physicist and the man of science." It is generally held that the physicist is one kind of the man of science. In this same preface the labours of the old philosophers receive but scant justice. We read of "the discovery of one logical fact and one physical truth after another." Surely the inquirer may here ask what is the meaning of a "logical fact?"

In the body of the work the author treats successively of the "Philosophers' Ideas of Heat," the Science of Thermodynamics, Heat-Transfer and the World's Industries, Air and Gas-Engines, their Work and their Promise, the Development of the Steam-Engine, and winds up with a summary. The view here given of heat and its laws is fully in accordance with the present state of our knowledge, and may therefore be accepted by the student as sound and trustworthy. On this very account it will call forth the wrath of the so-called "substantialists," a school of scientific heretics who have arisen in America, and who regard heat, and, we believe, even sound, as not modes of motion but substances. Mr. Thurston seems, however, if we may use the expression, to have his centre of gravity not so much in science as in industrial art. Hence he indulges somewhat magniloquently in the glorification of inventors. He forgets that in certain cases the good and the evil of invention are very nearly balanced, and that in others the latter may preponderate. Mechanical devices doubtless play the part formerly assigned to slaves; but like slaves they sometimes reduce those who are not their owners to a position similar to that of the former "mean whites" in the "slave States" of America.

We must enter our protest against a view here expressed: —"The fact illustrates a common experience—that practice and invention very often, if not generally, precede science, the latter coming in later to explain a result felt out by the inventor, or perceived by him by that peculiar intuition which is his birthright." The intuition of the inventor in lack or in defiance of the teachings of science leads sometimes to strange results. But putting this on one side, we must urge that as far as chemical inventions are concerned, their authors as a rule proceed on strictly scientific principles. The coal-tar colours are not the fruit either of "practice or of intuition."

In conclusion, we may say that to a numerous class this work will prove both welcome and useful. The index is very imperfect.

CORRESPONDENCE.

IMPURE POTASSIUM SULPHOCYANIDE.

To the Editor of the Chemical News.

Sir,—In working recently with a specimen of potassium sulphocyanide, I became suspicious of its purity. To test this I estimated its percentage of sulphur, which was found to be only 10·1. Pure potassium sulphocyanide contains 32·95 per cent. About 150 grms. of the salt were therefore taken, dissolved in water, and re-crystallised in vacuo. The first crop of crystals, about 40 grms., was rejected. The next crop was examined and found to consist of small, well formed cubes, containing 10·22 per cent of sulphur. Since potassium sulphocyanide crystallises in long slender prisms, the cubic form of these crystals led me to look for chlorides. The following method was devised to separate and estimate any chlorine present. The impure salt was oxidised with excess of permanganate. The hydrocyanic acid formed during the oxidation was then got rid of by continued boiling with nitric acid. I then estimated the chloride present in the usual manner with silver nitrate.

The mean of three determinations gave 28·75 per cent of chlorine.

Three fresh samples of sulphocyanide were then obtained from three different makers, and examined by the above method. In each case only the merest trace of chlorine was found.

Calculating the chlorine found in the impure salt, into potassium chloride, and the sulphur into potassium sulphocyanide, we find—

KCl	60·44 per cent.
$KCNS$	31·01 ,,
	91·45

As, except a trace of sulphate, no other impurities were found, it is probable that during the boiling with nitric acid some of the chlorine was lost. The above method does not, therefore, pretend to quantitative accuracy, but is a rapid and convenient method of discovering and approximately estimating chlorine in sulphocyanide.

Probably a considerable stock of the impure specimen has been cast upon the market: I think it well, therefore, to draw the attention of chemists to chlorine as a possible impurity in commercial sulphocyanide.

It may also be worthy of notice that in the presence of a large proportion of alkaline chloride, potassium sulphocyanide crystallises in cubes.—I am, &c.,

James Hendrick.

Chemical Laboratory, King's College, London.

ATOMIC WEIGHTS.

To the Editor of the Chemical News.

Sir,—With reference to the recent re-determinations of atomic weights in the platinum group, I should like to point out to readers of the Chemical News who may be in the habit of using Mr. Johnstone's useful little book, the "Analyst's Laboratory Companion," that the old erroneous weight of platinum is there given, viz., 197·2 instead of 194·3. The weight of osmium also is given as 198·5 instead of 190·3. The latter error is of course less material to the analyst, but it is very desirable that the exact equivalent of such a reagent as platinum should be used in calculating the results of our analyses.—I am, &c.,

F. H. P. C.

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. cxii., No. 8, February 23, 1891.

The Isolation of the Glycolytic Ferment of the Blood.—R. Lépine and Barral.—The experiment of the authors proves that the glycolytic power of the blood cannot be considered as a vital property of the albumen of the blood. In the series of three liquids, the serum, the first washings, and the second washings, the albumen decreases enormously, whilst the glycolytic power increases in the liquid and decreases in the globules. This transfer of the glycolytic power from the globules into the washing-water argues in favour of a soluble ferment.

On the Spectrum of α-Lyræ.—H. Deslandres.—The author, in opposition to Mr. Fowler, finds that the K ray of calcium in the spectrum of the star appears fine, distinct, and manifestly single; the nearest ray is at the distance of $\frac{7}{20}$ millimetre.

Testimonial to Professor Stas.—The Royal Belgian Academy is opening a subscription to present a gold medal to J. S. Stas on May 5th, by occasion of the 50th anniversary of his mastership of the Science section of the Belgian Academy.

The Compressibility of Mixtures of Air and Hydrogen. — Ulysse Lala. — The mixtures studied contained, respectively, 16·38, 28·12, 33·08, 39·28, and 49·89 per cent of hydrogen. The compressibility of mixtures in which the proportion of hygrogen increases from 16·31 is intermediate between those of air and of hydrogen for initially feeble pressures which increase with the proportion of hydrogen, and may rise to 175 c.m. of mercury for a mixture containing 49·89 per cent of hydrogen. But this compressibility deviates from Mariotte's law in the same direction as does that of hydrogen.

Position of the Luminous Vibration.—M. Carvallo.—The author's conclusions are that the laws of double refraction are not altered by dispersion. Calculation shows that M. Sarrau's system possesses the property that Briot's terms of dispersion do not introduce any perturbation in the laws of monochromatic double refraction, and that it is the only known system possessing this property.

Solubility of Potassium Bitartrate.—Ch. Blarez.—The solubility of cream of tartar in water, which is a function of the temperature θ, may be calculated by the quantity of the substance Q dissolved in 100 grms. of solution $Q\theta = 0{\cdot}351 + 0{\cdot}001510\theta + 0{\cdot}000055\theta^2$. Its solubility in water is decreased by the presence of potassium chloride.

Transformation of Starch into Dextrine by the Butyric Ferment.—A. Villiers.—Besides certain substances formed in very small quantities, the chief products of fermentation are dextrines not attacked by *Bacillus amylobacter.*

Distribution of Sodium Chloride according to Altitude.—A. Muntz.—The author mentions that in Alpine pastures sheep, &c., can smell salt. The rain-water and the herbage of elevated regions are much poorer in sodium chloride than those of the lowlands, and the milk and the blood of animals feeding on the mountains contain a decidedly less proportion of the same salt than do those of similar animals from the plains.

Revue Générale des Sciences Pures et Appliquées. Vol. ii., No. 2, January 30, 1891.

Photography of Objects at a Great Distance by the Intervention of the Electric Current.—Marcel Brillouin.—The author points out a difficulty which he thinks for the present insurmountable. To produce a luminous image, distinct to the naked eye, of 4 centimetres in diameter, the transmitting apparatus must completely obey the changes of illumination to which it it submitted in less than $\frac{1}{5000000}$ of a second in round numbers.

Annual Review of Applied Chemistry.—This consists of two distinct memoirs on the great chemical industries by Dr. G. Lunge, and on colouring matters and organic products by Ph. A. Guye. In the former are summarised an account of the invention of nickel oxychloride by Mond, Langer, and Quincke; remarks on water-gas; the recent improvements in the production of oxygen from air by the intervention of baryta, and by the ignition of a mixture of lead oxide and lime carbonate. The United Alkali Company is next discussed, and new methods of obtaining bleaching lime, or of bleaching without the use of this compound, *e.g.*, by electrolysis, are considered. In the paper on colouring matters it is stated that the red "de Saint Denis" is more brilliant than turkey red. Diamido azoxybenzene may be diazotised in each of its two groups NH_2; on causing the diazo compound formed to react upon α-sulpho α-naphthol the splendid scarlet colour just mentioned is formed. Concerning indigo, it is remarked that in spite of recent improvements the synthetic compound has not yet dethroned the natural product, and that the task of the assailants become from day to day more difficult. The yield of the plantations have been improved by a judicious selection of species. According to Schrottky there is still a possibility of utilising the natural product in a better manner by hindering or regulating certain phenomena of fermentation which take place in the vats at the cost of the colouring matter.

Bulletin de la Société Chimique de Paris. Series 3, Vol. iv., No. 9.

This issue contains no original papers.

MISCELLANEOUS.

The Chemical Laboratory of Wiesbaden.—The Chemical Laboratory of Geh. Hofrath Prof. Dr. Fresenius at Wiesbaden enjoys a very large attendance. In the winter term, 1890 91, there were 81 students on the books. Of these, 61 were from Germany, 4 from England, 3 from Austria, 3 from Russia, 3 from Spain, 2 from North America, 1 from Luxemburg, 1 from Belgium, 1 from France, 1 from Norway, and 1 from Bulgaria. Besides the director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, and Architect Brahm. The assistants in the instruction laboratory are 2 in number, in the private laboratory 17, in the Versuchs-station 2. The next summer term begins on the 24th of April. During the last term, besides the scientific researches, a great number of analyses were undertaken in the different departments of the laboratory, and in the Versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

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.

Removing Ink.—Can you inform me of any bleaching agents or chemicals that will remove writing and printing ink from paper? I have tried muriatic, also oxalic, acid applied with a brush, but find it does not quite remove the ink; so should be pleased to hear of something stronger, and the best means of applying the same. It does not matter if it bleaches the paper, so long as it *entirely* removes the ink and does not destroy the surface.—A. W.

MEETINGS FOR THE WEEK.

Monday, 16th.—Medical, 8.30.
—— Society of Chemical Industry, 8. "Observations made in the Working of Vitriol Chambers," by W. Crowder. "The Chemistry of Whisky and Allied Products," by A. H. Allen.
—— Society of Arts, 8. "Photographic Chemistry," by Prof. R. Meldola, F.R.S.
Tuesday, 17th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Society of Arts, 8. "Recent Development of Tasmanian Industries," by Sir Edward N. C. Braddon, K.C.M.G., Agent-General of the Colony.
—— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S.
Wednesday, 18th.—Society of Arts, 8. "Harbours, Natural and Artificial," by F. H. Cheesewright.
—— Meteorological, 7.
—— Microscopical, 8.
Thursday, 19th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "Modern Chemistry in Relation to Sanitation," by Professor C. Meymott Tidy.
—— Chemical Society, 8. "The Molecular Refraction and Dispersion of various Substances," by Dr. J. H. Gladstone, F.R.S. "Contributions to our Knowledge af the Aconite Alkaloids—Part I. The Crystalline Alkaloid of *Aconitum repellus*, by Prof. Dunstan and Dr. W. H. Ince. "The Crystallographic Character of Aconitine from *Aconitum napelius*," by A. E. Tutton.
Friday, 20th.—Quekett, 8.
—— Physical Society, 5. "The Theory of Dissociation into Ions, and its Consequences," by S. U. Pickering, F.R.S. "Some Points in Electrolysis," by J. Swinburne. "The Variation of Surface-Tension with Temperature," by A. A. Selby, M.A. "On Magnetic Proof-pieces and Proof-planes," by Prof. S. P. Thompson.
—— Royal Institution, 3. "Hydrophobia," by Prof. Victor Horsley, F.R.S.
Saturday, 21st.—Royal Institution, 3. "The Forces of Cohesion," by The Right Hon. Lord Rayleigh, F.R.S.

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THE CHEMICAL NEWS.
Vol. LXIII., No. 1634.

REPORT OF PROGRESS IN SPECTRUM WORK.*

By Professor HENRY A. ROWLAND.

During the past year or two a great deal of work has been done in the photography of the spectra of elements and the identification of the lines in the solar spectrum, which it will take a long time to work up, ready for publication. Hence, I have thought that a short account of what has been done up to the present time might be of interest to workers in the subject. In the prosecution of the work financial assistance has been received from the Rumford Fund of the American Academy of Arts and Sciences, as well as from the fund given by Miss Bruce to the Harvard Astronomical Observatory for the promotion of research in astronomical physics, and the advanced state of the work is due to such assistance.

The work may be summed up under the following heads:—

1. The spectra of all known elements, with the exception of a few gaseous ones, or those too rare to be yet obtained, have been photographed in connection with the solar spectrum, from the extreme ultra violet down to the D line, and eye observations have been made on many to the limit of the solar spectrum.

2. A measuring engine has been constructed with a screw to fit the above photographs, which, being taken with the concave grating, are all normal spectra and to the same scale. This engine measures *wave-lengths direct*, so that no multiplication is necessary, but only a slight correction to get figures correct to $\frac{1}{100}$ of a division of Angstrom.

3. A table of standard wave-lengths of the impurities in the carbons, extending to wave-length 2000, has been constructed to measure wave-lengths beyond the limits of the solar spectrum.

4. Maps of the spectra of some of the elements have been drawn on a large scale ready for publication.

5. The greater part of the lines in the map of the solar spectrum have been identified and the substance producing them noted.

6. The following rough table of the solar elements has been constructed entirely according to my own observations, although, of course, most of them have been given by others.

I do not know which are the new ones, but call attention to Silicon, Vanadium, Scandium, Yttrium, Zirconium, Glucinum, Germanium, and Erbium, as being possibly new.

Silicon has lines on my map at wave lengths 3905·7, 4103·1, 5708·7, 5772·3, and 5948·7. That at 3905·7 is the largest and most certain. That at 4103·1 is also claimed by Manganese.

These tables are to be accepted as preliminary only, especially the order in the first portion. However, being made with such a powerful instrument and with such care in the determination of impurities, they must still have a weight superior to most others published.

The substances under the head of "Not in the Solar Spectrum" are often placed there because the elements have few strong lines or none at all in the limit of the solar spectrum when the arc spectrum, which I have used, is employed. Thus boron has only two strong lines at 2497. Again, the lines of bismuth are all compound and so too diffuse to appear in the solar spectrum. Indeed, some good reason generally appears for their absence from the solar spectrum. Of course, this is little evidence of their absence from the sun itself.

Elements in the Sun, Arranged According to the Intensity and the Number of Lines in the Solar Spectrum.

According to Intensity.	According to Number.
Calcium.	Iron (2000 or more).
Iron.	Nickel.
Hydrogen.	Titanium.
Sodium.	Manganese.
Nickel.	Chromium.
Magnesium.	Cobalt.
Cobalt.	Carbon (200 or more).
Silicon.	Vanadium.
Aluminium.	Zirconium.
Titanium.	Cerium.
Chromium.	Calcium (75 or more).
Manganese.	Scandium.
Strontium.	Neodymium.
Vanadium.	Lanthanum.
Barium.	Yttrium.
Carbon.	Niobium.
Scandium.	Molybdenum.
Yttrium.	Palladium.
Zirconium.	Magnesium (20 or more).
Molybdenum.	Sodium (11).
Lanthanum.	Silicon.
Niobium.	Strontium.
Palladium.	Barium.
Neodymium.	Aluminium (4).
Copper.	Cadmium.
Zinc.	Rhodium.
Cadmium.	Erbium.
Cerium.	Zinc.
Glucinum.	Copper (2).
Germanium.	Silver (2).
Rhodium.	Glucinum (2).
Silver.	Germanium.
Tin.	Tin.
Lead.	Lead (1).
Erbium.	Potassium (1).
Potassium.	

Doubtful Elements.

Iridium.
Osmium.
Platinum.
Ruthenium.
Tantalum.
Thorium.
Tungsten.
Uranium.

Not in Solar Spectrum.

Antimony.
Arsenic.
Bismuth.
Boron.
Nitrogen (vacuum tube).
Cæsium.
Gold.
Indium.
Mercury.
Phosphorus.
Rubidium.
Selenium.
Sulphur.
Thallium.
Praseodymium.

Substances not yet Tried.

Bromine.
Chlorine.
Iodine.
Fluorine.
Oxygen.
Tellurium.
Gallium.
Holmium.
Thulium.
Terbium, &c.

Indeed, were the whole earth heated to the temperature of the sun, its spectrum would probably resemble that of the sun very closely.

With the high dispersion here used the "basic lines" of Lockyer are widely broken up and cease to exist. Indeed, it would be difficult to prove anything except accidental coincidences among the lines of the different elements. Accurate investigation generally reveals some slight difference of wave-length or a common impurity.

Furthermore, the strength of the lines in the solar spectrum is generally very nearly the same as that in the electric arc, with only a few exceptions, as, for instance, calcium. The cases mentioned by Lockyer are generally those where he mistakes groups of lines for single lines, or even mistakes the character of the line entirely. Alto-

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* *Johns Hopkins University Circulars*, Vol x., No. 85.

gether there seems to be very little evidence of the breaking up of the elements in the sun as far as my experiments go.

Even after comparing the solar spectrum with all known elements, there are still many important lines not accounted for. Some of these I have accounted for by silicon, and there are probably many more. Of all known substances this is the most difficult to bring out the lines in the visible spectrum, although it has a fine ultra violet one. Possibly iron may account for many more, and all the elements at a higher temperature might develop more.

Then, again, very rare elements, like scandium, vanadium, &c., when they have a strong spectrum, may cause strong solar lines, and thus we may look for new and even rare elements to account for very many more. Indeed, I find many lines accounted for by the rare elements in gadolinite, samarskite, and fergusonite other than yttrium, erbium, scandium, praseodymium, neodymium, lanthanum, and cerium, which I cannot identify yet, and which may be without a name. For this reason, and to discover rare elements, I intend finally to try unknown minerals, as my process gives me an easy method of detecting any new substance or analysing minerals, however many elements they may contain.

The research is much indebted to the faithful and careful work of Mr. L. E. Jewell, who has acted as my assistant for several years. Preliminary publications of results will be made in the *Johns Hopkins University Circulars.*

Among the latest results I may mention the spectroscopic separation of yttrium into three components, and the actual separation into two.

RESEARCHES ON "OIL FOR REDS" (ALIZARIN OIL).

By M. SCHEURER-KESTNER.

The sulphonic compound which is found in "oil for reds" may be isolated by treating this product with a suitable mixture of water and ether. The ether dissolves the fatty acids which are not sulphonised (or rather desulphonised by the action of water during the washing of the crude product obtained on allowing sulphuric acid to act upon castor oil), whilst the sulphonised substance remains in solution in the watery portion, separate from the ethereal stratum. To isolate it the aqueous solution is precipitated with a solution of sodium sulphate at 10° Baumé.

On evaporating the ethereal stratum we obtain the fatty acids, more or less polymerised, the weight of which may be determined, whilst the precipitation of the aqueous solution enables us to give account of the sulphonic body. In general two preparations made under conditions which seem identical do not always give the same results. The "oil for reds" obtained contains variable proportions of the two principal products. The fatty acids by the action of the water during the washings are thus changed to a greater or less extent, and the solubility of the oil in water is so much the greater as these desulphonised fatty acids are present in a smaller quantity. In fact, they are soluble only by reason of the presence of the sulphonised body, and they give the solution that fluorescence from which a solution of oil is never free.

As for the degree of polymerisation, it seems to be more considerable in the substances extracted by ether than in the soluble body. Thus the fatty acids withdrawn from one and the same preparation, and separated in the state of sulphonised and non-sulphonised bodies respectively, gave the molecular weights 402 and 472 (the molecular weight of the normal acid is 298).

Sulphoricinoleic acid, precipitated from its watery solution by sodium sulphate, forms a syrupy hydrate without any appearance of fluorescence when it has been freed from the non-sulphonised fatty acids by means of ethers. It enters into the composition of the most soluble "oil for reds" to the extent of 40 to 50 per cent, the remaining 50 or 60 per cent being formed of fatty acids insoluble in water. In this calculation the accompanying water is disregarded.

The sulpho-fatty acid in an isolated state has a composition approaching that of diricinosulphonic acid.

It is impossible to dehydrate it completely without decomposing it into sulphuric acid and fatty acid. If it is dried at a temperature not exceeding 60° its decomposition is very slight, and it then contains 4 per cent of sulphur.

We may give account of the composition of oil for reds by using in succession litmus and phenolphthalein as indicators. The litmus turns blue as soon as the sulphonic compound is saturated, whilst the phenolphthalein only becomes coloured much later, and then only if the non-sulphonised fatty acid has been saturated. Upon these properties the author has founded an analytical process, which by means of two simple titrations made successively gives the proportion of the two principal elements of oils for reds. The difference between the two values found on making use of a standard solution of ammonia and the indication above mentioned, shows the quantity of ammonia which has served for the saturation of the desulphonised acids.

Care must be taken to use always the same quantities of water, otherwise the results will not be comparable. This experiment may also be useful from a practical point of view, since the author has proved that the tone of the clearing of alizarin colours depends exactly on the presence of a larger or smaller proportion of the sulphonised compound.

The standard found with litmus corresponds to the weight of the barium sulphate which oil for reds gives if its sodium salt has been ignited. It is also easy to follow the polymerisation of ricinoleic acid, measuring it by its capacity for saturation, and making use of phenolphthalein.

Normal ricinoleic acid, if treated with sulphuric acid as castor oil is done, gives a product like that of castor oil. On analysing it by means of double titration the author has found a sulphonised acid and polymerised fatty acids in the proportion of 60—65 to 100 of the former.

He proposes to show ultimately that ricinoleic acid is easily polymerised, not merely by the action of heat, but by that of steam, and that it may be restored to its normal state by the action of soda under certain conditions.—*Comptes Rendus.*

THE DETERMINATION OF NITRIC AND NITROUS ACIDS IN SPRING WATER.

By MAX ROSENFELD.

Pyrogallic acid has not been duly appreciated as a reagent for nitric and nitrous acids. Many experiments have convinced the author that this reagent under certain conditions is not inferior to any other for the detection of nitric acid, and that it appears especially suited for the determination of the above acids in spring water.

For the determination of nitric acid we use a solution of 0·5—1 grm. pyrogallic acid in 100 c.c. water.

For carrying out the reaction the author pours 3 c.c. of the water under examination into a test-glass tapering to the bottom, and adds 6 c.c. of strong sulphuric acid, which is poured in as rapidly as possible from a small test-tube, adding carefully a drop of the pyrogallic acid solution. The upper stratum of the liquid takes at once or in the course of a few minutes (according to the proportion of nitric acid present) a violet to dark brown colour. It is advantageous, about two minutes after the addition of the pyrogallic acid, to turn the liquid carefully round, so that the coloured stratum may occupy the space of about 6 c.c. For this purpose it is well to make a mark on the test-glass indicating the volume (3 c.c.) of the liquid used for the test. If 5 milligrammes nitric acid (N_2O_5) per litre be present the colour appears very distinctly after a few minutes; with 10 milligrammes nitric acid per litre a violet colour appears at once after shaking; with 15 milligrammes the upper stratum appears brown either at once or after a short time. In this manner 1 milligramme of nitric acid may be detected per litre. If there are less than 3 milligrammes nitric acid (N_2O_5) per litre the colour is perceptible only after a time, and must then be compared with the colour which appears under the same circumstances in pure, distilled water. In such a comparative determination not more than one small drop of the reagent must be used, because pure sulphuric acid is turned a light rose by larger quantities of pyrogallic acid. It is further necessary to diffuse the pyrogallic acid through the space above mentioned by careful shaking immediately after it has been added. The difference in the colour of both liquids is distinctly perceptible with a proportion of 1 milligramme nitric acid per litre, and consists herein, that in the nitric acid solution the coloured stratum becomes more intense downwards, and thus appears to have a sharply-marked boundary. In pure distilled water the colour becomes less intense below, and fades away gradually.

In carrying out the reaction it is absolutely necessary to mix the liquid to be tested with sulphuric acid exactly in the proportions here indicated. It occurs in presence of large quantities of nitric acid that the dark colour which first appears disappears again on shaking. In such a case several drops of the pyrogallic acid must be added to the solution.

As the difference of intensity in the colour produced by pyrogallic acid according to the quantity of the nitric acid present, may be distinctly recognised (up to the proportion of 15 milligrammes per litre), and admits of a comparison with the tones of colour obtained in the same conditions in solutions containing a known amount of nitric acid, this method may serve for an estimation of the nitric acid in spring water.

If this estimation is only rough it allows us to decide very rapidly whether a potable water contains more or less than the permissible maximum of nitric acid.

The test-glasses in which the operation is performed must not be previously wiped out with linen or cotton cloths, since even small quantities of cellulose in contact with sulphuric acid produce the colouration of pyrogallic acid.

The author has examined the sensitiveness of Schœnbein's reaction, and finds that there may be founded upon it a comparative colorimetric method for the estimation of small quantities of nitric acid.

The reagent is a solution of 0·5 grm. pyrogallic acid in 90 c.c. of water, to which are added 10 c.c. of concentrated sulphuric acid.

In order to perform the reaction 100 c.c. of the water in question are placed in a narrow cylinder of colourless glass, 18—20 c.m. in height, and mixed with 2 c.c. solution of pyrogallic acid. If the liquid contains 0·4 m.grm. nitrous acid (N_2O_3) per litre, the yellow colour appears immediately; with 0·3 m.grm. in six minutes; with 0·2 in about twenty-three minutes; whilst with 0·1 m.grm. nitrous acid per litre the colour appears only after the lapse of about seven hours. The difference in the colour is perceptible with a difference of 0·005 m.grm. nitrous acid in 100 c.c. of water if this quantity does not contain more than 0·05 m.grm. nitrous acid. With larger proportions the colour, if seen from above through the column of liquid, is too intense to allow of the difference of colouration being distinguished. Within the above limits (0·01—0·05 m.grm. nitrous acid in 100 c.c. of liquid) the differences of colour remain perceptible, so that the limit of error per litre is less than 0·1 m.grm. Pyrogallic acid is also turned yellow by free alkalies.—*Zeitschrift Anal. Chemie.*, vol. xxix., p. 661.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

March 5th, 1891.

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

MR. A. W. OXFORD was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. William Bate, National Explosives Company, Hayle, Cornwall; Alexander Lauder, University College, Bangor, North Wales; Cecil George Freer Thonger, Colonial College, Hollesley Bay, Suffolk.

The following papers were read:—

14. "*Crystalline Form of the Calcium Salt of Optically Active Glyceric Acid.*" By ALFRED E. TUTTON, Royal College of Science, London.

This paper presents the results of a complete crystallographical investigation of the calcium salt, $Ca(C_3H_5O_4)_2,2H_2O$, of the optically active (dextrorotatory) form of glyceric acid described (*Trans.*, 1891, p. 96) by Frankland and Frew. The crystals belong to the monoclinic system, and are hemihedral, the forms $\{111\}$ and $\{011\}$ being only developed at the right-hand extremity of the symmetry axis, and the forms $\{\bar{1}\bar{1}1\}$ and $\{2\bar{1}\bar{1}\}$ at the left extremity. The hemihedrism is also manifested by a difference in the prism faces of the form $\{110\}$, those upon the right side of the symmetry plane being much more brilliant than those upon the left side. The ratio of the axes is $a:b:c = 1·4469:1:0·6694$. A complete table of angles is given, the result of the measurement of a dozen crystals. The optic axial plane is perpendicular to the symmetry plane, and the first median line is nearly perpendicular to the basal plane. The true angle of the optic axes is $2Va_{Li} = 34° 56'$, $2Va_{Na} = 35° 28'$, $2Va_{Te} = 36° 16'$. The mean refractive index β is 1·4496, 1·4521, and 1·4545 for lithium, sodium, and thallium light respectively. The sign of double refraction is positive. The calcium salt of this dextrorotatory glyceric acid must therefore be added to the list of optically active substances whose crystals are also hemihedral, a list which includes all the hitherto well investigated cases.

15. "*Fermentations Induced by the Pneumococcus of Friedländer.*" By PERCY F. FRANKLAND, Ph.D., B.Sc., (London), ARTHUR STANLEY, and WM. FREW.

That this well known micro organism is capable of inducing fermentative changes in suitable solutions of glucose and cane-sugar was first pointed out by Brieger, *Zeit. f, Physiol. Chem.*, vol. viii., p. 306—331, and vol. ix., 1—7). The authors have confirmed these observations of Brieger's, and have further found that the organism ferments maltose, milk-sugar, raffinose, dextrin, and mannitol, but that, like the *Bacillus ethaceticus*, it does not attack dulcitol. They have made a special study of the fermentations of glucose and mannitol, determining quantitatively the proportions in which the several products are formed. These products are in each case ethyl alcohol, acetic acid, generally accompanied by a little formic acid and a trace of succinic acid, carbon dioxide, and hydrogen. Both the glucose and mannitol were in all cases only partially fermented, and the decomposition of the glucose was especially incomplete, glucose being apparently less readily attacked by the organism than mannitol and cane-sugar. The fermentation was not rendered more complete by furnishing the organism with a more abundant supply of nitrogenous food.

In the first instance, fermentations were conducted on 60 grms. of glucose and mannitol respectively, with the following results:—

	I. Grms. glucose.	I. Grms. mannitol.	III. Grms. mannitol.
Ethyl alcohol	0·5897	4·11	5·06
Volatile acids calculated as acetic acid	1·6578	2·9921	3·1617

The products of the mannitol fermentations are not only qualitatively similar to those obtained in the fermentation of the same substance by the *Bacillus ethaceticus*, but the relative proportions in which they are formed are almost identical, the ratio corresponding closely to the molecular proportions

$$2C_2H_5\cdot OH : CH_3\cdot COOH.$$

In the subsequent experiments, in which the volume and composition of the evolved gases were determined, only 12 grms. of mannitol were employed; in this case also very similar ratios were obtained, although a period of two years had elapsed since the above fermentation had been carried on.

The following results of analysis show the composition of the gas evolved in a fermentation with 12 grms. mannitol, after the air in the apparatus had been displaced:—

	16th day.	23rd day.	34th day.	41st day.	Average.
CO_2 ..	51·77	61·29	66·18	65·47	61·18
O_2 ..	0·09	0·15	0·22	0·09	0·14
H_2 ..	47·97	38·26	33·47	34·19	38·47
N_2 ..	0·17	0·30	1·13	0·25	0·21
	100·00	100·00	100·00	100·00	100·00

The lower proportion of carbon dioxide in the earlier part of the fermentation is doubtless due to the liquid saturating itself with the gas, and the excess at the end to the slow decomposition of the calcium bicarbonate formed in the first instance. The average composition of the gas may be taken to be 6 volumes or molecules of carbon dioxide to 4 volumes or molecules of hydrogen. Taking into account the actual volume of gas given off, the several products are in very close accord with the molecular proportions; $9C_2H_6O : 4C_2H_4O_2 : 12CO_2 : 8H_2$, derived from 6 mol. props. of mannitol, 2 mol. props. of carbon dioxide being formed by the action of the acetic acid on the added calcium carbonate.

By plotting out the volumes of evolved gas on a diagram, in which the ordinates represent the volumes in cubic centimetres, and the abscissæ the time of fermentation in days from the date of inoculation, the authors obtain a curve for which the equation is—

$$v = \frac{6\cdot73t^2}{1 - 0\cdot006t + 0\cdot00574t^2}.$$

16. "*The Volumetric Estimation of Tellurium. Part II.*" By B. Brauner, Ph.D.

The author finds that although a solution of iodide in potassium iodide acts on alkaline tellurates in accordance with the equation

$$Na_2TeO_3 + I_2 + 2NaOH = Na_2TeO_4 + 2NaI + H_2O,$$

the action is very slow and incomplete at the ordinary temperature, so that heat must be applied for its completion. On acidification the excess of iodine is set free, but it has hitherto been found impossible to exactly determine the end of reaction by titration with thiosulphate.

The titration of solutions of tellurium dioxide in chlorhydric acid with permanganate is found to be impracticable, as varying quantities of chlorine are evolved during the process.

When a solution of tellurium dioxide in sulphuric acid is titrated with permanganate, the following interchange occurs:—

$$2KMnO_4 + 4H_2SO_4 + 4TeO_2 = K_2SO_4 + \\ + Mn_2(SO_4)_3 + 4H_2O + 4TeO_3.$$

In order to destroy the manganic salt which is formed, either decinormal ferrous sulphate or oxalic acid is added until decolorisation takes place, after which permanganate is added in slight excess. After subtracting the volume of permanganate corresponding to the ferrous salt or to oxalic acid from the total of permanganate added, the quantity of tellurium dioxide is calculated from the volume of permanganate necessary for its oxidation, as if the following action had taken place:—

$$2KMnO_4 + 3H_2SO_4 + 5TeO_2 = K_2SO_4 + \\ + 2MnSO_4 + 3H_2O + 5TeO_3.$$

Owing to the evolution of some oxygen, the quantity of tellurium dioxide found is greater by 1 per cent than that calculated from the equation.

In alkaline solution the change which takes place is that indicated by the equation

$$2KMnO_4 + 3TeO_2 = K_2O + 2MnO_2 + 3TeO_3.$$

After addition of an excess of sulphuric acid oxalic acid is used for re-titration in the manner previously stated, but the results are 0·35 per cent too high. The results obtained by both methods are accurate when the corrections mentioned are applied.

17. "*Chloro- and Bromo-derivatives of Naphthol and Naphthylamine.*" By Henry E. Armstrong and E. C. Rossiter.

This communication is a continuation of one published in the *Proc. Chem. Soc.* in 1889.

1 : 4-*Dichloro-β naphthol.*—A better yield of this compound than is obtained by Zincke's method appears to result from the gradual interaction of chloro-β-naphthol and sulphuryl chloride at ordinary temperatures, about 30 per cent of the chloro- being converted into the dichloro-compound. The mixture obtained on steam-distilling the crude product is sulphonated, and the mixture of salts resulting from the direct neutralisation of the acid solution with potassium carbonate is extracted with boiling alcohol, which dissolves the dichloro- but not the monochlorosulphonate. The dichloronaphthol is recovered by heating the sulphonate with dilute sulphuric acid at 210°.

1 : 4 : 4'-*Trichloro-β-naphthol.*—The oily by-product obtained in preparing a large quantity of trichloro-β-ketonenaphthalene, when allowed to stand during many months, was found to slowly give off hydrogen chloride and to become partially solid; the solid was freed from oil by washing with acetic acid and was re-crystallised from this solvent. The substance thus obtained proved to be a trichloro-β-naphthol, and as it yields 1 : 2 : 3-chlorophthalic acid on oxidation, and is reduced by sodium amalgam to 1 : 4-dichloro-β-naphthol, it is most probably the 1 : 4 : 4'-modification. It crystallises in short soft needles melting at 157—158°; its acetyl derivative melts at 129°.

Chloro-β-naphtholsulphonic Acid.—1-Chloro-, 1 : 3-, and 1 : 4-dichloro-, and 1 : 3 : 4'- and 1 : 4 : 4'4-trichloro-β-naphthol are all sulphonated with the greatest care, each yielding a derivative of 1 : 3'- (Schaefer's) β naphtholsulphonic acid, proof that this is the case being afforded by the formation of this acid from each of the chloro-acids on reduction. This result is noteworthy inasmuch as 3' : 1-dibromo- and bromochloro-β-naphthol—in which the position occupied by the sulpho-group in Schaefer's acid is occupied by bromine—are distinctly less readily sulphonated than any of the chloronaphthols referred to; and it is a matter of interest also that neither is a derivative of the Weinburg β-acid, isomeric with Schaefer's formed from them; hence it would seem that a β-sulphonic acid only results when the β-3'-position is free, viz., that which is symmetrically situated relatively to the β-OH group.

1 : 3'-*Dibromo and Bromochloro-β-naphthol.*—In the previous communication it was stated, that on brominating either bromo- or chloro-β-naphthol, the bromine is introduced into the second nucleus. To determine the position taken up by the bromine, the bromochloronaphthol was

distilled with PCl_5; 1 : 2 : 3′-trichloronaphthalene was one of the products obtained, and it would seem therefore that it occupies the position 3′-. As both dibromo- and bromochloronaphthol afford 1 : 3 : 4-bromophthalic acid on oxidation, this conclusion may be regarded as established. Independent confirmation of this result is afforded by the observation that chloro β-acenaphthylide is converted by bromine almost quantitatively into a bromochloracenaphthalide (m.p. 216°), which affords a bromochloronaphthylamine (m. p. 119°) and a bromochloronaphthalene (m.p. 60°) in which the bromine atom occupies the β- 3′-position; also by Claus's recent statement that when brominated bromo-β-acenaphthalide in like manner yields 1 : 3′-dibromo-β-naphthylamine (*J. pr. Chem*).

The conclusion thus arrived at, however, is in opposition to that to be deduced from Smith and Meldola's statement, that tetrabromo-β-naphthol, when oxidised, yields the bromophthalic acid whose anhydride melts at 134°, *i.e.*, the 1 : 2 : 3-acid. The authors have, therefore, studied the action of bromine in excesss on β-naphthol. They find that, contrary to Smith's statement, the preparation of tetrabromonaphthol is attended with very considerable difficulty, the product chiefly consisting of tribromonaphthol; the separation of this latter by crystallisation is difficult, but is easily accomplished by acetylating the crude product and re-crystallising the acetate from benzene and from acetic acid. The acetate crystallises in long fine needles melting at 184°, and is very easily hydrolysed. Tribromonaphthol melts at 155—156°; on oxidation with alkaline permanganate it yields 1 : 3 : 4-bromophthalic acid. The authors are still engaged in investigating this compound and the other products of the action of bromine in excess on β-naphthol.

Action of Nitric Acid and of Oxidising Agents on Chloro- and Bromo-naphthols.—Nearly all the chloro- and bromo-derivatives of β-naphthol yield characteristic quinone derivatives when submitted to the action of nitric acid; in most cases the formation of these is preceded by that of an unstable intermediate compound, the determination of whose composition presents great difficulties. The final product of the action of nitric acid is phthalic acid. Alkaline permanganate is not always a suitable agent to employ if the object be to completely oxidise the naphthol: thus the main product of its action on dibromo-β-naphthol, for example, is the acid—

$$C_6H_3Br<^{CH-\!-COOH,}_{CO>O}$$

which, on distillation, yields bromophthalide.

Anniversary Meeting.
Wednesday, March 25th, at 8 p.m.

THE CHEMICAL SOCIETY.

Jubilee Meeting.

A meeting in celebration of the Jubilee of the Society was held in the Theatre of the London University on Tuesday, the 24th February, 1891, Dr. Russell (the President) being in the Chair, and a numerous audience of Fellows and visitors being present.

The proceedings were opened by the following address from the President:—

We meet to-day to celebrate the fifty years' existence of our Society, a time, if measured by the progress which our science has made, equal to centuries of former ages, but which in years is so brief a space that we have, I am happy to say, with us to-day some of those who were present and who took an active part in the foundation of the Society, and I need hardly say with how much interest we shall listen to their reminiscences of the time and circumstances connected with the birth of our Society.

I would, by way of introduction, say a few words, first, with regard to our Society, and afterwards with regard to the state of chemistry in England when our Society was founded. We boast, and I believe rightly, that our Society holds the distinguished position of being the first which was formed solely for the study of chemistry. Chemistry and physics, twin sisters, had hitherto always dwelt together, and many were the societies, both in this country and abroad, devoted to their joint study and development.

In London there was the Royal Society, which had hitherto received the most important chemical papers; there was also the Society of Arts, which is 110 years, and the British Association, which is ten years senior of our Society. In Manchester the Literary and Philosophical Society had been founded and actively at work since 1781; and we admit that our neighbours at Burlington House, the Astronomical, Antiquarian, Linnean, and Geological Societies are all our seniors: they had a distinct individuality and literature of their own, which called them into existence some forty to eighty years before the commencement of our Society. Small private chemical societies, no doubt, existed; they are the natural fore-runners of a large society, and become merged into it. The Chemical Section of the British Association, which is an ephemeral and peripatetic Chemical Society, had existed from the founding of that body. If we turn to other countries we find that, much as our science had been cultivated on the Continent, it did not, until later times, engross a whole society to itself, the French Chemical Society not having been formed until 1857, and the now great Berlin Chemical Society not until 1868. Our interest, however, at the moment is rather in the growth of chemistry in this country than in what occurred elsewhere.

To-day we may learn how it came about that the first Chemical Society was established in England. I may, however, state that the reason for our meeting depends on the official record that on the 23rd of February, 1841, twenty-five gentlemen "interested in the prosecution of Chemistry" met together at the Society of Arts to consider whether it be expedient to form a Chemical Society. Of the twenty-five who then met I am happy to say three are present—Sir W. Grove, Sir L. Playfair and Mr. Heisch, and Dr. Longstaff and Mr. J. Cock are others of this band who are still alive but not present.

These twenty-five gentlemen appear without dissent to have come to the conclusion that it *was* expedient to form a Chemical Society, and appointed a committee of fourteen to carry this resolution into effect. So expeditious were they in their work, that in little more than a month the first general meeting was held, and the provisional committee brought forward a report embodying a plan for the constitution and government of the Society, and this plan remains essentially the same, save in one point, to the present day. I refer to the formation of a museum of chemical specimens; this project was abandoned some years ago. It is worth recording that at this first general meeting Thomas Graham was elected President; W. T. Brande, Esq., J. T. Cooper, Esq., J. F. Daniell, Esq., R. Phillips, Vice-Presidents; Arthur Aikin, Esq., Treasurer; Robert Warington, Esq., E. F. Teschemacher, Esq., Secretaries; Council—Dr. T. Clark, Rev. J. Cumming, M.A., Dr. C. Daubeny, T. Everitt, Esq., T. Griffiths, Esq., W. R. Grove, Esq., H. Hennell, Esq., G. Lowe, Esq., W. H. Miller, Esq., M.A., W. H. Pepys, Esq., R. Porret, Esq., Dr. G. O. Rees. Also that the Society then numbered seventy-seven members. We hail Sir W. Grove as being the most active member who is still among us in founding our Society, for he was a member of the first council, was present at the first meeting, and was a member of the provisional committee. I must here add to the official record, for it does not tell us how these twenty-five gentlemen "interested in the prosecution of chemistry" were collected together at one time and place. Obviously, some special force was required to build up this complicated molecule; that special force was embodied in and exercised by Robert Warington. By his activity and energy he brought about this meeting, and we can imagine how difficult and troublesome a work it probably was, how some of these gentlemen had to be instigated to action, others repressed, some convinced that the aim was desirable, others that it was feasible. But whatever the difficulties were Mr. Warington succeeded, and to him we are indebted for the formation of our Society. Although he has passed away, he is ably represented here to-day by his son. The love for the Chemical Society has proved to be hereditary: Mr. Warington of to-day is a most active and valued member; is one of our Vice-Presidents; and, as our programme shows, is about to present to us records connected with the early history of our Society which are of great interest now and will become of increasing value as time goes on.

I turn now at once from these matters immediately connected with our Society to the consideration of what was being done in chemistry in this country fifty years ago. At that time public laboratories for the systematic teaching of chemistry did not exist in London. The number of real students of chemistry in this country was very small. They were looked upon by their friends as being eccentric young men, who probably would never do any good for themselves, and these few students found practical instruction in the private laboratories of some of the London teachers.

The practical teaching of chemistry appears to have been undertaken in Scotland much earlier than in England, for Dr. D. B. Reid held practical classes at the University of Edinburgh as early as 1832. Graham came to London from Glasgow in 1837, and until the opening of the Birkbeck Laboratory in 1846, he had from time to time private students working in his laboratory. And so with the other teachers, who all had private or articled pupils. I doubt whether the pupils received much systematic instruction, but they gained an insight into laboratory work, saw how apparatus was put together, and how analyses were made. We have, indeed, to wait some years before public laboratories are established, for not until 1845 is the College of Chemistry opened, and this appears to have been really the first first public laboratory in London, and its object, as stated by its founders, is "to establish a practical School of Chemistry in England." About the same time both University and King's College establish laboratories. The Council of our Society recognised the importance of these occurrences, for in the Annual Report in 1847 we read, although an event not immediately connected with the Society, the Council has much pleasure in commemorating the late successful establishment in London of chemical laboratories, expressly designed to further the prosecution of original research. The new laboratories of the College of Chemistry, and of the two older Colleges of the London University, now offer facilities for practical instruction and research not surpassed, we believe, in any foreign school.

While speaking of laboratories in London, I should, however, mention that the Pharmaceutical Society established a laboratory especially, if not exclusively, for its own students as early as 1843.

It was not till several years later—till 1850 and 1851—that the medical schools in London established classes of practical chemistry.

If we consult the scientific journals of the time immediately preceding the formation of our Society, we find it was by no means a time of chemical activity in this country, but was rather a dull time, given more to the study and slow development of the science than to discovery. Methods of analysis, both organic and inorganic, had been much improved, and the dominant idea was the determination of the empirical composition of bodies, and the preparation of new compounds, whose existence was predicted by a study of Dalton's Atomic Theory. Graham, Kane, and Johnson, of Durham, were the leaders in scientific chemistry, and the authors of the most important chemical papers of the time. Graham had very lately published his notable paper on the constitution of salts—a paper which gained for him, some years after its publication, a Royal medal. Kane was an active worker and bold theorist, and at this time his reputation was much increased by a paper on the Chemical History of Archil and Litmus. Johnson was also a most active chemist. His contributions relate to many branches of the science, but especially to the chemical composition of minerals. In 1841, however, he is engaged on a long series of papers on the constitution of resins. He will probably be best known and remembered as an agricultural chemist. Faraday we can hardly claim as a chemist at this time, for he was then rapidly publishing his long series of Experimental Researches in Electricity. While speaking of electricity I should state that it was in 1840 that Smee described his battery, and the Society of Arts awarded him a gold medal for it. An important branch of our science was, however, coming into existence—a branch which has found many and successful investigators in this country; I mean photography. It was in 1840 that Herschel published in the *Philosophical Transactions* his elaborate paper on the chemical action of the rays of the solar spectrum, a paper in which he recognises a new prismatic colour beyond the violet, and chemical activity in the spectrum beyond the red, and besides discussing many other matters, establishes his previously discovered hyposulphite of soda as the best agent for the fixing of sun pictures. Fox-Talbot had previously given an account of Photogenic drawing, and claims that as far back as 1835 he took pictures of his house by means of a camera and chloride of silver paper, but it is not till 1838 that the Secretary of the Royal Society extracts from him a clear account of the details of his process, and it is in 1841 that he is granted a patent for improvements in obtaining pictures or representations of objects. Again, in the following year, Herschel publishes another paper of much importance. I can here only mention how actively this line of research was prosecuted by Robert Hunt, how many ingenious and interesting experiments he made, and how valuable was the account he afterwards gave of this subject in his "Researches on Light." Thus the work done in this branch of chemistry at the time of which I am speaking is certainly noteworthy, probably more so than in other branches of chemistry. In fact, of other advances in chemistry there is little to record, but I may mention that Clarke's process for determining the hardness of water also holds its jubilee this year, for it was in 1841 that a patent was granted to Dr. T. Clarke for a new mode of rendering certain waters less impure and less hard.

Not a single chemical paper appears in the *Phil. Trans.* for 1841, but there are two papers which were much discussed at this time, and although they were readily shown to be erroneous, still are interesting as indicating the chemical ideas of the day. One is by Robert Rigg, who is carrying on an experimental inquiry on Fermentation, being termed "Additional Experiments on the Formation of Alkaline and Earthy Bodies by Chemical Action when Carbonic Acid is Present"; it is published in the *Proceedings of the Royal Society*. The other is a paper by Dr. S. M. Brown entitled "The Conversion of Carbon into Silicon," published in the *Transactions of the Royal Society of Edinburgh*.

With regard to the first paper, Mr. Rigg believes that he has demonstrated that when fermentation takes place, a great and direct increase in alkaline and earthy salts, viz., of potass, soda, and lime occurs, an increase varying from 15 to 19 times the original amount. Denham Smith, who has only very lately passed away, showed that the theory simply rested on inaccurate experiment.

The object of the other paper is to demonstrate that on heating paracyanogen, nitrogen is given off, and a residue of silicon remained. Dr. Brett and Mr. Denham Smith controverted this, and in a paper in the *Phil. Mag.* proved that the supposed silicon was simply carbon in a very incombustible state. So important an experiment was this alleged conversion of carbon into silicon considered to be at the time of its publication, that it attracted Liebig's attention, and in a letter to Dr. Playfair, which was communicated to the meeting of the British Association at Plymouth in 1841, Liebig says, he has repeated Dr. Brown's experiment on the production of silicon from paracyanogen, but has not been able to confirm one of his results.

As far as pure chemistry is concerned it was rather a time of repose. The beginning of the century had been a brilliant time for chemistry in England. Dalton had published his atomic theory; Davy had decomposed potash and soda, and had demonstrated that chlorine was an element; and Cavendish and Wollaston were then still at work. In fact, the most important discoveries of that time were made in this country, but I fancy that during this later period a feeling grew up that the age of brilliant discoveries was over, and that apart from the preparation of a few new compounds, the essential work of the time was analysis, and the determination of the percentage composition of bodies. Still, much quiet study of the science was going on, as is indicated by the considerable demand which existed for good text-books. Henry's, Turner's, Kane's, and Graham's Chemistry—all these, without mentioning others, went through numerous editions, and played a very important part in the spread of chemical knowledge in our country.

Another text-book, which is interesting as showing how little organic chemistry was studied in this country, is Dr. Thomas Thompson's work on "Vegetable Chemistry." Dr. Thompson states in his preface that the object of the book is to lay before the British public a pretty full view of the present state of the chemistry of vegetable bodies, and further he says, "that the ultimate analyses he gives have, with very few exceptions, been made upon the Continent, and principally in Germany and France. British chemists have hardly entered on the investigation." Evidently, then, at this time organic chemistry had been but little studied in this country.

When our Society was founded, Thomas Graham was certainly the most distinguished chemist in England. He came to London in 1837 as professor of chemistry at University College, succeeding Edward Turner. The work he had already accomplished was of a high order, and he was now occupied in writing his book which appeared in 1842.

The book was an admirable account of the chemistry of the time; it contained a well-arranged and clearly written introduction, describing the principles and latest discoveries in those branches of physics which bear most directly on chemistry. There was also an able and succinct account—probably the best which had then appeared in this country—of organic chemistry; and with regard to physiological chemistry, he states in the preface that he gives a "condensed view of the new discoveries in this department, which now enters for the first time into a systematic work on chemistry."

There are, however, indications that a knowledge of the discoveries and discussions going on the Continent only slowly reached this country. This is strongly insisted on in the *Phil. Mag.* of 1841, by Messrs. Francis and Croft, who state that "but little of what is done abroad, especially in Germany, seems to find its way into England, or at least until the lapse of some years." In proof of this statement they mention results lately published by Dr. Apjohn, Prof. Johnston, and Dr. Golding Bird, all of which had been known on the Continent some time previously. A valuable series of communications described as "Notes of the Labours of Continental Chemists," is afterwards communicated by these chemists to the *Phil. Mag.*, and continued for several years.

The visit of Liebig in 1837, when he attended the meeting of the British Association at Liverpool, must have given some stimulus to the study of organic chemistry in England, and we find that he undertook to report to the British Association on "Isomeric bodies," and also on organic chemistry, and this great undertaking resulted in his two works, the one "Chemistry, in its Application to Agriculture and Physiology," and the other, "Chemistry, in its Applications to Physiology and Pathology." Both books were dedicated to the Briti Association, the first appearing in 1840, the second in 1842. It is very difficult for us now to realise the importance of these works, and properly to appreciate not only the large amount of new knowledge which they contained, but, what is of still greater importance, the novelty of treating such subjects in a truly scientific spirit. Gradually this treatment of the subjects became understood and appreciated, and people took a higher view of chemistry, and regarded it as a true science, and not merely as a study which might lead to useful results.

If, then, it be true that chemistry at this epoch was not rapidly progressing in this country, we naturally ask how it came about that our Society from its very foundation was so successful. The explanation is not difficult to find, nor doubtful, for we have only to turn from our own country to the Continent and learn what is happening there. Liebig is at Giessen, Wöhler at Göttingen, Bunsen at Marburg, Dumas, Laurent, Gerhardt, and a host of distinguished and active chemists in France, and at this time even Berzelius and Gay-Lussac are alive. Liebig, with his wonderful energy and ability, was powerfully advocating the theory of compound radicles, and was extending in every direction our knowledge of organic chemistry, and inspiring all who came within the range of his influence with a love for investigation. Dumas, at the same time, both as a chemist and a finished advocate, was advancing his views on substitution and chemical types. Laurent, and afterwards Gerhardt, were, with conspicuous ability, showing how these theories were to be extended and modified so as to assume a form which has even with the lapse of time been but little altered. Thus on the Continent it was a time of wonderful activity; chemistry was every day becoming more of a true science, and the constitution as well as the composition of bodies was actively being discussed and investigated. This activity on the Continent took time to reach and really affect us here. The older chemists thought the new theories were visionary and unsound, the simple theories of their younger days were being swept away, and only slowly did they realise the meaning of the newer form of their science; but the wave of progress could not be stopped, and in this country we had been ripening for the change. Clearly the immediately cause of this sudden increase of chemical activity in England was Liebig. His famous school had now been established for several years at Giessen, and if the older men in this country did not altogether put their trust in him, the younger men, breaking through all restraint, flocked from this country to his laboratory, there to become indoctrinated with his enthusiasm for the study of chemistry, and to learn how scientific investigation was to be carried on. At this epoch our Society was founded, and our Journal shows how successful Liebig's teaching was, how a new spirit was instilled into English chemistry, and how much valuable work his students did. Our Society gave them a ready means of publishing their discoveries, and a meeting place for discussion and mutual interchange of ideas. Thus do I explain the success which from the first has attended on our Society; and having now led you to this point I stop, for my part was merely to speak the prologue, and I leave the story of the development of our Society in other hands.

A Gas-Balance with a Compensator.—A. Siegert and W. Durr.—This apparatus differs from that of Lux by the circumstance that the hollow sphere suspended to the weigh-beam is essentially closed and filled with air.—*Zeit. f. Anal. Chem.*, Vol. xxix, Part 4.

PHYSICAL SOCIETY.

March 6th, 1891.

Prof. W. E. Ayrton, F.R.S., President, in the chair.

Mr. H. A. Miers, M.A., and Mr. W. Lucas, M.A., were elected Members of the Society.

Mr. James Swinburne read a "*Note on Electrostatic Wattmeters.*"

After referring to the history of the electrometer method of measuring power developed by alternating currents, the author pointed out that the necessity for taking two readings from which to determine the watts might be obviated by having the quadrants separate instead of connected in pairs as in the ordinary method. Non-inductive resistances are connected to the transformer, motor, or other apparatus in which the power is to be measured, so as to be in series with the apparatus, and on opposite sides of it; and the four ends of these two resistances are connected with the four quadrants. Under these circumstances the deflection of the needle is a measure of the watts. To increase the maximum deflection obtainable so as to make an instrument capable of being read by a pointer, the needle is made in two halves, fixed one below the other on the same stem, and, instead of quadrants, semicircular boxes are employed. In this way a range of 130 degrees is obtainable.

Prof. Perry enquired as to what kind of *law* the instrument had, and Mr. Blakesley asked whether it was convenient to use.

Mr. E. W. Smith pointed out that there was no necessity to take two observations in the ordinary electrometer method, for, by using a false zero, one deflection gave the watts. Further, the use of the false zero rendered it unnecessary to employ any other voltmeter when experimenting at constant pressure.

The President said the historical part of the paper was not quite correct, and recalled attention to the fact that when high pressures were used a single reading obtained with the ordinary method of counting up gave the power. For ordinary low voltages, however, the false zero method described by Mr. Smith was very convenient.

Mr. Swinburne, in reply to Mr. Smith, said the observation of the false zero really meant another reading. As to the law of his wattmeter, referred to by Prof. Perry and the President, he said he never calculated a law, but calibrated the instruments directly.

Prof. S. P. Thompson, D.Sc., now took the chair, and a paper on "*Interference with Alternating Currents,*" by Prof. W. E. Ayrton, F.R.S., and Dr. Sumpner, was read by the latter.

The paper relates to the phenomena which occur when alternating electric pressures are impressed on circuits made up of various combinations of resistances, condensers, arcs, and inductive coils; to the characteristics of alternators; to the properties of transformers; and to the peculiarities exhibited by the Ferranti mains.

In one of the experiments an inductive coil and a condenser were connected in series, and a pressure of 25 volts as measured by a Cardew voltmeter, impressed on its terminals; the pressure on the two parts, measured in the same way, were 110 and 104 volts respectively, thus showing that each of the two parts was much greater than the whole. On joining a condenser and inductive coil in parallel, an ammeter in the main circuit indicated 5·5 ampères, whilst those in the branches showed 6·4 ampères passing through the condenser, and 10 ampères through the coil. Other experiments of a similar nature were described, and it was pointed out that the ratio of the sum of the two parts to the measured total may be large, being about 8 in the case first mentioned. Theoretically, this ratio might be anything, its maximum value being equal to the ratio of the impedance of the coil to its resistance; practically, however, it is not easy to get this number more than 8 or 10 for ordinary frequencies.

Alternate currents, arcs, and condensers give results of the same general character as those above described, as also do arcs and inductive coils, such as the regulating coils of lamps; this may cause considerable error in estimating the power supplied to such lamps. The magnitude of the error was found to depend greatly on the quality of the carbons and the character of the arc. With bad carbons and a hissing arc the error was very great, but with good cored carbons, burning steadily, it was not very serious.

Combinations of inductive and non-inductive coils exhibit marked peculiarities, particularly if the inductive one be a transformer coil. This last arrangement gave distinct evidence of interference, or difference of phase when the secondary of the transformer was open, but when closed, and with a moderate load, the difference of phase disappeared, thus showing, under these circumstances, that the primary coil had no appreciable self-induction.

On the subject of alternator characteristics, a graphical method of drawing the E.M.F. curve from the terminal curve was described, and the dependence of the terminal curve on the character of the external circuit pointed out. Keeping the speed, exciting current, and armature current constant, the pressure between the terminals was shown to be dependent on whether the external circuit consists of condensers, resistances, or inductive coils, the pressure being greatest in the former and least in the latter. The true E.M.F. of the dynamo, however, was the same in all the cases, but it became less as the armature current increased. From these results, the authors conclude that the drop in E.M.F. with large currents is due to reaction on the field, but that the change of terminal pressure cannot be all attributed to this cause.

Transformers, it was shown, are powerful controllers of phase, for the primary and secondary currents are nearly always circulating in opposite senses: the phase angle for a 1 to 1 Mordey transformer experimented on, varying from 170° at no load to 180° at full load. The relation between the strengths of the primary and secondary currents, A_p A_s, was found to be a linear one, of the form—

$$\frac{P}{S} A_p = \alpha + \beta A_s,$$

where P and S are the number of turns in the primary and secondary respectively, and α and β constants; α representing the exciting current, and β being nearly unity. The phase angle, ϕ, between the currents was given by the equation—

$$-\cos\phi = \frac{\frac{1+\beta^2}{2} A_p + \alpha\beta}{\beta A_s + \alpha}$$

The results of numerous experiments on a transformer of the Mordey type, in which coils having different numbers of turns were put in parallel with each other were given. In some cases resistances were put in circuit with the coils, and in others one or more of these resistances were cut out. Remarkable interference effects were thus produced, for in some combinations the volts or currents were additive, whilst in others they were nearly differential.

In connection with the Ferranti effect, experiments had been made by putting a condenser on the terminals of the secondary of a transformer, and noting the resulting increases in pressure, both in the primary and secondary circuits. The results obtained with a given condenser and approximately constant secondary pressure show:—

1. That whether the transformation be up or down, the percentage rise in the secondary is greater than that in the primary.
2. That these percentage rises diminish as the secondary current increases.
3. That they increase with the ratio of transformation,

4. That the rise in the secondary may be considerable, without that in the primary being appreciable.
5. That the rise in the secondary still persists even when large currents are flowing.

These facts lead the authors to believe that the "Ferranti effect" is due to some kind of interaction between the cable condenser and the self-induction of the transformer, and that is not wholly due to armature reactions in the dynamo.

In the discussion on the paper, Mr. Swinburne said the character of the "Ferranti effect" had been wrongly stated, for he understood Prof. Ayrton to say that the pressure between the Ferranti mains was greater at the London end than at Deptford. This, he contended, was impossible. He also said the effects now described, of putting a condenser on the secondary of a transformer and noticing the rise in both primary and secondary volts, were due to the waste field of the transformer. In large transformers, such as those at Deptford, the magnetic leakage was proportionately much less, and no such effects would be noticeable with them. Referring to the relation between the primary and secondary currents in transformers, he said it was convenient to look at the primary from two points of view, and consider one part of it as producing the magnetisation and the other as neutralising the effect of the secondary current.

Mr. Mordey described an experiment on armature reactions in alternators, in which one of the armature coils of a 50 H.P. machine was isolated from the rest and connected directly to a Cardew voltmeter. On varying the load from 0 to the full output (20 ampères), the voltmeter on the isolated coil was quite stationary, thus showing that no appreciable armature reaction occurred.

Mr. E. W. Smith remarked that the formula connecting the primary and secondary currents holds true over a very wide range, for he had experimented on a Kapp transformer, which gave (a) constant and (β) = 1 for frequencies varying from 20 to 200.

Mr. Blakesley gave the following formula as applying to transformer currents generally:—

$$\left(\frac{\mathrm{A}p}{\mathrm{A}s}\right)^2 = \frac{n^2}{m^2}\left\{(1 + k r_2^2) + \frac{q r^3}{v}\right\};$$

where r_2 = resistance of secondary, v is proportional to the frequency, m and n the primary and secondary turns, and k and q are the constants depending on the disposition of the iron. This formula he found to very nearly represent Ferrari's results, and he hoped others would test its applicability to various types of transformers. He believed himself to be the first who carried out an interference experiment, when he put a condenser in parallel with an inductive coil, six years ago. He mentioned the matter now because that arrangement had been put forward by Mr. Glazebrook in explanation of the "Ferranti effect." Mr. Glazebrook, however, had made an error in stating that under certain conditions one of the currents may become infinite.

Dr. Thompson thought the word interference had been used in a somewhat different sense to its ordinary usage in optics, and asked for an authoritative definition of its meaning in the paper under discussion. The experiments on the alternating arc he considered very remarkable, as well as those on the dynamo, which give various terminal pressures when its E.M.F. and current were the same, but the external circuit of different character.

Prof. Ayrton pointed out that the measurements on the rise of volts by putting on condensers, mentioned in the paper were not strictly analogous to those made by Mr. Ferranti, for his were made by pilot transformers, one placed between the primary terminals of the Deptford transformer, and the other on the secondary of the London transformer; whereas in the cases now brought forward the volts measured were those at the primary and secondary of the same transformer. On the subject of arc lamps, he said that Messrs. Kolkhorst, Thornton, and Weekes, who made the experiments, found that great lag only occurred when the carbons were bad and the arc hissing. If the apparent and the true power spent in such an arc were measured, a great difference existed between them. Dr. Hopkinson, he said, had shown that this might be expected if the arc had a constant back E.M.F. which changed sign with the direction of the current.

A paper on "The Theory of Dissociation into Ions and its Consequences," by Prof. S. U. Pickering, F.R.S., and another on "Some Points on Electrolysis," by Mr. J. Swinburne, were postponed.

Addendum to Report, February 27th, 1891.—The transformer on which the tests described in Prof. Aryton and Mr. Taylor's paper were made was of the Mordey type, having been kindly lent by the Brush Electrical Engineering Corporation.

CORRESPONDENCE.

DR. CARRINGTON BOLTON'S "CATALOGUE OF SCIENTIFIC AND TECHNICAL PERIODICALS."

To the Editor of the Chemical News.

Sir,—My letter in the Chemical News (vol. lxiii., p. 71), giving some account of my Catalogue of Scientific and Technical Periodicals, 1665—1882, and the chronological tables contained therein, has brought me several communications from both England and America, making inquiries as to the price of the work and the method of securing a copy.

I therefore beg leave to inform such correspondents through your columns that this volume can be had by applying to the secretary of the Smithsonian Institution, Washington, D.C., or for the convenience of residents of Great Britain to the agents of the Smithsonian, Messrs. Wm. Westley and Son, 28, Essex St., Strand, London. The price is 3 dollars or its equivalent. I may be allowed to add that I have no financial interest in the work, and I gave the MS. to the Smithsonian for the convenience of scholars.—I am, &c.,

H. Carrington Bolton.

University Club, New York, U.S.A.,
March 2, 1891.

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. cxii., No. 7, February 16, 1891.

On the Conductivity of the Organic Acids and their Salts.—Prof. Ostwald.

Reply to the Preceding Paper of Prof. Ostwald's. —Daniel Berthelot.—A continuation of the controversy opened in the memoirs on pp. 229 and 230 of the present volume.

On Certain Compounds of Pyridine.—Raoult Varet. —An account of pyridine bromo-cadmiate, of argento-pyridic cyanide, pyridine cyanomercurate, cyanocuprite, and iodocuprite.

On Sodium Amidide and on a Disodammonium Chloride.—M. Joannis.—Sodammonium is decomposed spontaneously at common temperatures into hydrogen and sodium amidide, NH_2Na. This change takes place in the dark as well as in the light, though rather more rapidly in the latter. It appears to tend towards a limit in proportion as the pressure of the hydrogen liberated increases.

Researches on Red Oil (Turkey Red Oil).—M. Scheurer-Kestner.—(See p. 134).

Bulletin de la Société Chimique de Paris.

Series 3, Vol. iv., No. 11.

Action of Isopropyl Iodide upon Aqueous Ammonia in Equimolecular Proportions above 100°. Limit to the Progression of the Isopropylamines.—H. and A. Malbot.—The reaction studied yields chiefly monoisopropylamine hydriodate with a perceptible though smaller proportion of di-isopropylamine hydriodate. The proportion of the latter compound is limited by the work of destruction and reproduction which it undergoes in presence of isopropyl iodide, the consequence of which is the formation of an increasing quantity of propylene.

Transformation of Isobutyl Chloride at 100° in a Closed Vessel in Presence of Aqueous Ammonia. Influence of Time and of an Increasing Proportion of Ammonia.—H. Malbot.—Not adapted for abstraction.

On Alcoholic Fermentation and the Transformation of the Alcohol into Aldehyd occasioned by Saccharomyces Albicans.—G. Linossier and Gabriel Roux.—This microphyte causes fermentation in glucose, levulose, and maltose; it is developed at the exposure of saccharose, but without occasioning either inversion or fermentation. Lactose is not affected. Besides the sugars, properly so called, a certain number of substances may serve as a hydrocarbonic nutriment for this Saccharomyces, but without undergoing fermentation. Such are dextrine, mannite, alcohol, sodium lactate, lactic acid, gum, and glycerin. Tartaric acid and the tartrates form the outside limit of the substances upon which this microphyte can nourish itself. Starch, erythrite, acetic acid and its salts, oxalic acid and the oxalates, aldehyd, acetone, and the aromatic bodies in general do not nourish the *Saccharomyces albicans*. Besides the secondary products of normal alcoholic fermentations, such as glycerin and succinic acid, we find in liquids which have undergone the action of this ferment a considerable quantity of acetic acid and acetaldehyd.

Can Ozone be Formed on Lowering the Temperature of Flame? Is there Ozone near the Flame?—Prof. Ilosvay de N. Ilosva.—The author criticises the affirmative conclusions of O. Loew and of F. Cundill. All the researches which he has lately made strengthen his conviction that brisk combustion cannot be the source of the ozone supposed to be in the air. Our heating appliances are not fitted up in such a manner that the air mixed with the products of combustion can withdraw from the flame immediately after the reduction of its temperature to that of the decomposition of ozone, and if this could happen the reductive products of the fuel would quickly destroy it. Again, if the combustion were effected in the open air a perfect hurricane would be required to lower the temperature of a flame of a large surface without the condition just mentioned being fulfilled.

Determination of Sulphur not Combined with Hydrogen in Coal-Gas.—Prof. L. Ilosvay de N. Ilosva.—This paper will be inserted in full.

On Certain Combinations of Camphor with the Phenols and their Derivatives.—E. Léger.—The compounds studied are monocamphoric phenol, hemicamphoric phenol, monocamphoric resorcine, bicamphoric resorcine, the α and β camphoric naphthols, camphoric salicylic acid, and camphoric salol.

On a very Sensitive Reaction of Tartaric Acid.—Ed. Mohler.—If we throw a few crystals of tartaric acid into a sulphuric solution of full strength containing 1 per cent of resorcine, and apply heat, there is produced at about 125° a fine violet-red colouration which may be preserved indefinitely on dilution with acetic acid, but which is at once destroyed on adding water. In order to detect $\frac{1}{100}$ milligramme of tartaric acid, it is needful to evaporate the liquid to dryness in a small porcelain capsule, to moisten the residue with 1 c.c. of the sulphoresorcine reagent, and to raise the temperature gradually to 125—130°. Reddish stripes appear first at the bottom of the capsule, and the entire liquid becomes coloured. The reagent has no action upon succinic, malic, citric, and benzoic acids. The mineral acids do not interfere, except the nitric and nitrous acids, which give with resorcine a blue colour so intense as to mask the reaction.

On the Sulpho-Conjugated Phenols or Camphosulpho-Phenols Derived from Ordinary Camphor.—P. Cazeneuve.—The author gives an account of amethylcamphophenol sulphone, of amethylcamphophenol-sulphonic acid, of camphophenol-trisulphuric acid, of camphophenol sulphuric acid, and of a distinct compound to which he also gives the name last mentioned.—*Bull. de*

Series 3, Vol. iv., No. 12.

Contributions to a Knowledge of the Diphenylic Bases.—E. Noelting and Paul Werner.—The authors have studied di-tolidine (an isomer of ortho-tolidine), bromo- and iodo-diphenylene, the transposition of meta-di-iodazobenzene, and of azobenzene parasulphonic acid, the diphenylic bases obtained by means of oxyazo derivatives, and further a number of derivatives of phenol, of ortho-cresylol, and of para-cresylol.

On the Formation of Diphenylic Derivatives by Means of the Ethers of Hydroquinone.—E. Noelting and Paul Werner.—The substances examined are diethylhydrotoluquinone, diethoxyldimethyldiphenylquinone, diethyltetraoxyditolyl, monobromodimethylhydroquinone, dimethylparaxylohydroquinone, diethylparaxylohydroquinone, diethylmetaxylohydroquinone, and diethylorthoxylohydroquinone.

Researches on the Double Rhodium Nitrites.—M. Leidié.—The author describes the double rhodium and potassium nitrite, the corresponding rhodium salt, the rhodium and sodium and rhodium-barium nitrites.

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.

Separation of Iron Sulphide from Calcium Phosphate.—I venture to trespass on your space to enquire what process is recommended for the separation of sulphuret of iron from phosphate of lime? A large deposit of the latter has lately been discovered, but analysis shows that there is enough sulphuret of iron present to destroy its value.—JAS. E. PICKERING.

MEETINGS FOR THE WEEK.

MONDAY, 22rd.—Medical, 8.30.
—— Society of Arts, 8. "Photographic Chemistry," by Prof. R. Meldola, F.R.S.
TUESDAY, 24th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Society of Arts, 8. "Uses of Cloisonné or Decoration in Ancient and Modern Times," by Clement Heaton.
WEDNESDAY, 25th.—Chemical Society, 8. (Anniversary Meeting) Election of Office Bearers and Council.
—— Geological, 8.

THE CHEMICAL NEWS.

Vol. LXIII., No. 1635.

THE ISOMERIC FORMS OF THE HYDRAZON OF ORTHONITROPHENYLGLYOXYLIC ACID.

By A. KRAUSS.

Some time ago H. Fehrlin showed that this body, if treated in the cold with alcoholic potassa, is converted into an isomeric compound, concerning which nothing definite is known.

If hydrazon is dissolved in an aqueous solution of potassa, and immediately precipitated with dilute acids, the hydrazon is recovered unchanged, but if the solution is allowed to stand, the sparingly soluble potassium salt of the isomer is deposited. The complete conversion in the cold requires some hours. On decomposing the salt with dilute hydrochloric acid, the isomer is obtained as a yellow powder, which, after re-crystallisation from alcohol, has the melting-point 188°—189°. Soda effects no change in hydrazon.

The composition of hydrazon is expressed by the formula $C_{14}H_{11}NO_4$. The isomerism is not physical, but chemical.—*Berichte Deutsch. Chem. Gesellschaft*, xxiii.

HYDRAZOIC ACID.

H.H. Curtius and Radenhausen have continued the study of this strange compound, HN_3, and have communicated their results to the *Journal fur Prakt. Chemie.* This acid, when anhydrous, is gaseous at temperatures above 37°, but on cooling it condenses to a very explosive gas. In the Torricellian vacuum it explodes, as also under a variety of conditions not as yet thoroughly determined. This behaviour has already occasioned one very serious accident, Dr. Curtius being the sufferer. Its explosive force is very violent. In one case every article of glass was not merely shattered, but pulverised.

The azoates, *e.g.*, BaN_6, explode if exposed to a strong green light. The silver salt behaves in a very similar manner.

The acid is found to be stronger than the acetic, and it possesses one property which it is surprising to find in any acid of organic origin, or, indeed, in any single acid. Its aqueous solution dissolves gold, forming a red salt. It seemed not unlikely that the ammonium salt of the new acid might yield an isomeric compound analogous to urea, but this is found not to be the case.

The first method taken for obtaining the free acid was by the action of dilute sulphuric acid upon the sodium salt. An improved process sets out from the hydrazine derivative of hippuric acid, which is converted into a nitroso-derivative by treatment with sodium nitrite and acetic acid at a temperature about 0°. The crystalline compound obtained is dissolved in aqueous caustic soda, and dilute sulphuric acid is then let fall drop by drop into the solution, which is kept at a boil. Weak hydrazoic acid distils over and is allowed to flow into a solution of silver nitrate, forming N_3Ag. This salt is dried at a temperature of 60°—70°, and is then decomposed by dilute sulphuric acid.

The name adopted for this compound is not very happy, since the "azoates" may easily be confounded with "azotates"—the French name for nitrates. Further discoveries on this acid and its salts may be expected.

AN IMPROVED METHOD FOR THE SAPONIFICATION OF TALLOW TO ASCERTAIN THE SOLIDIFYING POINT OF ITS FATTY ACIDS.

By H. N. WARREN, Research Analyst.

The action of the fixed alkalies upon the fatty bodies in general, as is well known, results in the formation of a soap corresponding to the alkali employed; and since the production of these compounds are necessary, in order to produce and examine further their allied acids, so as to ascertain the solidifying point of the same, an accurate and expeditious method of saponification should be considered by no means unwelcome.

The simplest method of saponification recorded is that of boiling for a considerable period a sufficiency of the sample under examination in contact with an excess of caustic soda. This reaction, as granted, proceeds tranquilly until the formation of a certain quantity of soap has been reached; the remaining unsaponified fat becomes then in a large manner protected by mixing intimately with the resulting soap, and thus escaping for some time the further action of the alkali. To obviate this an alcoholic solution has been employed; this may have preference over an aqueous solution, but its drawbacks, on the other hand, are twofold. Only quite recently during the examination of a number of samples of tallow, the author accidentally employed for saponifying the same a combined mixture of caustic potash and soda, and being struck with the ease with which they saponified was led to adopt this method in preference to others. The operation is conducted by selecting about 20 grms. of the sample, introducing the same into a copper pan containing in excess a boiling solution of equal parts of potassium and sodium hydrate; a complete saponification of the fat is brought about by exposing the same for about ten minutes at the boiling-point. To the contents are then added a slight excess of dilute sulphuric acid, and the heat maintained until the fatty acids thus separated float uniformly upon the surface of the liquid, the acids being afterwards washed by means of hot water in a separating funnel, until free from impurities. They are then introduced into a flask of convenient dimensions surrounded by salt water and raised to an elevated temperature by boiling the same, during which time a slow current of air is injected through a glass tube into the flask; by this means the whole of the moisture is expelled, and the solidifying point observed in the usual manner. By this means I have worked as many as twenty samples in less than five hours.

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

ON THE INFLUENCE OF PRESSURE ON THE SPECTRA OF FLAMES.*

By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and
J. DEWAR, M.A., F.R.S., Jacksonian Professor,
University of Cambridge.

We have already described (*Phil. Trans.*, A, 1888) the remarkable spectrum of the oxy-hydrogen flame burning at the ordinary atmospheric pressure. Recently we have examined the spectrum of the same flame at various pressures: hydrogen burning in excess of oxygen up to a pressure of 40 atmospheres, and oxygen in excess of hydrogen up to a pressure of 25 atmospheres, also that of the mixed gases burning in carbonic acid gas.

The apparatus employed was an adaptation of one of the tubes used in our experiments on the absorption spectra of compressed gases (*Phil. Mag.*, September, 1888,

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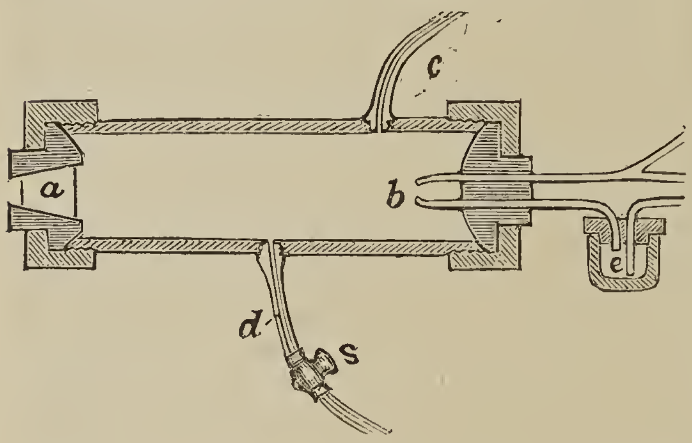
* Abstract of a Paper read before the Royal Society, Feb. 19, 1891.

and *Roy. Soc. Proc.*, vol. xlvi., p. 222). It consisted of a steel cylinder, about 50 m.m. in internal diameter, and 225 m.m. long, fitted at one end with a quartz stopper, *a*, in the annexed figure, and with a jet, *b*, for burning the gas, adapted by a properly fitting union joint to the opposite end. There were two tubes, *c* and *d*, connected to the cylinder at the sides, of which one, *c*, served for the introduction of gas, while the other, *d*, was fitted with a stopcock and was used to draw off the water formed, or to reduce the pressure of the gas in the cylinder if that was desired. The flame was observed, nearly end on, through the quartz stopper. The whole apparatus was kept cool by a stream of cold water running on to a sponge cloth wrapped round the cylinder. In the course of the tube conveying gas to the jet *b* was interposed a small cylinder, *e*, in which sodium was placed, and by heating this, the gas entering could be charged with sodium vapour.

The gases were supplied from steel cylinders into which they had been compressed, and the pressure was registered by a gauge attached to the tube by which the gas entered the experimental cylinder. Commercial compressed gases were used, containing a sensible percentage of air.

When hydrogen was the gas forming the burning jet, it was lighted at the end of the tube *b* before introducing it into the experimental cylinder. When it was desired to have a jet of oxygen burning in hydrogen, this could be managed by introducing oxygen through the second tube and increasing the supply of hydrogen until the flame passed over to the oxygen jet. The same result was sometimes attained by first filling the experimental cylinder by a gentle stream of hydrogen through the side tube *e* before the end with the tube *b* was screwed on; the hydrogen as it issued was then lighted, and the jet, with a gentle stream of oxygen issuing, inserted and screwed down. The stopcock, *s*, was kept open until this was done, and then by closing *s*, and admitting more gas from the reservoirs, the pressure in the experimental cylinder could be increased at pleasure.



Hydrogen Burning in Oxygen.

The first observations were made with a jet of hydrogen burning in oxygen. As the pressure rose, the luminosity of the flame increased, as long ago described by Frankland ("Experimental Researches," p. 905). The colour of the flame, viewed end on, was yellow, as if it contained sodium; but on examining it with a spectroscope, it was found to give a continuous spectrum intersected by many shaded bands, and the D lines of sodium were only faintly present. The shaded bands were faint at a pressure of 5 atmospheres, but at pressures of 20 atmospheres and upwards they came out strongly. They were evidently the absorption bands of NO_2, derived from the residue of atmospheric air mixed with the condensed gases. We took a photograph of them, and on comparing this with a photograph of the NO_2 bands, we found the two to be identical. Except for the bands, and the bright lines of sodium, the spectrum appeared to be continuous, and to extend from about λ 6200 to λ 4150, with the brightest part about λ 5150. It increased in brilliance as the pressure increased, as well as in extent, being visible at 3 atmospheres pressure from about λ 6720 to λ 4040. The greater distinctness of the NO_2 bands at the higher pressures was due both to the greater brightness of the continuous spectrum and to the greater quantity of NO_2 formed. A large quantity of water accumulated in the experimental tube, and when this was drawn off by the stopcock, *s*, it effervesced with escape of NO, and was found to be strongly acid. A specimen titrated was found to contain very nearly 3 per cent of nitric acid. The observations were continued up to a pressure of 40 atmospheres. There was no indication that the continuous spectrum had any connection with the line spectrum of hydrogen. There was no increase of brilliance in the neighbourhood of the C, F, or G lines of hydrogen. The characters of the spectrum were, however, better seen in the absence of NO_2, and will be described in the next section.

Oxygen Burning in Hydrogen.

In this case the colour of the flame was very different from that of hydrogen burning in oxygen. Instead of being yellow, it appeared, to the unaided eye, to have a lavender hue. In the spectroscope it showed a perfectly continuous spectrum, brightest in the green, about the region of the Fraunhofer line *b*, and very gradually fading away on either side. On the red side it could be just traced up to about λ 6150, and on the violet side to about λ 4285, at ordinary pressures. The sodium lines were absent. With increase of pressure it increased very much in brightness, and at 8 atmospheres pressure it could be traced as low as λ 6630 and as high as λ 3990.

The dispersion used was that of a direct-vision spectroscope (such as was described by us, *Roy. Soc. Proc.*, vol. xli., p. 449), equivalent to three prisms of white flint glass, but the collimator and telescope very short, so as to obtain plenty of light. With less dispersion, perhaps, the continuous spectrum might have been traced further. Photographs, however, showed that it scarcely extended into the ultra-violet. There was no indication that this spectrum was due to an expansion of the lines of either the first or second spectrum of hydrogen. It is true that the maximum brightness (which could not be determined with any great accuracy) was not very far from F, but no indication of any second maximum in the neighbourhood of either C or G, or anywhere else, could be detected. The pressure was carried up to 12 atmospheres, and at this pressure the visible spectrum was brilliant, but in the ultra-violet, photographs showed that the spectrum consisted only of what we have called the "water-spectrum," very strong and sharp. The lines of this spectrum showed no signs of expansion even at a pressure of 12 atmospheres, and, though much more intense than at ordinary pressures, remained clearly defined.

Observations were continued with the eye up to 25 atmospheres pressure, but no trace of emission, or absorption, corresponding to either spectrum of hydrogen, could be detected, and it is doubtful if either spectrum can be produced in such a flame. Since the formation of steam from its component gases is attended with a diminution of volume, increased pressure will increase the stability of the compound, and the flame will contain a larger proportion of steam, as well as have a higher temperature, than at ordinary pressures.

The water formed when the flame was a jet of oxygen burning in hydrogen was found to be alkaline, and to contain ammonia. But the proportion of ammonia was much less than the proportion of nitric acid formed when the jet was hydrogen burning in oxygen; a specimen titrated contained 0·0004 per cent of ammonia.

Effects of Pressure on the Sodium Spectrum.

In order to see what effect would be produced by increased pressure on the spectrum of other substances in the flame, we charged the hydrogen with sodium vapour by making it pass, before entering the experimental cylinder, through a small iron cylinder, *e*, in the figure, containing metallic sodium, heated by a lamp. As the D lines of sodium are very easily expanded and self-reversed in a flame at ordinary pressure, some care was needed to discriminate the effects which were really to be ascribed to pressure. The gas was easily charged with sodium vapour, and when burning in oxygen, not only the D lines, but the citron and green pairs, and sometimes the blue pair (λ 467), and the orange pair (λ 616), were well seen; but we could not find that they were expanded by increase of pressure. A sudden change of pressure generally produced an expansion, but it did not last; the lines fined down again when the pressure was steady, whether that pressure was high or low. These experiments were continued up to a pressure of 40 atmospheres without any definite effect on the width of the lines which could be ascribed to the pressure.

It may be said that at the higher pressure the evaporation of the sodium would be slower, and so the proportion of sodium vapour to hydrogen be diminished; also, when the lines are diffuse at the edges to begin with, it is extremely difficult to judge whether there is any expansion. At all events, we may say that there is no expansion produced by pressure at all comparable with that produced in a flame at ordinary pressure by increasing the quantity of sodium in the flame. We noticed, however, that the presence of sodium, which produces a feeble continuous spectrum in a flame at an ordinary pressure, seemed to increase the continuous spectrum of the flame under pressure, especially in the orange and green.

(To be continued).

ON THE POTASSIUM CYANIDE ASSAY OF LEAD ORES.

By ARTHUR W. WARWICK,
Assayer at the Phœnix Test Works, Battersea.

(Concluded from p. 30).

Owing to press of other work, I have been unable to finish the experiments upon the cyanide assay of lead quite as soon as I expected. The experiments have been continued upon the remaining ores of commercial value, viz., anglesite, pyromorphite, and mimetisite, and with the two former minerals results have been obtained exceeding all expectations. As was to be expected, with the last named mineral, the result was vitiated owing to the reduction of arsenic, giving too high a result. The lead-antimony minerals such as jamesonite, &c., were not treated, since the lead and antimony would be reduced together. Of course, the lead and antimony might be estimated in the button by the usual wet process, but such a mode of procedure offers no advantage over the usual chemical analysis.

Anglesite.—The anglesite employed for the following experiments contained a *small* quantity of cerussite, and here and there a minute crystal of galena was seen glistening. It contained 59·62 per cent of lead as shown by chemical analysis. The mineral was crushed and passed through a 60 sieve, samples being taken when required by the method detailed in my first paper (Chem. News, vol. lxiii., p. 30). 100 grains of the ore were mixed with 600 grains of "stick" KCy, and placed in a small Battersea crucible with the precautions observed in the galena assay. This mixture was heated for twenty minutes, using a low red heat rising gradually to a bright red. A good finishing temperature was required, otherwise the slag would have been too viscid. The button of lead was obtained in the usual way by breaking the crucible.

Exp. No.		Grains.	
21.	Button of lead obtained	59·3	Mean 59·35 p.c.
22.	,, , ,,	59·4	

The slag was of a light pink with a white crystalline core. This result is as good as it is possible to get with any furnace assay, since it is only 0·27 per cent below that given by chemical analysis.

Pyromorphite containing 74·01 per cent of lead was the mineral next worked upon. A sample was made as above, and 100 grains of the ore treated, in duplicate, as in experiments 21 and 22, finishing, however, with a moderate red heat. The crucible showed only a spongy mass at the bottom instead of the expected button. Further experiments were made using a higher finishing temperature as well as modifying the starting temperature. In experiments 23 and 24 the temperature at the commencement was a low red.

Exp. No.		Grains.	
23.	Button of lead obiained	72·85	Mean 72·77 p.c.
24.	,, ,, ,,	72·70	

In experiments 25 and 26 a moderate red heat was used at the start, and finishing at a bright red as in experiments 23 and 24.

Exp. No.		Grains.	
25.	Button of lead obtained	73·0	Mean 73·05 p.c.
26.	,, ,, ,,	73·1	

The mean of five experiments gave a result of 73·1 per cent. From these experiments it is obvious that a higher temperature is required to complete the reaction with pyromorphite than with any of the preceding minerals. The result is rather astonishing considering the high temperature used, and certainly points to the loss in the galena assay being a chemical one, and not so much to loss by volatilisation. This assay yields 0·91 per cent lower than the chemical process. For comparison, two assays were made, using the mixture of

Ore	200 grs.
Carbonate of soda ..	250 ,,
Argol	60 ,,

Covered with 100 grs. borax.

This mixture was fused for twenty-five minutes, using a bright red heat, and the fused charged poured into a warm mould. The following results were obtained:—

Exp. No.		Grains.	
27.	Button of lead obtained	142·2	Mean 71·05 p.c.
28.	,, ,, ,,	141·9	

The slag thus obtained is viscid, and there is great danger of it enclosing small globules of metal unless the crucible is handled rapidly. This result is 2·06 per cent below the cyanide method.

A sample of impure mimetisite was next experimented upon, with, however, very varying results. The button of lead obtained was brittle and of a very dark colour, due to the presence of arsenic. Under these circumstances, after making four experiments with similar results, no more work was done upon this mineral.

The fact that one flux gives good results with all the commercial ores of lead is of great value. As galena, cerussite, and anglesite frequently occur together, it is of great advantage to be able to assay all these minerals with the same flux. Of course this method does not give such accurate results as the sulphate chemical method, but as the furnace method is still largely used (and in all probability will continue to be used) in most lead mines, any method which will give higher results than those now in use is well worth considering.

It is true, as Mr. Cooper states (Chem. News, vol. lxiii., p. 73), that with lead ores containing other reducible metals the lead button obtained contains a notable quantity of those metals. In those cases where the impurity is large, the furnace method is inapplicable, and the chemical method must perforce be employed. The galena used in experiments 15 and 16[*] contained nearly 2 per cent of copper pyrites, and most of the copper was in all probability carried off in the slag, as the lead button obtained was quite clean and soft. Percy made a number of experiments some years ago in the Metallurgical Laboratory of the School of Mines upon cupriferous galena. A galena containing 10 per cent of copper pyrites was reduced, using a carbonate of soda and argol flux, and the amount of copper determined in the button of metal obtained. It was found that the button of lead contained 98·9 per cent of lead and 1·1 per cent of copper; with a galena containing 25 per cent of pyrites; the button of metal contained 96·5 per cent of lead and 3·5 per cent of copper, the rest of the copper being contained in the slag. From these figures it is evident that with a galena having less than 5 per cent of copper pyrites the error introduced is negligible, since the button would contain less than 0·4 per cent of copper. I may point out, however, that the quartz worked on by Mr. Cooper could hardly be called a *lead* ore, inasmuch as it only contained 3 per cent of galena and about 10·5 per cent of copper pyrites; surely this is more like a copper ore. The results obtained from a mineral of this character do not warrant the condemnation of the cyanide assay of lead ores.

DETERMINATION OF FERRIC OXIDE AND ALUMINA IN PRESENCE OF PHOSPHORIC ACID, ACCORDING TO THE MOST RECENT RESULTS.

By Dr. von GRUBER.

The determination of ferric oxide and alumina in phosphates is of the greatest importance for the manufacture of superphosphates, as it is the only method of foreseeing the results of the process and the value of the finished article. Even the phosphoric acid which has been rendered soluble goes back and becomes insoluble in proportion to the proportion of ferric oxide and alumina in the manure.

This fact is admitted, although the process of reversion is still unexplained. The author suggests that the strong attraction of water by the gypsum as it passes from the precipitated to the crystalline state deprives the existing phosphates of sesquioxides of their constitutional water, and thus converts them into an insoluble modification; at least certain experiments made point in this direction. The object of the present communication is to discuss the methods of determining the sesquioxides which have only just been perfected, which, considering the practical importance of the question, is truly surprising.

There has been hitherto employed a so-called "conventional method," the result of which showed the most striking discrepancies. It was customary to dissolve in acetic acid the precipitate obtained by adding ammonia to the hydrochloric (or nitro-hydrochloric) solution of the phosphate, containing the phosphates of the alkaline earths, of ferric oxide, and alumina. Calcium and magnesium phosphates were supposed to be completely dissolved, whilst ferric and aluminium phosphate remained undissolved. But as a considerable quantity of calcium phosphate always remained in the precipitate the precipitate was re-dissolved in hydrochloric acid, re-precipitated with ammonia, and the precipitate dissolved a second time with acetic acid. The precipitate was thus rendered purer, and was, indeed, generally free from lime; but whilst the first result was too high in consequence of the presence of calcium phosphate, the second precipitate gave too low a result, as the cold acetic acid has a solvent action, especially on the aluminium phosphate.

Still this conventional method was retained, though it could not claim the rank of a scientific process, and must even be regarded as insufficient for the demands of practice. There was no other method of determination.

From this point of view we can understand the discrepancies announced from the laboratories of leading analysts:—

	A.	B.	C.	D.	E.
			Per cent.		
I.	0·60	0·56	0·23	0·39	2·67
II.	0·85	—	0·26	—	—
III.	1·38	2·93	0·93	0·99	3·40
IV.	—	—	—	—	0·60

The letters A—E stand for the various materials examined, and the numbers I.—IV. stand in place of the names of the analysts. It is seen that there can scarcely be any idea of an agreement. It seems as if one analyst had precipitated only once and others twice.

Whilst making known these conflicting results the author endeavoured about six years ago to draw attention to the unsatisfactory nature of this method of determination, and expressed the wish that as long as no better process was known this "conventional method" might be developed by fixing exactly the quantity of acid to be used for the crude phosphate, the quantity of ammonia to be used for neutralising, and the quantity of acetic acid, so that the results obtained might at least be concordant if not strictly correct. He also made the request that the experience gained in seeking for a better method might be mutually communicated.

Not one reply was obtained to this circular letter sent out by the author and his collaborator, Herr Otto Schönherr, though he does not venture to infer that the subject was ignored. There was never found an absolutely correct result even when working with pure materials. Among other expedients he tried the precipitation of the phosphoric acid of the precipitate with molydenum as proposed by Stutzer. The worst point was that no explanations for the deviations—often considerable—could be given.

The method of Eugen Glaser (published in November, 1889) solved the question in a manner sufficiently accurate for technical purposes, and avoided the errors of the conventional method. This so called "alcohol method" is very simple:—

5 grms. phosphate are dissolved in the usual manner in 25 c.c. nitric acid of sp. gr. 1·2, and about 12·5 c.c. hydrochloric acid of the same sp. gr., and made up to 500 c.c.; 100 c.c. of the filtrate (= one-fifth of the sample) are placed in a ¼-litre flask, with the addition of 25 c.c. sulphuric acid of 1·84 sp. gr. The flask is let stand for five minutes, shaking occasionally; about 100 c.c. alcohol (95 per cent) are added; the flask is cooled, filled up to the mark with alcohol, and well shaken up. After standing for half an hour the liquid is filtered. 100 c.c. of the filtrate (= 0·4 grm. of the sample) are evaporated down in a platinum capsule until the alcohol is expelled. The solution is then mixed with 50 c.c. water in a beaker and heated to a boil. Ammonia is added to the solution until the reaction is alkaline, but not whilst boiling, to avoid a violent effervescence.

The excess of ammonia is boiled away; it is let cool, filtered, the precipitate washed with hot water, ignited, and weighed as ferric and aluminium phosphate. On trying this method the author obtained results which agree with those of calculation. The precipitate obtained was pure, consisting entirely of ferric and aluminium phosphates.

In January, 1890, Stutzer published another method for the determination of ferric oxide and alumina in phosphates. The first (calciferous) precipitate which remained on precipitation with ammonia and treatment with acetic acid, is collected and treated with molybdic solution in the usual manner to remove the phosphoric acid. In the filtrate the ferric oxide and alumina are precipitated with ammonia in the usual manner.

This method seems, theoretically speaking, to ensure

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[*] Chemical News, vol. lxiii, p. 30.

absolutely correct results. In the meantime the author has tried it years ago, and not obtained satisfactory results. On repeated trial it was the same. Sometimes he obtained several satisfactory analyses in succession, but then all at once the method failed without any perceptible reason. Dr. Stutzer himself has had similar experiences; whence the method cannot be pronounced satisfactory until the necessary precautions have been discovered. However, a combination of Glaser's method with that of Stutzer meets the objection that half the quantity of ferric and aluminium phosphate found is calculated as sesquioxides. This objection is justified in view of the different molecular weights of ferric oxide and alumina if scientific accuracy is required, but for technical purposes no scruples need be entertained. If it is necessary to remove the error the precipitate obtained, according to Glaser's method, which is free from lime and magnesia, is re-dissolved and treated with molybdic solution, so that the pure sesquioxides can be precipitated from the filtrate with ammonia and separated in the usual manner.

The "alcohol method" was formally accepted at the Congress of German Experimental Stations held on September 18th.—*Zeitschrift Anal. Chemie.*, xxx., p. 9.

DISCUSSION ON THE THEORY OF SOLUTION.*

The following discussion ensued on the reading of the paper on "The Present Position of the Hydrate Theory of Solution," by Mr. S. U. Pickering, F.R.S., which appeared in the Chemical News, vol. lxii., pp. 185 and 194:—

Dr. **Gladstone** made a communication on "The Molecular Refraction of Substances in Solution," in which he reconsidered the five reasons given in 1865 and 1869 for believing that "the specific refractive energy of a solution is the mean of the specific refractive energies of the solvent and the substance dissolved." In describing the present state of our knowledge, he brought forward some facts which have a bearing on the views under discussion.

In the first place, although it may be accepted as a rule that a solid when dissolved retains its former refractive power, it is a rule not without exceptions. Thus the experiments, both of the speaker and of Dr. Bedson, on rock salt agree in giving 14·6 as the molecular refraction of chloride of sodium for the solar line A or R; in which R represents the value $\frac{\mu - 1}{d}$ multiplied by the molecular weight. But the molecular refraction for the same ray as calculated from aqueous solution is 15·3, showing that the water has perceptibly increased the refractive power. And this is not an isolated instance, for the observations of Topsoe and Christiansen on crystals of potassic bromide and iodide show a molecular refraction for the line D, or R_D, of 24·85 and 36·29 respectively, while the solutions indicate 25·7 and 36·9 respectively. In fact, the chlorides, bromides, and iodides, in general, when dissolved in water, are known to exhibit a higher refraction and dispersion than would be calculated by adding together the generally received values for the metal and the halogen, and this increase is uniform for each series of salts.

It is also known that there is a slight change in the molecular refraction of certain liquid substances, such as acetic acid, when they are mixed with water.

In the second place the molecular refraction of a substance in solution is not varied by varying the amount of the solvent. In the case of water, however, there are some marked exceptions. With the hydracids the values increase with the dilution up to a certain extent, when they become stationary. Nitric and sulphuric acids are also exceptional. It is evident that the difference here noted does not depend upon whether these binary compounds are electrolytes or not.

In the third place there is a great deal of evidence that the molecular refraction of a substance is the same whether it be deduced from its solution in alcohol, ether, benzene, bisulphide of carbon, or any other solvent that does not act chemically upon it. The same rule applies in some instances to solution in water; thus the molecular refraction of ammonia in alcohol, or in different quantities of water, was found to be about 8·96. The value for gaseous ammonia, as deduced from Dulong's observations, is 8·60.

A notable exception is hydrochloric acid. Very early in the history of refraction equivalents it was recognised that this acid in aqueous solution gave a value much larger than the gas itself, or than what would be obtained by adding together the values for chlorine and hydrogen in combination, as deduced from other sources. Dr. Perkin found a similar great increase of magnetic rotation in an aqueous solution of hydrochloric acid, but on dissolving the gas in isoamyloxide and examining the solution he found it rotated the plane of polarisation to very little more than the theoretical amount. The speaker therefore determined the refraction of this solution, and found the hydrochloric acid in it to have practically the theoretical value.

HCl, theoretical value	11·2 or 11·3
HCl, in water	about 14·4
HCl, in isoamyloxide	11·36

It would not be safe to use this increase of refraction of hydrochloric acid in aqueous solution as an evidence either of dissociation or of the formation of a hydrate. For the sum of the molecular refractions of free hydrogen and free chlorine, as determined by Dulong or Mascart, would be only 10·3, rather less than the theoretical, instead of more, as might be expected on the dissociation hypothesis,* while, on the other hand, the addition value of H_2O in recognised hydrates (such as crystallised alums) seems to be the same as that of pure water, namely, 5·93.

The general inference drawn by the speaker from the accumulated evidence was that the old conclusion is substantially correct; that molecular refraction and dispersion may be safely deduced from substances in solution where the solvent is chemically inactive, but that in the case of water there is some profound change effected upon the constitution of hydracids, haloid salts, and probably some other compounds by the act of solution. What this change may be cannot at present be inferred from optical analysis.

Dr. **James Walker** read the following translation of a communication from Dr. **Arrhenius**:—

"In the *Journ. Chem. Soc.* for 1890, p. 355, Mr. Pickering writes:—'It is indeed surprising that van 't Hoff, Arrhenius, and others should not have recognised that every known deviation from the so-called normal depression, when induced by increase of strength of the solution, is in exactly the opposite direction to that which it should be if the law of osmotic pressure were really correct.' That the depression of the freezing-point per grm. molecule should decrease with increasing concentration is no deduction (as Mr. Pickering seems to imagine) from the law of osmotic pressure; and the corresponding statement for the analogous case of highly compressed gases has been proved to be false by the researches of Regnault, Netterer, and others. . . . Besides, it is not correct that 'every known deviation' is in the opposite direction to that expected by Mr. Pickering.

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* British Association (Section B), Leeds Meeting, 1890.

* These numbers would have been brought more closely together if the calculation had been made by means of Lorenz's formula, $\frac{\mu^2 - 1}{\mu^2 + 2} \times \frac{1}{d}$ instead of the simpler $\frac{\mu - 1}{d}$. With liquids and solids it is practically unimportant which formula is employed.

H_2SO_4 per cent.	Sp. gr.	Gr.-equiv.	$i.=1+2a$	Freezing-point.			Differences in 1-1000 deg. Cent.	
				Obs.$_1$	Obs.$_2$	Calc.	Obs $_1$-calc.	Obs.$_2$-calc.
3·993	1·0278	0·8376	2·036	−1·61°	—	−1·62	−10	—
3·967	1·0274	0·8324	2·036	1·58	—	1·61	−30	—
3·492	1·0243	0·7300	2·042	1·37	—	1·42	−50	—
3·008	1·0210	0·6267	2·051	1·19	—	1·22	−30	—
2·806	1·0193	0·5835	2·058	1·10	—	1·14	−40	—
2·496	1·0174	0·5182	2·064	0·981	—	1·016	−35	—
1·996	1·0140	0·4130	2·082	0·788	—	0·817	−29	—
1·785	1·0126	0·3688	2·088	0·705	0·699	0·731	−26	−32
1·596	1·0112	0·3293	2·094	0·633	0·627	0·655	−22	−28
1·398	1·0100	0·2882	2·102	0·558	0·550	0·575	−17	−25
1·212	1·0087	0·2496	2·112	0·484	0·480	0·501	−17	−21
1·024	1·0073	0·2058	2·126	0·417	0·412	0·416	+1	−4
0·8188	1·0059	0·1681	2·136	0·334	0·332	0·333	+1	−1
0·7138	1·0051	0·1464	2·146	0·297	0·294	0·298	−1	−4
0·6145	1·0044	0·1260	2·156	0·255	0·254	0·258	−3	−4
0·5146	1·0037	0·1054	2·168	0·219	0·217	0·217	+2	0
0·4061	1·0029	0·08312	2·210	0·178	0·177	0·175	+3	+2
0·3562	1·0025	0·07288	2·236	0·160	0·155	0·155	+5	0
0·3063	1·0022	0·06264	2·272	0·138	0·137	0·135	+3	+2
0·2594	1·0019	0·05281	2·304	0·115	0·116	0·116	−1	0
0·2056	1·0015	0·04203	2·352	0·095	0·093	0·094	+1	−1
0·1539	1·0011	0·03144	2·406	0·067	0·072	0·072	−5	0
0·1401	1·0010	0·02861	2·422	0·062	0·067	0·066	−4	+1
0·1012	1·0007	0·02067	2·476	0·052	0·049	0·049	+3	0
0·0771	1·0005	0·01574	2·544	0·038	0·035	0·038	0	−3
0·0519	1·0003	0·01060	2·594	0·026	0·028	0·026	0	+2
0·0264	1·0001	0·00539	2·702	0·016	0·014	0·014	+2	0
						Sum ..	+7	−10

From Beckmann's excellent determinations (*Zeitsch. fur Physik. Chem.*, ii., 715) it appears that in the great majority of cases the molecular depression does diminish with increasing concentration when benzene and acetic acid are the solvents. Mr. Pickering can find numerous other examples in Eykman's observations, and I shall show below that it is even the case with the sulphuric acid solutions which were the subject of his own investigation. . . .

"Mr. Pickering, in comparing his 'theoretical' with the observed values for the depression of the freezing-point in dilute solution of sulphuric acid, remarks that 'the molecular depression, *even in this extreme region*,* instead of being constant, as it should be according to the theory of osmotic pressure, varies between 2·95° and 2·1°.' Mr. Pickering has overlooked the fact that sulphuric acid is an electrolyte, and that the deviations may be accounted for by the theory of electrolytic dissociation. For the purpose of comparison with the experimental results, I have calculated the values of the depression for dilute solutions, such as Mr. Pickering investigated. In the calculation I have taken the freezing-point of an aqueous solution of a non-electrolyte containing 1 grm. molecule per litre to be −1·90° C., in accordance with van 't Hoff's theory. I have further made the molecular conductively of $\frac{1}{2}H_2SO_4$ at infinition dilute ($\mu\infty$) equal to $356/10^7$ Siemens's units (Kohlrausch, *Wied. Ann.*, xxvi., 196). From Kohlrausch's numbers we then find the degree of dissociation—

a for	1	0·5	0·1	0·05	0·03	0·01	0·006	0·002*
to be	0·511	0·533	0·585	0·658	0·707	0·802	0·844	0·910

* Normal solutions.

By interpolation we get a for other concentrations (*Zeitsch. f. physik. Chem.*, v., 5). From the percentage composition and the specific gravity (Pickering) I have calculated the number of grm.-equivalents per litre solution. The subjoined table corresponds to that on p. 363 of the *Jour. Chem. Soc.*

"Under obs.$_1$ are the (corrected) observed numbers obtained with thermometer 65108; under obs.$_2$ are the numbers for the same concentrations interpolated from the series made with themometer 65561. This comparison affords an indication of the experimental accuracy.

"It is at once evident from the table that the observed numbers agree within the limits of experimental error (obs.$_1$—obs.$_2$) with the theoretical values so long as the concentration is less than 1 per cent. The agreement, in fact, is so extremely good as to lead one to put more faith in the calculated than in the observed values. In stronger solutions (1 to 4 per cent) the depressions found are less than the theoretical depressions, in direct contradiction to Mr. Pickering's statement that the opposite is always the case. On this last circumstance, however, we need not lay too much weight, for the theory has not yet been sufficiently advanced in this direction, and the deviations besides only amount here to 3·6 per cent at most. Instead, then, of these experiments of Mr. Pickering finally disproving 'all existing physical (*sic!*) theories of solution,' and in especial 'the theory of osmotic pressure,' they afford the most striking proof of the applicability of van 't Hoff's theory and the hypothesis of electrolytic dissociation of dilute solutions, with which alone these theories have hitherto been concerned."

Dr. Walker drew attention to the fact that in almost all the combinations of solvent and dissolved substance tabulated electrolytic dissociation played a great part, entirely neglected by Mr. Pickering. The comparison of observed with "theoretical" values was thus open to the same objection as Dr. Arrhenius urged in the case of dilute solutions of sulphuric acid, and so the great discrepancies found in the tables were from this cause alone rendered illusory.

Professor Ramsay suggested that it might well be the case that complex molecular aggregates were capable of existence alongside of dissociated molecules where ions are present. In the case of solutions of sulphuric acid, for example, it is by no means unconceivable that aggregates of several molecules of sulphuric acid $(H_2SO_4)_n$, or of compounds of acid and water, such as $H_2SO_4.2H_2O$,

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Mr. P.'s italics.

&c., might exist along with the ions of dissociated sulphuric acid 2H and SO_4, or more probably H and HSO_4. The abnormal results in the freezing-points of solutions of sulphuric acid observed by Mr. Pickering might well be due to some such cause.

Dr. ARMSTRONG, after remarking that thus far the physical aspects of the main problem under discussion—the constitution of solutions which conducted electrolytically—had alone been dwelt on, said that it would be impossible, in the time at disposal, to consider more than one of the conclusions arrived at by the advocates of the dissociation hypothesis, which did not appear to be in accordance with the chemist's experience. It had hitherto been customary to regard the neutralisation of an acid by an alkali as a case of interchange or double decomposition, as represented, for example, by an equation such as $KOH + HCl = KCl + HOH$. But now that it was argued that hydrogen chloride, potassium hydroxide, and potassium chloride underwent almost complete dissociation when dissolved in water to form a dilute solution, it became necessary to suppose that in such cases the only new compound formed in solution was water, and the main action which occurred on mixing solutions of potassium hydroxide and hydrogen chloride was consequently represented by the equation

$$H+Cl+K+OH=K+Cl+H_2O.$$

Such a conclusion, although undoubtedly a necessary and logical one from the dissociationist's point of view, involved the admission that hydrogen chloride and water were compounds of a totally different order; that these two hydrides were so different that while that of chlorine underwent practically complete dissociation that of oxygen remained practically unchanged. Chemists, however, were in the habit of teaching that chlorine and oxygen were comparable elements, and the facts of chemistry appeared to afford the strongest evidence that hydrogen chloride and oxide were in all ways comparable compounds. Moreover the behaviour of the two compounds at high temperatures afforded no grounds for any such belief in the instability of the one and the stability of the other.

Referring to the series of numerical agreements between theory and practice relied on by the dissociationists, the speaker said that in his opinion these afforded no necessary proof of the correctness of the theory. The correlation of chemical activity and electrical resistance which had been established by Arrhenius, Ostwald, and others was undoubtedly of the highest importance, but the successful use which they had made of the data at their disposal appeared to him to depend on the fact that by observations of electrical resistance they were enabled to classify electrolytes in the order of their activity, whether physical or chemical; and that, having done this, they were in a position to apply the correction required to discount the superior activity of such compounds in comparison with dielectrics, *i.e.*, compounds producing the so-called normal effect in depressing the freezing-point, for example.

Professor FITZGERALD said—It is important to distinguish between what is implied and what not by experiments: *e.g.*, osmotic pressure, change of freezing and boiling points are in no way independent; we can deduce one from the other by applying known principles. There seems to be a very important connection, which cannot be deduced from known principles, between conductivity, the variation of osmotic pressure from its value calculated from molecular weights, and the chemical activity of a substance in certain relations. The quality upon which these properties depend is, I think, certainly the same quality in each case, and its existence and importance have been brought to light by the labours of our renowned visitors and their collaborateurs, and the discovery is one of the most valuable contributions to chemical physics that has been made of recent years. The visitors call this quality the "ratio of dissociation." Professor Armstrong would rather call it "measure of affinity." I would be inclined to point out that the term "dissociation" is not happily chosen, and that "affinity" really explains very little, and that it would be better to call it by a new name whose full meaning will require further investigation, and would call it "measure of ionisation."

In the first place as to the term "dissociation." In all other cases of dissociation, *e.g.* in an electric arc, the elements are so far free from one another that they diffuse independently of one another. The term "dissociation" is no doubt vague, but it is time we had a more definite notion of it. I would certainly confine the use of the term to such cases that there was no link connecting the elements that would prevent their diffusing independently of one another. As long as there is any link connecting the elements of molecules together which essentially prevented one of them getting away without the others following, I would not agree to say that the elements were dissociated. Hence I object to the term dissociation as applied to the ions in an electrolyte. All agree that one cannot escape or diffuse without the other following; it may be due to electrical forces between them, it may be for other causes; but in either case I would refuse to call them dissociated. The possibility of independent diffusion I look upon as a test of dissociation. I would therefore appeal to both sides to adopt some neutral term such as "ionisation" to express the state of ions in electrolytes. Now as to the proofs that the ions are absolutely independently mobile in the liquid, and the assumption from this that they are free like the molecules of a gas being kept apart by the molecules of the solvent. This seems a very misleading way to speak of the condition. In the first place it is acknowledged that different solvents have different powers of ionising a given substance, thereby conclusively proving that the function of the solvent cannot be properly described as merely giving the ions space to resolve themselves. And those who speak so acknowledge that it is only an analogy, or a *façon de parler*. But it seems a very misleading analogy, which leaves out the really active part that the solvent plays, and attributes to it a purely passive part. The argument of van 't Hoff that the osmotic pressure in very dilute solutions depends only on the kinetic pressure, and not on the forces between the molecules, seems to cut against the conclusion that these forces must necessarily be small; it seems to show that, *whatever* forces there are between the ions, they will produce the right amount of osmotic pressure if only they are so far independent that each ion can carry on its bombardment independently of the other. As this only requires the space within which they are bombarding about to be small compared with the space rate of variation of the force between the elements, and as this is quite consistent with there being plenty of connection between the elements, it follows that the laws of osmotic pressure so explained do not in the least militate against there being bonds between the elements. The whole argument is, however, I think, fallacious, in that it assumes a particular theory as to the action between the semi-permeable membrane and the liquid. It would follow from this theory that one molecule of a salt could never produce osmotic pressure in its own neighbourhood by any forces of attraction between it and the solvent. Now if we apply this on a large scale to the case of an ocean 1000 miles deep surrounding the world with a membrane in it, say, 100 miles deep, through which the water could go, but the world could not because the holes were only, say, about a square mile in area, we see at once that, if this membrane were made of a material lighter than water, *i.e.*, less attracted by the world than water, it would tend to burst out with a great force, *i.e.*, it would float out from the world because the pressure in the water near the earth was much greater than at a distance from it. This shows where van 't Hoff's argument fails. He has neglected the difference of pressure in the solvent near and far from the salt, or at least has assumed that this difference of pressure could not act upon his semi-permeable membrane because the membrane is permeable to the solvent. It is, however, quite evident that the water can press very hard even on a membrane permeable to it, as is explained by the example I have just mentioned. Considering the complex nature of the problem, I think it is quite too soon to assume that the state of affairs assumed by van 't Hoff is at all like reality. I would much rather look for an explanation in the direction I have pointed out in this year's report of the Committee on Electrolysis. The argument there tends to show that the distances between molecules would arrange themselves so that the forces due to different kinds of molecules would be independent of their kind and depend on their numbers, and this would lead to the laws of osmotic pressure. It seems to me much more likely that a state of affairs such as I have supposed existing near the earth is the one existing in a liquid.

As regards the argument for the independent mobility of the ions founded on the laws of electrolysis, I think that just as in the case of osmotic pressure this does require a certain kind of independent mobility, but just as in that case I do not see that the required amount of independence cannot be attained without supposing a complete independence. There seems no doubt that conductivity and double composition are essentially connected with the same quality in the solution, and this property I have proposed to call "ionisation." Now, Williamson's hypothesis as to the nature of double decomposition and Clausius's as to the nature of electrolytic conduction only require that the ions shall be so far free as that they shall be frequently exchanging partners; neither hypothesis *requires* that they shall be during a finite time without partners, which I consider to be an essential condition of any right use of the term dissociated ions. If during the time the ions are paired they can move independently within the little chinks they have to move in between the molecules of the solvent—and be it observed that this is the same condition as for the extra osmotic pressure, *i.e.*, if their chinks are small compared with the variation of force between the ions—then there seems quite sufficient independence for any theory of electrolysis, if, whenever two molecules were within the same chink, there were, as there would be, sufficient independence for an exchange of partners. Thus these two phenomena would be explicable upon the same hypothesis, and that without assuming that ionisation was a true dissociation. I have already explained that even those who insist most strongly upon the dissociation hypothesis yet guard themselves from its being supposed that this dissociation is an actually complete independence of the ions from one another. On all these grounds then I would appeal against the use of the word dissociation in this connection. Professor Ostwald says that there will result two theories leading to the same result. I dissent from this. The two theories are *essentially* the same. There have been unnecessary assumptions no doubt made as to how far an absolute independence of motion of the ions is required by the experiments, and I combat this unnecessarily absolute independence, but in all essential respects my theory is the same as the other. This unnecessarily absolute independence has been introduced in order to make what is acknowledged to be an "analogy" appear as if it were more than an analogy, to give verisimilitude to what is at the same time said to be merely a *façon de parler*, to make what is known to be complicated appear unreally simple.

It may be worth while following Professor Armstrong's suggestions that the way in which the double decomposition is facilitated by a solvent is by the two salts entering into combination with the solvent and forming a large molecule. Then by a process of tautomerism* by which the elements within a molecule exchange places, the double decomposition is effected. A similar but regulated rearrangement under electric forces would account for electrolysis. That solution is a true chemical combination seems undoubted. There is change of nature, *e.g.*, solid salt and ice change into liquid, re-distribution of energy, change of volume, every change significant of chemical action, and that solution can be saturated shows that there is combination in definite proportions, even though some doubt may exist as to the existence of cryohydrates. In speaking of solvents as merely giving molecules space wherein to resolve themselves into ions, it seems as if the part of Hamlet were left out. The action of the solvent is to cause ionisation, some solvents do it and some do not, and it is rather hard on these strangely active solvents not to recognise this activity, one of the most wonderful and effective of all chemical actions known to us.

As regards the energy required for dissociation, or, as I would prefer to call it, ionisation, I agree with Professor Ostwald that any required supply can be obtained by assuming either an affinity of the element for electricity (a form of words I object to for reasons to be presently stated) or by supposing the ionic state to be an allotropic form of the atom with a different internal energy in it from that in the atom when in combination. The reason I object to the term affinity of the atom for electricity is that all we know of electricity seems to show that if any body attracts positive electricity it repels negative, and in that case the atom and its electrical charge combined would not be acted on by electrical forces as is required in order to explain electrolysis. I do not like the idea of an allotropic form of the atom, and think the facts of solution, &c., can all be explained by chemical combination between the salt and its solvent, as I have described, without this assumption. A good deal of weight has been laid on the explanation of the equality of heats of neutralisation of ionised bodies by supposing them to be dissociated. The explanation only pushes the difficulty one step further back. How does it happen that the heats of ionisation or dissociation during solution are many of them so nearly balanced by the allotropism of the ionic state? We are only explaining the obscure by the more obscure in thus reasoning. It is perfectly plain that double exchanging can never be continually taking place between molecules unless the heats of combination are the same, and consequently anything that explains one will explain the other. I would rather look for an explanation of both in the direction I have already pointed towards as to the dependence of the forces between molecules upon their distance apart and on the way these and their internal energy are all bound together by the conditions of temperature equilibrium. The question is evidently in the highest degree complicated, and for a complete discussion must introduce the theory as to the nature of temperature equilibrium, and in the meanwhile it is misleading to pretend that a matter is simple which is in reality most obscure by speaking of acknowledged analogies as if they really explained anything.

It may be of interest to remark in connection with the question of the chinks within which molecules move that very rough estimate can be made as to their size by considering the crude hypothesis that each ion is moved by the electric force near it acting on its ionic charge, and by calculating how long it would be in getting up its ionic velocity. Assuming that the ion moves like a body in a viscous liquid, the time it takes to get up its velocity must be a very small part of the time during which a current acts on it, and for which it obeys Ohm's law, because, for this to hold, the velocity must be independent of the time during which the current is acting. By some rough estimates as to the quantities involved it appears that the time during which an atom is acquiring its ionic velocity is somewhere about 10^{-15} of a second, and that the space it would acquire it in is about 10^{-20} of a centimetre. This seems as if the intermolecular bombardment distances were probably very small, and it shows that we can hardly expect Ohm's law to fail for electrolytes due

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* Professor J. Emerson Reynolds informs me that such redistributions are recognised as occurring in complex molecules.

to this cause until the rate of alternation of our current is comparable with that of light. Of course the actual jostling of an atom through the molecules can hardly be fairly represented by such a crude hypothesis as that it is like a body moving in a viscous fluid; yet such a calculation as the above may be of use in showing the sort of quantities we may have to deal with.

Professor **Oliver Lodge** said he had not been closely attending to these subjects during the past year or two, and accordingly only made a very few remarks, mainly with reference to the views he formerly expressed.

He had always endeavoured to moderate between the extreme dissociation views on the one hand, and those which require the molecule to be electrolytically torn asunder on the other. One reconciling fact is the chemically proved fact of double decomposition whenever two substances are mixed; this seemed to him to establish clearly that molecules are accustomed to interchange their atoms. Now, during the moment of interchange there is an instant of freedom, an instant of potential dissociation, and it is upon this that he had looked as the opportunity demanded by electric force to cause a slight diversion, sufficient in the long run to result in opposite atomic processions.

But, as Fitzgerald has somewhere pointed out, an infinitesimal moment of time is not sufficient to permit any finite effect, unless the forces acting are enormous, which in the middle of the liquid they certainly are not. This is therefore a difficulty, for if the atoms are solitary for any reasonable time, that amounts at once to actual dissociation, as postulated by Clausius. One may have to fall back, therefore, on the outlying atom stragglers from gross complex molecules as giving the necessary pseudo-freedom or potential dissociation which is all that Ohm's law and electrolytic facts demand, if one is to avoid admitting that extreme state of dissociation which physically seems to be so satisfactory and chemically so abhorrent.

But on this head it seems that no logical argument definitely asserting this latter view has been adduced. The fact that solutions do, in many respects, as shown by their osmotic pressure for instance, obey gaseous laws, is of high interest; but to argue from it that therefore their atoms must be in the same state of independent freedom as the atoms of a gas, is to commit the fallacy called by logicians "the illicit process of the major."

Moreover it is not quite apparent why (in Mr. Pickering's paper, for instance) the antithesis of the hydrate theory is supposed to be the dissociation theory. Free *molecules* in solution, rather than free *atoms*, would seem to be the opposite to the formation of definite chemical hydrates.

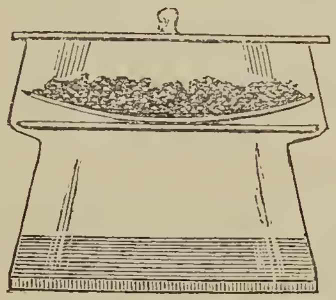
Lastly he hoped he might be permitted one more word on the subject of an old communication by Professor Ostwald relating a hypothetical experiment on statically electrifying an electrolyte, which he controverted some year or two ago, and which has been referred to by Mr. Pickering as if it were equivalent to a perpetual-motion device. He wished to dissociate himself entirely from Mr. Pickering's position on this point, and to explain what he had not yet had a good opportunity for explaining, that his published hostile remarks were made at first with the idea that the experiment was related as an experiment, and subsequently with the view that it is not very safe to use hypothetical experiments as controversial weapons. The view held by Professor Ostwald, that an electrolyte charged positively is so charged by reason of its hydrogen atoms looking outwards, while if charged negatively its oxygen atoms look outwards, is an extremely probable and instructive mode of regarding the matter. But an experiment establishing the truth of this view would have no necessary bearing on the dissociation controversy; in other words, the experiment suggested by Professor Ostwald, even if it could be performed, would not be a crucial one. The accepted laws of electrolysis already enable one to say what will happen when the minute current of a displaced electrostatic charge is passed through a liquid, with as much clearness as one can say what happens when a battery is applied to it. There is really no difference between the two cases, except the presence or absence of electrodes; for, as Professor Fitzgerald has said, the facing-out atoms exist in each case, only in one they face the electrodes, and in the other they face the air.

(To be continued).

IS SULPHURIC HYDRATE VOLATILE AT THE ORDINARY TEMPERATURE OF THE AIR?*

By GEORGE A. KOENIG.

The question proposed in the heading of this communication arose under the following circumstances. I had received a number of skeleton crystals of metallic iron which had formed in a steel block. To prevent them from rusting they had been coated with shellac. Previous to the analysis, the shellac was removed by alcohol, and after drying on water-bath, the material not needed for the purpose in view was placed upon a perfectly clean watch-glass into a desiccator of the common pattern. The watch-glass was supported by an iron wire triangle; its rims did not touch the sides of the desiccator. Upon the latter's bottom was pure sulphuric acid about one inch deep. The lid fitted with a film of vaseline. The desiccator was then placed upon a shelf and remained there undisturbed for about nine months. Being needed for another purpose I took it down, and found to my astonishment that both the iron-wire triangle and the iron crystals were covered with a clean white crust. What could this crust be? My first supposition reverted to the nitrous compounds frequently found even in re-distilled sulphuric acid. The crust was very coherent and peeled off in scales, leaving a bright metallic surface. I noticed that those parts of triangle which had rested in immediate contact with the glass were not incrusted. Likewise the watch-glass was bright and free from dust. The crust dissolved readily in distilled water, and proved to be composed of *anhydrous ferrous sulphate*. The test for nitric and nitrous acid resulted negatively. A quantitative analysis was not made under the circumstances.



How was this ferrous sulphate formed? Two possibilities only seem to present themselves:—

a. The acid has crept up the side of the vessel, and also from the triangle along the watch-glass, by capillary force. This hypothesis is not well sustained. In the first place the sides proved themselves dry and clean, and so did the watch-glass. In the second place, one should expect the strongest action where the triangle rested on the glass. But the fact obtained that these contacts were not corroded.

b. The acid is volatile at ordinary temperature, similarly to other liquids with high boiling-point, such as mercury. It might even be proposed that this volatilisation is induced by the strong basic character of metallic

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* Read at the Chemical Section of the Franklin Institute, January 20, 1891.

iron, and the minute quantities volatilised being immediately absorbed by the iron, there would not be any appreciable tension. There must have been produced, of course, a corresponding quantity of hydrogen, which would cause tension. I neglected to collect at once the gas in the desiccator, and a test was thus impossible. On the other hand, the lid was not so tight that such a thin gas could not readily escape.

There seems to me at present no escape from admitting the volatility of sulphuric hydrate at temperatures not exceeding 30° C., and more particularly in the presence of bodies exerting chemical attraction.

It will be probably of use to many to bear this fact in mind when they employ sulphuric acid as a desiccating medium. I propose to institute—and, in fact, have already instituted—several sets of conditions for proving or disproving this volatilisation. They will necessarily be time taking, as time seems the chief factor in the case.

NOTICES OF BOOKS.

Fresenius' Quantitative Analysis. Vol. II. Translated by C. E. Groves, F.R.S. Part III.

This issue of the *magnum opus* of the great master of analytical chemistry includes the special part from §215 (acidimetry), to §245 (zinc-dust). We may safely say that it is a decided improvement on former editions. New methods and new precautions are given whenever necessary, and causes of error are pointed out whenever they have been detected.

In the directions for acidimetry, it is to be noted that the author, upon the whole, still prefers litmus to all other indicators, though he recognises that they may in certain cases have an advantage.

We remark that the translator, possibly in accordance with the wish of the author, retains a nomenclature which the majority of chemists have abandoned. He writes, *e.g.*, not sodium carbonate but carbonate of soda. No chemist, we feel sure, will willingly dispense with this standard book of laboratory reference, and we can only hope that it may soon reach its completion.

CORRESPONDENCE.

ATOMIC WEIGHTS.

To the Editor of the Chemical News.

Sir,—I have read the letter of "F.H.P.C." in the Chemical News (vol. lxiii., p. 130), in which he draws attention to the fact that in my little book, "The Analyst's Laboratory Companion," I have given "erroneous" atomic weights of platinum and osmium. The latter, as he justly remarks, is "less material to the analyst," but, as he goes on to state, "it is very desirable that the exact equivalent of such a *reagent* (*!*) as platinum should be used in calculating the results of our analyses." It certainly *is* eminently desirable that the practising analyst should use correct *factors* for calculating the results of his analyses, and it is for this very reason that, after much careful consideration, I finally adopted the value Pt = 197·2, because this gives the most correct factors for calculating K_2PtCl_6 into K_2O, &c., and for converting the corresponding ammonio-compound into N, &c. In fact, when preparing the MS. of the work, the very first thing I did was to settle the matter of atomic weights in a manner that would commend itself to the analytical profession generally as indicated in my preface, and I went to a great deal of trouble in comparing the lists of atomic weights in a number of standard works before making out my final list. I will now quote the authorities which determined me to take Pt = 197·2.

1. In Crookes's "Select Methods of Chemical Analysis" (last edition), we read, regarding the estimation of potassium, that Messrs. Teschemacher and Smith's method gives results which are "very accurate." The authors take 244·2 as the equivalent of the potassium platino-chloride." I take 488·2, which, being almost exactly double, gives results that are practically identical when worked out consistently.

2. In Dittmar's "Exercises in Quantitative Chemical Analysis," p. 236, we are told that after drying the double chloride at 100°, $PtCl_6K_2 \times 0{\cdot}30627$ (an empirical factor), = KCl, the author adding the following remark: "The factor 0·30707 calculated from (Seubert's) Pt = 194·8, does not afford so close an approximation." Further back in the book we find (by Tatlock's method), $PtCl_6K_2 \times 0{\cdot}1940$ (also an empirical factor), $= K_2O$. My factors are—

$$PtCl_4, 2KCl \times 0{\cdot}19254 = K_2O.$$
$$,, \quad \times 0{\cdot}30520 = KCl.$$

3. Lunge and Hurter in their "Alkali Makers' Pocket Book," agree exactly with me in the above factors. Moreover, they expressly state in their preface that the atomic weight taken for platinum is "the figure adopted by all German potash manufacturers and analytical chemists."

4. Adriance, in his "Laboratory Calculations," adopts F. W. Clarke's list of atomic weights, with the single exception of platinum, on which he has the following note:—"It has been carefully determined that the atomic weight of platinum should be taken as 197·18, while really it is 194·41, since the factor obtained from 197·18 gives more correct results in calculations (*vide* Fresenius, *Zeit. für Anal. Chem.*, vol. xxi., 1882, p. 234)." Nevertheless, the factor he gives—$K_2PtCl_6 \times 0{\cdot}30697 = KCl$—is undoubtedly too high (see 2 above). In his more recent work "Chemical Arithmetic" Dittmar again supports me in my sets of factors for both the ammonic and the potassic platino-chlorides. He takes Pt = 195·5.

As regards osmium Clarke gives Os = 198·49, Dittmar 191·5 in the work last named, but 195·0 in his former work; and "F.H.P.C." gives 190·3. There are such wide divergences that the matter seems to me to require further elucidation. I took what seemed to me, and still seems to me, the most probable value.—I am, &c.,

A. E. Johnson.

10, Victoria Street, Wolverhampton,
March 17, 1891.

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. cxii., No. 9, March 2, 1891.

On the Composition of Drainage Waters.—P. P. Dehérain.—The author continues his observations on the drainage waters from fields, which he finds vary excessively in different soils. Thus the nitric nitrogen found in the drainage of a hectare of land at Wardrecques (Pas de Calais), from March to November, 1890, was 152·4 kilos.; at Blaringhem (Nord), 128·1; at Marmilhat (Puy de Dôme), 62·5, and at Palbost, in the same department, only 45·2. The black soils of the two last localities are much richer in organic matter than the light brown soils of the North. The researches of Warington and Winogradski have shown that an abundance of organic matter in a soil retards nitrification. Nitrification is useful in spring, and often requires to be supplemented by the use of Chilian nitre. An abundant nitrification in autumn occasions considerable loss. To prevent this waste he proposes to sow vetches and colza immediately after harvest.

On Certain Alkaline Derivatives of Erythrite.—M. de Forcrand.—The author has obtained an anhydrous potassium erythrate and three new hydrates, as well as an anhydrous sodium erythrate, which may also be obtained by the action of erythrate upon sodium methylate. The formula of the hydrates have not yet been determined.

On Cotton-Dyeing.—Leo Vignon.—This fibre shows very feeble chemical functions in comparison with animal fibres. The author inquires if the chemical inactivity of cotton is the cause, or the effect of its deficient aptitude for fixing colouring-matters? To decide this question he treats cotton in sealed tubes with an excess of aqueous ammonia or of ammonium-calcium chloride, at temperatures between 100° and 200°. The quantity of nitrogen thus taken up varied from 1·05 to 2·86 per cent. The samples became capable of absorbing considerable proportions of colouring matters, such as orange, roccelline, soluble rosaniline blues, &c.

On a Vegetable Hematine, Aspergilline—the Pigment of the Spores of Aspergillus Niger.—Georges Linossier.—Aspergilline presents striking analogies with the hematine in blood. Both contain a notable quantity of the same metal, iron. Both furnish by the action of energetic reducers a product which is oxidised in contact with air, and thus returns to its original state.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. v., No. 2.

Essay on the Laws of Berthollet.—Albert Colson.—It is necessary either to preserve the laws of Berthollet, restricted, however, to the bases of the same order, as the author has done, or else add to the principle of maximum work other indispensable considerations as Berthelot has done. In the precipitation of aniline salts by pyridine the latter chemist considers that the decomposing action of water upon the salts of aniline must be admitted to intervene.

Oxidation Products of Dimethylaniline.—Ch. Lauth.—It is well known that dimethylaniline submitted to the action of certain oxidising agents yields Paris violet. The reaction is different if we take as oxidising agent lead dioxide. On adding PbO_2 to an acetic solution of dimethylaniline we obtain a very fine green colour, or an orange-yellow if the acid is in excess. Fischer has observed the formation of violet and of formic aldehyd by the reaction of MnO_2 upon dimethylaniline sulphate in a dilute aqueous solution.

Coloured Reactions of the Aromatic Amines.—Ch. Lauth.—Already noticed.

New Process for Determining Oxygen Dissolved in Water.—G. Linossier.—This paper will be inserted in full.

Supplementary Paper on a Process for Identifying Free Chlorine, and on the Detection of Chlorides in Presence of Bromides and Iodides.—The author refers to a method for identifying free chlorine which appeared in the *Bulletin de la Soc. Chimique* for October 20th, 1890. For identifying chlorine he now proposes the reaction of aniline phenate indicated by Jacquemin. The reagent is prepared by dissolving in 1 litre of water, and without alcohol, 40 grms. of phenol and 5 c.c. of aniline. A few c.c. of this solution heated nearly to the boiling-point and then mixed with very small quantities of a hypochlorite, rendered strongly alkaline with soda, give at once a fine blue colouration.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. v., No. 60.

Contains a continuation of the researches of Sir J. B. Lawes and Dr. Gilbert, from the *Proc. Roy. Soc.*

MISCELLANEOUS.

Royal Institution of Great Britain.—The following are the probable arrangements for the Friday Evening Meetings after Easter, 1891:—

April 10th. Sir William Thomson, D.C.L., LL.D., Pres. R.S., "Electric and Magnetic Screening."

April 17th. Professor A. W. Rücker, M.A., F.R.S., "Magnetic Rocks."

April 24th. The Rev. Canon Ainger, M.A., LL.D. "Euphuism—Past and Present."

May 1st. James Edmund Harting, Esq., F.L.S. F.Z.S., "Hawks and Hawking."

May 8th. Professor W. Ramsay, Ph.D., F.R.S., "Liquids and Gases."

May 15th. Professor G. D. Liveing, M.A., F.R.S., "Crystallisation."

May 22nd. Professor J. A. Ewing, M.A., F.R.S., "The Molecular Process in Magnetic Induction."

May 29th. David Gill, Esq., LL.D., F.R.S., Her Majesty's Astronomer at the Cape of Good Hope, "An Astronomer's Work in a Modern Observatory."

June 5th. St. George J. Mivart, M.D., F.R.S.

June 12th. Professor Harold Dixon, M.A., F.R.S., "The Rate of Explosion in Gases."

The following are the lecture arrangements after Easter:—

Mr. J. Scott Keltie, three lectures on the "Geography of Africa, with special reference to the Exploration, Commercial Development, and Political Partition of the Continent"; Dr. E. E. Klein, three lectures on "Bacteria: their Nature and Functions" (the Tyndall Lectures); Mr. William Archer, four lectures on "Four Stages of Stage History (the Betterton, the Cibber, the Garrick, and the Kemble Periods)"; Professor Dewar, six lectures on "Recent Spectroscopic Investigations"; Dr. A. C. Mackenzie, four lectures on "The Orchestra considered in connection with the Development of the Overture"; Professor Silvanus P. Thompson, four lectures on "The Dynamo"; Mr. H. Graham Harris, three lectures on "The Artificial Production of Cold"; Professor A. H. Church, three lectures on the "Scientific Study of Decorative Colour."

Programme of the Société Batàve de Philosophie Experimental at Rotterdam.—The Society proposes among others the following questions:—

9. *Question* 154.—The best and most economical method of heating large buildings, having in view the demands of hygiene.

10. *Question* 155.—An experimental research on the cause of phosphorescence, especially among animals of a lower order.

12. *Question* 159.—A new and very exact determination of the variability of the specific heat of mercury with reference to temperature.

14. *Question* 164.—An exact determination of the refraction indices of substances which are abnormally dispersive and determination of the absorption-spectrum of these substances and of the spectrum of the superficial colour which often appears in these substances.

16. *Question* 166.—An examination of the specific heat of rhombic sulphur above 100°; of monoclinic and amorphous sulphur at different temperatures; of red phosphorus above 100°, and of ordinary phosphorus at different temperatures.

21. *Question* 176.—Monographs of an element, *e.g.*, sulphur; of a compound, *e.g.*, carbon disulphide or quinine; in a class of compounds, *e.g.*, the nitro-derivatives; on a phenomenon or a series of phenomena, *e.g.*, the action of sulphuric or nitric acid upon other bodies.

22. *Question* 177.—Very careful experimental determinations of the atomic weight of at least one element which is not yet well known.

25. *Question* 181.—A description of the vital conditions

of one or more species of moulds, ferments, or bacteria, which are important in horticulture, agriculture, the manufacture of butter, cheese, beer, vinegar, &c., and the manner in which these organisms affect the practice of such branch of industry.

The prize offered for the best answer to any of these questions is the Society's gold medal of the weight of 30 ducats. The papers must be drawn up in Dutch, French, English, German, or Latin, legibly written in the italic character (a prudent reservation as excluding German script), not in the hand of the author, and marked with some motto. Each must be accompanied by a sealed paper bearing the same motto and containing the name and address of the author. They must be sent post free to the Chief Secretary, Dr. G. J. W. Bremer, on or before February 1st, 1892.

MEETINGS FOR THE WEEK.

Thursday, April 2nd.—Chemical, 8.
Friday, 3rd.—Geologists' Association, 8.
—— Quekett, 8.

TO CORRESPONDENTS.

W. Naylor.—We know of no method of sterilising sewage.

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THE CHEMICAL NEWS.

Vol. LXIII., No. 1636.

BOGUS LETTERS.

The anxiously-awaited Anniversary Meeting of the Chemical Society has been held. As was only to be expected, motions of which notice had not previously been given were ruled out of order by the chairman, and for this reason the section of the Society which is discontented with the present conditions under which Fellows are elected, can hardly be said to have had that opportunity for discussing what they consider to be their grievances which they probably hoped for.

Rumours of a special meeting were afloat later in the evening, and it is to be sincerely hoped that such may be held, for it is obviously unhealthy to have a fermentation in our midst which cannot be properly ventilated.

But whether or not it be right that only such should be admitted to the Chemical Society as have taken an active part in the advancement or practice of the science, certain it is that prompt steps should be taken to prevent those who are not Fellows of the Society from using the letters F.C.S. It is therefore a matter for congratulation that the President was able to announce that steps were being taken, in conjunction with the Royal Society and other learned societies, for the introduction of a Bill in Parliament to render such fraud punishable.

Unfortunately, the system of Government under which this country labours renders the passing of a Private Bill a slow and tedious process. Meantime the wicked flourish like a green bay tree, and weekly advertisements appear in which the advertisers allege that they are "F.C.S."

Under these circumstances, the Chemical Society might do much for itself. Whenever it becomes known that any person is using these letters when he has no right to do so, let the Society publish far and wide the fact that he is not a Fellow. Of course, an immediate objection will be made to this suggestion: that such a course would merely serve to advertise the advertiser, and would do no real good; but this objection is not valid if the assertion that the public believe the letters F.C.S. to have a professional value be adopted, and we have good reason for supposing that this view is generally accepted.

We have pointed out what we believe to be an easy way of preventing that which is becoming a very serious fraud, not only upon the public, but upon the chemical profession. If it is adopted, we shall expect to see the bogus letters after the names of so-called analysts rapidly disappear.

ON THE INFLUENCE OF PRESSURE ON THE SPECTRA OF FLAMES.*

By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge.

(Concluded from p. 145).

Oxy-hydrogen Jet in Carbonic Acid Gas.

For this experiment a two-branched tube (the upper one in the figure) was used. The jet of mixed oxygen and hydrogen was first lighted and introduced into the experimental cylinder while the latter was full of air and the stopcock *s* open. The air was then replaced by CO_2 entering by the tube *c*. The effect of this was at once to brighten the flame and change its colour from yellow to blue. Seen in the spectroscope, the change consisted in an increase of continuous spectrum, especially towards the more refrangible end. When the stopcock *s* was closed so that the pressure rose in the experimental cylinder, the flame increased in brightness, but there was no other change in the spectrum. It remained continuous with no bright or dark lines, or bands, except the D lines of sodium. It resembled an ordinary flame of CO. The jet would not burn in CO_2 unless there was some excess of oxygen, and even with an excess of oxygen we could not get it to continue to burn in CO_2 at a pressure higher than two atmospheres.

Ethylene in Oxygen.

A jet of ethylene burning in oxygen gave, when the flame was small, the usual candle-flame spectrum, together with a band in the indigo (λ 431) shading towards the violet; but as the pressure was increased, the continuous spectrum brightened and completely overpowered the bands, and at the same time the absorption spectrum of NO_2 appeared. We carried the pressure up to 33 atmospheres, and at that pressure the flame seemed to give nothing but a continuous spectrum, intersected by the absorption bands of NO_2. In our tube the flame was viewed almost directly end on, and it is possible that if we had seen the flame sideways we might have detected the hydrocarbon flame spectrum near the nozzle. At the high pressure much soot separated. We tried burning a mixture of ethylene and oxygen. The mixed jet burnt well in air, and when the supply of oxygen was sufficient, gave the hydrocarbon flame spectrum. In the experimental tube in oxygen, the jet burnt well at the atmospheric pressure, but we failed to get it to continue burning when the pressure was increased. The shaded band, commencing with a sharply defined edge about λ 431, seems to be independent of the pressure, and has been before observed in a gas flame (Huggins, *Proc. Roy. Soc.*, vol. xxx., p. 580). In fact, the only effect of pressure in this, as in the former cases, seemed to be the increase of the continuous spectrum.

Cyanogen and Oxygen.

As we could not obtain cyanogen at such pressures as we had used in the case of the other gases, we were obliged to content ourselves with exploding mixtures of cyanogen and oxygen in an iron bottle, fitted with a quartz stopper like that of the experimental tube above described. The bottle, having been exhausted by an air-pump, was filled with the mixture of gases, and exploded by an electric spark. With less than 3 vols. of oxygen to 1 vol. of cyanogen, there was always a considerable deposit of carbon, which covered the quartz and impeded vision; but, with 3 vols. of oxygen to 1 of cyanogen, the carbon was all burnt. Notwithstanding the brilliant banded spectrum of a flame of cyanogen in oxygen at ordinary pressure, nothing but a continuous spectrum could be seen in the flash of the exploded gases, except the ubiquitous D lines of sodium. The continuous spectrum was bright. Photographs showed a continuous spectrum with lines of iron, calcium, potassium, and sodium, but no cyanogen or carbon bands, or carbon lines. When a little hydrogen was added to the mixture of gases, no trace of the hydrogen red or green line could be detected in the spectrum of the exploding gas.

In every case, the prominent feature of the light emitted by flames at high pressure appears to be a strong continuous spectrum. There is not the slightest indication that this continuous spectrum is produced by the widening of the lines, or obliteration of the inequalities, of the discontinuous spectra produced by the same gases at lower pressures. On the contrary, it seems to be developed independently. This is, on the whole, quite in accordance with what would be expected, considering that under pressure the molecules of the gases have much less freedom, encounters amongst them are much more frequent, and they have much less chance

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* Abstract of a Paper read before the Royal Society, Feb. 19, 1891.

of vibrating independently, and of taking up exclusively, or chiefly, the fundamental rates of vibration which are natural to them when free. Their condition, during a large part of any given time, approximates to that of the molecules of a liquid, and their spectra approximate to that of a liquid to at least a like extent. On the other hand, the higher temperature which, in many flames, attends an increased pressure ought to give some intensity to the special radiation which the molecules emit during their time of free motion; and this we have noticed to occur in the principal sections of the discontinuous spectrum of the oxy-hydrogen flame. Whether the continuous spectrum is due to the mutual action of the molecules of the compressed gases may perhaps be best determined by some photometric measures of the rate at which the brilliance increases with the pressure. Frankland ("Experimental Researches," pp. 892 *et seq.*) has made some such measures, but not sufficient to solve the question. We have made an attempt to measure, not the total intensity of the light, but that of rays of definite refrangibility.

Photometry of Oxy-Hydrogen Flame under Pressure.

The apparatus used for these measures was a spectro-photometer of the pattern employed by Crova (*Annales de Chimie*, series 5, vol. xxix., p. 556). In this, the rays of one of the sources of light to be compared are passed through two Nicol's prisms, and then reflected into one half of the slit of the spectroscope, while the light from the other source passes directly into the other half of the slit. By turning one of the Nicol prisms, the light from the first source can be reduced at pleasure, and any small section of the spectrum can be separately observed by cutting off the rest by means of a shutter in the eye-piece. We found it by no means easy to get good concordant observations. A much larger vessel was used than for the earlier experiments, one which contained several litres, and so we may presume a more uniform pressure was maintained within it. The results of the best series of observations on the photometric intensity of the jet of oxygen burning in hydrogen are given in the following table. The comparison light was a petroleum lamp.

I.	II.	III.	IV.
15 lbs.	3°	274	$30 \times 3^2 = 270$
35 ,,	7	1485	$30 \times 7^2 = 1470$
55 ,,	11	3641	$30 \times 11^2 = 3630$
75 ,,	14	5853	$26 \times 15^2 = 5850$
95 ,,	19	10600	$29 \times 19^2 = 10469$

The first column gives the pressure of the gas, the second the mean of four to six observations of the angular deviation of the Nicol's prisms from the position of complete extinction for each pressure. The third column gives the squares of the sines of the angles in the second column multiplied by 100,000.

It will be seen from the last column that the numbers in the third column, which should be proportional to the photometric intensities at the respective pressures, are approximately proportional to the squares of the pressures.

This may be taken to indicate that the brightness of the continuous spectrum depends mainly on the mutual action of the molecules of gas.

A series of similar observations on hydrogen burning in oxygen gave somewhat different results, tabulated below:—

I.	II.	III.
15 lbs.	6°	1093
35 ,,	13	5060
55 ,,	18	9549
75 ,,	22	14033
95 ,,	28	17861

The flame was brighter than that of oxygen burning in hydrogen at ordinary pressure, but the rate of increase with increased pressure was not so rapid as in the former case. It seems as if the continuous spectrum were made up of two parts, one varying as the square of the pressure and another according to some other law. The flame is evidently not the same in the two cases. The products of combustion derived from the small quantity of air are different, and also the hydrogen jet always showed the presence of sodium, sometimes calcium. The appearance of the flame was also different; the hydrogen jet being faintly visible and yellowish in the elongated part, whereas the light from the oxygen jet was concentrated near the base, the point being invisible. The measures of which the means are tabulated above were also less concordant than the corresponding measures for the oxygen jet. We were unable to carry our measures beyond a pressure of 95 lbs., because at higher pressures a cloud was formed in the apparatus which prevented our seeing the flame directly. We hope to prosecute these measures with flames of other gases, and, if possible, at higher pressures.

The conclusions to which our experiments have led seem inconsistent with these which have been drawn from Plücker and Hittorf's well-known observations on the widening of the hydrogen lines in vacuous tubes with a residue of hydrogen when that residue increases. That the widening of the lines in a Plücker's tube results from increasing the density of the residue of hydrogen in the tube cannot be gainsaid, but we are wholly ignorant of the mechanism by which the gas is lighted up by the electric discharge. It is sometimes assumed, but without any sufficient reason, that the energy of the electric current is first converted into heat, and then in turn into radiation; but the electric energy may equally well be directly converted into the motion of radiation. As a fact, we have never yet been able to obtain either the emission or the absorption spectrum of hydrogen without the aid of an electric current, so that, in reasoning on this spectrum, we are much more in a region of speculation than when treating of flames. Whether the hydrogen lines, bright or dark, in the solar spectrum are produced directly by the high temperature of the sun, may even be called in question. And though we may admit that the density of the hydrogen in the sun's atmosphere, outside the photosphere, is but slight, it does not follow that the total pressure of all the gases forming that atmosphere is so very small as Messrs. Frankland and Lockyer (*Proc Roy. Soc.*, vol. xvii., p. 288) have, from the width of the lines, concluded it to be. After all, it is not so easy to connect the temperature, even of a flame, with its radiation, for it is only when the condition of a gas is steady that we can assume that there is a definite relation between the motion of agitation, on which temperature depends, and the vibratory motions, on which radiation depends. In speculating on such questions, chemical, as well as electrical, changes must not be lost sight of, although the latter may be more directly concerned in radiation.

Experiments which we have commenced upon the arc in an atmosphere of compressed gas tend to the same conclusion. It does not appear that the metallic lines in the arc are sensibly affected by a steady pressure up to 15 atmospheres. The details of these observations, which are complicated by the variation of resistance with change of pressure, we defer until the experiments are finished.

On the Ptomaines.—M. Oechsner de Coninck.—A completion of the study of the ptomaine $C_{10}H_{15}N$. Its iodomethylate was dissolved in absolute alcohol; to the solution whilst still hot there was added a single drop of strong potassa lye. A bright red colouration appears at once and soon turns brown. The dark liquid in about an hour presents a blueish-green fluorescence which lasts a long time. The two ptomaines, $C_8H_{11}N$ and $C_{10}H_{15}N$, certainly belong to the pyridic series, but are not hydrides.—*Comptes Rendus*, vol. cxii., No. 11.

ON THE BISULPHITE COMPOUNDS OF ALIZARIN-BLUE AND CŒRULIN AS SENSITISERS FOR RAYS OF LOW REFRANGIBILITY.*

By GEORGE HIGGS.

The determination of the relative wave-lengths of the Fraunhofer lines, by photographing all the orders of spectra given by any particular grating, includes certain subjects which present more or less difficulty, and that of selecting or producing a dye-bath adapted to the requirements of the two or more orders comprising the subject is intimately connected with that of the choice of absorbing media.

Having been engaged for some time in investigations of this nature, I had occasion, during the summer of 1889, to require an impression of the 2nd order, about w.l. 3300, contiguous with that of the red end of the 1st order, and finding that the ordinate of an actinic curve for a plate immersed in a very dilute alcoholic ammoniacal solution of cyanin (1 : 30,000), reduced to about one-fourth of that for an unprepared plate, I abandoned its use for this purpose. The results appeared to be unaffected by the addition of quinine.

Subsequently, induline, cœrulin, alizarin-blue, and the bisulphite compounds of the two latter were used, and when obtained in a state of sufficient purity the alizarin-blue S leaves little or nothing to be desired, for, whilst possessing, in a high degree, sensitising properties for rays throughout the region comprised between w.l. 6200 and 8000, it does not, as in the case of cyanin, lower the sensitiveness to the violet and ultra-violet.

The following is one of the processes I employed in the preparation of the dye-stuff in a pure state:—

To a saturated solution of sodium bisulphite in a mortar is added alizarin-blue paste, disintegrated with a pestle, and poured into a glass vessel capable of holding an additional quantity of sodium bisulphite, in all 10 parts of the paste to 20 parts of bisulphite, and another 10 parts of water. The vessel is well stoppered, set aside in a cool place for five or six weeks, and shaken daily, but left undisturbed during the last eight or ten days.

The solution is decanted, filtered, and treated with alcohol, to precipitate the greater portion of the remaining sodium bisulphite. 50 parts of water are now added with a sufficiency of sodium chloride to form a concentrated solution. Again set aside in an open-mouthed glass jar, covered with bibulous paper, for seven or eight days, a deposition of the dye in a crystalline state, together with sulphite of calcium, will take place, which latter, owing to its insolubility in water, may be removed by filtration.

The alizarin-blue S is separated from any unaltered substance left in the original stoppered vessel by solution, and added to the brine, now purified from lime salts, and once more set aside to crystallise, the final purification being effected in a beaker containing alcohol and a small percentage of water to remove the last traces of sodium chloride, collecting the crystals on a filter-paper and drying at ordinary temperatures.

The needle-shaped crystals are of a deep red. Dilute solutions are of a pale sherry colour, changing, with the addition of a few drops of ammonia, to a green, which immediately gives way to magenta and every shade of purple, till oxidation is complete, when it assumes a blue colour, the absorption spectrum of which is continuous and strongest in the least refrangible end, presenting the appearance of extending into the infra-red.

Plates immersed in a solution containing 1 : 10,000 and 1 per cent of ammonia give the most perfect results the day after preparation, but rapidly deteriorate unless kept quite dry.

With a slit $\frac{1}{1000}$ inch in width, and an exposure of forty minutes, results have been obtained in the region of Great A of the 2nd order, which possess all the detail and definition usually so characteristic of the violet end. Numerous lines are sharply depicted which were previously not known to exist. W.l. 8400 has been reached, giving almost equal detail.

The process for the preparation of pure cœrulin S is a slight modification of the preceding. The results obtained, as well as the actinic curve, are almost identical. The pure substance is almost white; dilute solutions pass rapidly from pale yellow to a bright green; a trace of ammonia produces an olive-green.

For several samples of paste I am indebted to the kindness of Messrs. Schott, Segner, and Co., of Manchester, agents to the Badische Anilin- und Soda-Fabrik, Ludwigshafen, who hold the patent rights for the manufacture of alizarin-blue S. It is hoped this company may be induced to manufacture this substance free from the minute crystallisable impurities which render it unsuitable for use in investigations of such delicate nature.

DISCUSSION ON THE THEORY OF SOLUTION.*

(Continued from p. 151).

Professor Ostwald read the following communication "On the Electrical Behaviour of Semipermeable Membranes":—

If we fill two glass beakers with copper sulphate solution, put in them two copper wires connected with a couple of Leclanché cells, and a galvanoscope, and close the circuit by a siphon filled with any electrolyte, which is prevented from mixing with the copper sulphate by covering the ends of the siphon with parchment paper, no phenomenon of special interest is to be noticed. We have an electrolytic circuit without polarisation, as used by Paalzow for the determination of the specific conductivities of liquids. By varying the liquid in the siphon only the total resistance of the circuit varies, and polarisation does not generally occur. If we fill the siphon with potassium ferrocyanide, nothing novel seems to go on at the first glance. But if we remember that on the contact of copper salts with ferrocyanides a *semipermeable membrane* of copper ferrocyanide is formed, through which, according to the observations of Traube, no copper salt can diffuse, we are led to a somewhat strange question. The fact that no copper salt can pass through the membrane is evidence that the copper ions existing in the salt solution are likewise unable to pass. But as the electricity in electrolytes travels only with the ponderable ions, we are met by the alternative either that the refusal of the copper (and ferrocyanide) ions to pass through the membrane will cause the current wholly to stop, or that the electricity will deposit the copper ions on the membrane and itself alone pass through. The semipermeable membrane must in the first case act as an *insulator*; in the second case it must act as a *metallic diaphragm*. Both these cases are so unexpected that the described experiment at once acquires a special interest.

By performing the experiment we find that the second alternative holds good. The current becomes rapidly weaker, and after ten minutes we can easily observe a very marked polarisation current in inverse direction to the primary current. After some hours of current the parchment paper containing the semipermeable membrane on the positive side is coated with a layer of metallic copper, and this is evidence *that the copper ions are filtered off by the semipermeable membrane*.

From this experiment it follows that the semipermeable membrane really acts as a sieve, not only as regards compounds, but also for ions, allowing some of them to pass

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* Read before the Royal Society, March 12, 1891.

* British Association (Section B), Leeds Meeting, 1890.

and retaining others; for we know, for example, that potassium chloride can pass the membrane of copper prussiate, and therefore the ions K and Cl do so, while barium chloride and potassium ferrocyanide are retained. In the two last-mentioned cases one of the ions has the power of passing, but is retained by the other. At the first moment the Cl ions of the barium chloride will of course go through the membrane, while the barium ions stay behind. But by this separation a separation of positive and negative electricity also takes place, and thereby forces will arise tending to draw the Cl ions back. Finally a double layer of electricity is formed, causing a potential difference on both sides of the membrane, whose value depends only upon the molecular concentration of the electrolyte, and in no way upon its nature.

If the formation of the double layer is prevented, free diffusion of the passing ion takes place. By adding to the barium chloride some salt whose metal can pass through the membrane—for instance, some salt of potassium—the Cl ions at once will traverse the membrane, but the same number of K ions must go along with them. In this case, however, it may be assumed that the added potassium salt undergoes a double decomposition with the barium chloride, forming potassium chloride, which is able to diffuse through the membrane. But we can also cause the Cl ions to pass by putting some diffusible negative ions on the *outside* of the membrane—for instance, copper nitrate. Then we soon find chlorine outside and a nitrate inside the membrane. In this case it is impossible to assume a double decomposition, because both the salts are separated by the membrane, which prevents the diffusion of the barium chloride, as well as of the copper nitrate, and the explanation, by taking into account free migrating ions, seems to be the only sufficient one.

The above-mentioned double layers and potential differences, occurring at semipermeable membranes, when one of the ions of the electrolyte is retained, are probably the source of the potential differences and currents we meet with in living matter, because the cells of organisms are all coated with such semipermeable membranes. It is perhaps not too rash to hope that the ancient mystery of electrical fishes will find its solution on these lines.

Referring to the discussion Professor OSTWALD said—Professor Fitzgerald has asked why the ions, when they are free, do not separate by diffusion. The answer is that they do. If we have a solution of HCl, for example, consisting to a great extent of H and Cl ions, in contact with pure water, the H ions, moving much faster than the Cl ions, take the lead in wandering into the water. But a separation of electricity hereby takes place, and every ion being charged with a great amount of either positive or negative electricity, the electrostatic forces resulting from the initial separation soon prevent further separation. Therefore water must take a positive potential against a solution of hydrogen chloride, and in general water must show against every electrolytic solution the potential of the faster ion.

These considerations, which lead to the whole theory of the potential differences between electrolytes, were first developed by W. Nernst (*Zeitsch. f. phys. Chem.*, ii., 613, and iv., 129), who has confirmed them by various experiments; and further by M. Planck (*Wied. Ann.*, xl., 561). As far as I am aware, no theory of fluid-cells (*Flüssigkeitsketten*) had hitherto existed, and the possibility of developing one consistent with experiment from the principles first stated by Arrhenius is strong evidence in favour of his views.

Secondly, Professor Fitzgerald seeks for the source of energy required for the separation of, *e.g.*, Cl and H by dissolving HCl in water. This question is in accordance with the widely-spread assumption that a great expenditure of work must be done to effect this separation. As a great amount of heat is developed by forming HCl from its elements it seems evident that the same amount of energy must be restored to the elements in separating them. This is quite true if common hydrogen and chlorine were formed, but the ions H and Cl, existing in the aqueous solution of hydrogen chloride, are by no means identical with the so-called free elements. To use a word to which chemists are accustomed, the ions H and Cl are *allotropic forms* of these elements, similar to yellow and red phosphorus, and contain very different amounts of energy from those which they contain in their common state of hydrogen and chlorine gases. Therefore it is impossible to say anything *à priori* about the evolution or absorption of energy connected with the change from HCl gas to positively charged H ions and negatively charged Cl ions; we must interrogate facts; and these teach us that the ions generally contain much less energy than the elements in the common state, and therefore a great amount of energy is not called for in the transformation of, *e.g.*, HCl into the free ions H and Cl.

The elements in the state of ions being charged with great amounts of electricity, the very different tendency of the elements to assume the state of ions can be conveniently called their different affinity for electricity. This expression is of course only a *façon de parler*, but it gives a good description of the behaviour of the elements. The action, for example, of zinc on cupric sulphate solution, containing the ions Cu and SO_4, depends on the greater tendency of the zinc to form ions; therefore the zinc tears the positive electricity necessary for its existence as an ion from the copper ions, and deposits the latter as unelectrical, *i.e.*, common metallic copper. The SO_4 ions, being no closer connected with the zinc than with the copper, act only as, owing to their negative charges, they render possible the existence of an equal number of positive ions, no matter of what nature.

If I am right Professor Fitzgerald is now ready to acknowledge the views of Arrhenius as *possible* ones, but he assumes that the facts explained by these views can also be explained by some other views, of which he has given some specimens. It is, of course, impossible to deny this. But as the theory of Arrhenius has done its work up to the present, and the new theory has yet its way to make, the former seems to have certain claims to be preferred. As the theory of Arrhenius has shown itself to be consistent with a very great number of facts, in the most various branches of physics and chemistry, the new theory must of necessity lead in all these cases to the same result as that of Arrhenius. Then the scientific world will have the wonderful spectacle of two theories, starting from different points of view, but leading everywhere to the same result. Science will then possess a twofold means of further investigation of some of its most difficult problems; a state of matters that cannot be too urgently wished for by all who have devoted their powers to such investigations.

In reply to Mr. Pickering's remark that the induction experiment upon electrolytic solutions described by me is opposed to the first principles of science, especially to the first law of thermodynamics, I wish only to remind him that by carrying out the common lecture experiment with two metallic balls and a charged body, we can get from the balls a spark, and therefore also an amount of energy. As no one hitherto has found in this experiment a contradiction to the law of the conservation of energy, I can leave the defence of my experiment to all teachers who annually perform this experiment in their lectures.

Professor Lodge has asked if the experiment in question has been carried out, and in what manner. The description of a series of such experiments has been given in the *Zeitschr. f. phys. Chem.*, iii., 1889, p. 120. The easiest way to demonstrate the liberation of ions in electrolytes by induction is to fill a glass jar covered on the outside with tinfoil with dilute sulphuric acid, to connect the outside with a source of positive electricity, and to insert in the sulphuric acid an earth-connected capillary electrode, *i.e.*, a short Lippmann electrometer. The very minute bubbles of hydrogen developed by electrostatical actions can then easily be observed in the capillary tube on the boundary of the mercury and the sulphuric acid by help of a microscope.

Professor Armstrong has declared that the dissociation theory of electrolytes is unacceptable to chemists. As far as I am aware, there exists nowhere a real contradiction between chemical *facts* and the dissociation theory, but this theory only runs against all the time-honoured *feelings* of chemists. As feelings, although very powerful things, are at least variable with time and custom, it is to be expected that they will change sooner or later. The time is not very long past when the assumption that, in the vapour of ammonium chloride, hydrochloric acid and ammonia, which have "so great an affinity for each other," should exist separate from one another ran in quite the same manner against the feelings of chemists. Now we are accustomed to this conception, and in the same manner chemists will speak in a year or two as quietly of the free ions as they now speak of the uncombined mixture of hydrochloric acid and ammonia in the gaseous state.

But it should not be forgotten that a great many purely chemical facts—in the first place the great generality and regularity of the chemical reactions of electrolytes as used in analytical chemistry, in opposition to the variability and irregularity of the behaviour of non-electrolytes, especially of organic bodies—have found their first explanation in the theory of electrolytic dissociation. The objection against this theory, that if the ions of salts exist in a free state this would not be any ground for the law of constant proportion between acid ions and metals, is easily refuted. For, according to Faraday's law, all chemically equivalent amounts of positive and negative ions are charged with equal amounts of electricity; in an electrically neutral solution, as all ordinary solutions are, there cannot but exist an exact equivalent number of positive and negative ions. We see, therefore, the law of Faraday connected in the closest manner with Richter's law of chemical equivalents; if the one holds good, the other must also hold good, and *vice versâ*.

Professor Armstrong has asked why water does not split into ions, while hydrogen chloride, a body similar to water, does. But has Professor Armstrong forgotten that liquid hydrogen chloride, like pure water, is an *insulator* for the electric current, as was found long ago by Gore, an observation afterwards confirmed by Bleekrode? It has been stated by F. Kohlrausch that at ordinary temperatures no pure liquid is a good electrolyte. The theory of Arrhenius is still in this point the only one which explains this strange fact; pure liquids do not conduct, because their molecules have no space to resolve themselves into ions.

It is therefore not improbable that water would conduct electrolytically if we could find a suitable solvent for it. An investigation in this direction would be of very great interest, but not without grave difficulties.

To a certain, but very small extent, water too contains ions, namely, H and OH. This is shown by the hydrolytic action of water on the salts of weak acids and bases, the amount of H or OH ions dissociated from these acids or bases being in such cases comparable with the amount of the same ions in water. Then the latter acts as a very weak acid or base, and the action follows the common law of masses, as J. Walker has shown (*Zeitsch. f. phys. Chem.*, iv., 319).

(To be continued).

STUDIES ON THE EARTHS OF THE CERIUM AND YTTRIUM GROUP.*

By A. BETTENDORFF.

The material for the following researches was orthite, obtained from the establishments of Dr. Marquart, of Bonn, and Dr. Schuchardt, of Goerlitz, and said to have been derived from Strömboe, near Arendal, and from Hitteroë. From the analysis of Angström and Clève, it appears that all the orthites contain varying quantities of the earths of the cerium and yttrium groups, in which considerable quantities of thoria are also present.

The rare earths of the orthite were separated according to the known methods which are also used for the decomposition of cerite. To remove the cerium and thorium oxide, the author used the process given by Debraye (*Comptes Rendus*, xcvi., 828). The nitrates of the earths are fused with six parts of potassium nitrate, a method which is expeditious and gives excellent results. The cerium compound is so completely removed that on treating the hydroxides of the earths with chlorine gas no trace can be discovered. On the other hand, very small quantities only of the other earths remain in the cerium oxide. After the removal of this oxide and of thoria, the earths of both groups are separated by means of potassium sulphate.

This separation has hitherto been effected exclusively by Mosander's method. The author has introduced a modification which has an influence upon the complete separation of the two groups. The cerium group contains certain oxides, the double potassium sulphates of which are only precipitated from a saturated solution of potassium sulphate very slowly and on vigorous agitation. The separation is therefore undertaken by preference in corked bottles which are filled with a solution of potassium sulphate, saturated when hot, and allowed to cool. The bottom of the bottle is then coated with a firmly adherent saline crust. If the separation is to take place without shaking, the bottle, after the introduction of the chlorides or nitrates of the earths, is completely filled with the saturated solution of potassium sulphate, corked up, and inverted; these are the conditions prescribed by Mosander. In the other case, the bottles are only filled partially. When both the groups have been separated, and the earths have been set free from the double sulphates, the separation of the two constituents is commenced.

The author has used the method of the partial decomposition of the nitrates, as it permits larger quantities to be worked up in a relatively short time. It is easily practicable to melt up the nitrates of the yttrium earths to a clear liquid, as their point of fusion is low and remote from their decomposition heat. Small quantities of the nitrates of the cerium earths can also be melted to a transparent liquid in a platinum crucible on an open fire. But if we attempt to operate on larger quantities, it appears that long before complete fusion is effected a part of the mass is decomposed, with separation of oxide and basic nitrate. Under these conditions the access of heat is not in harmony with the thermic conductivity of the solid nitrate, whence the portions lying nearest to the fire are melted and decomposed before the entire mass enters into fusion. This defect may be remedied by placing the platinum crucible containing the nitrates in a porcelain crucible in such a manner that there remains everywhere between the two an interval of from 1 to 2 m.m. As the porcelain crucible is very apt to crack, it is wrapped round with some rings of platinum wire, after which hundreds of fusions can be undertaken in it. In this manner large quantities of nitrate can be fused to a clear liquid, and, if heated more strongly, begin to decompose. As soon as small crystalline leaflets of basic nitrate appear on the surface of the melt, the contents of the crucible are poured into a large platinum capsule. The cold mass forms a perfectly clear solution in 10 parts of water; and, on boiling, basic nitrate separates from the solution in dense flocks, which are easily removed by filtration. From the concentrated filtrate a second separation is then obtained, and so further.

The earths, freed from cerium oxide and precipitable by potassium sulphate, after the last portions of the yttrium earths had been removed had an equivalent of RO = 109·0 to 110·2. It is readily practicable to remove all lanthanum by systematic fractional precipitation of the nitrates of

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* From *Liebig's Annalen*

these oxides. Small quantities of didymium oxide are still present, but the product has a high degree of purity, as is proved by the equivalent of the oxide RO = 108·76.

The separation is carried so far that in the basic nitrates ultimately obtained no lanthanum lines can be obtained in the spark-spectrum of the chloride. The united basic nitrates, when completely freed from La, furnish a brown oxide with the equivalent of RO = 113·2 to 114·0. They contain all the didymia and samaria bands, larger or smaller quantities of gadolinia or terbia, according as the separation of the yttrium earths by means of potassium sulphate has been effected by Mosander's process, or by the modification above described.

The author now communicates the observations made whilst obtaining pure lanthanum compounds from the above-mentioned mixtures RO = 108·76.

A further purification by a systematic fractionated decomposition of the nitrates on fusion presents serious difficulties. Though the melting-point has become rather high, it is practicable, by the process above described, to obtain a clear melt from which leaflets of basic nitrate separate; but, on cooling, the congealed mass is scattered about as dust—the more, the richer it is in lanthanum nitrate—sometimes with such force that considerable quantities are lost. This phenomenon was observed by Berzelius, and is described in his "Lehrbuch."

It is more advantageous to apply the method described by Auer von Welsbach, which depends on the circumstance that in a solution of the mixed didymium and lanthanum-ammonium nitrates, the double salt of lanthanum first crystallises out, being much less soluble. Auer von Welsbach conducts this separation in a strong nitric solution. The author—as his preparation contained but little didymium—found it more convenient to allow crystallisation to take place in a solution as neutral as possible.

(To be continued).

MILK ANALYSIS BY THE ASBESTOS METHOD.*

By **FRANK T. SHUTT**, M.A., F.I.C., F.C.S.

To render complete the results of feeding experiments conducted at the Central Experimental Farm with thoroughbred stock, a comparatively large number of analyses of milk is required to be made. At the outset of this work, therefore, a process was sought by which the composition of the milk (*i.e.*, total solids and fat) could be accurately and rapidly ascertained.

After working Adams's, Wanklyn's, the plaster-of-paris, sand, and other methods, a trial was made of the asbestos method as described by Thomas Macfarlane, F.R.S.C., Chief Analyst, Department Inland Revenue, in a paper read before this Society in May, 1887. This process proved so satisfactory, both as to accuracy and rapidity, that I have been led to adopt it in the laboratory of the farm.

The object of this paper is to bring before your notice the results of some experiments contrasting this process with others in which (*a*) the total solids are estimated by evaporation in platinum dishes, and (*b*) in which the fat is determined by direct weighing in flasks after exhaustion of the milk solids in a Soxhlet tube. A series of experiments (the results of which are depicted in Table III.) was also undertaken to compare the percentages of fat obtained by the use of Soxhlet and Stutzer tubes respectively, the fat being estimated by difference. Lastly, as shown in Table IV., the results are given of a number of consecutive analyses, copied seriatim from the analyses book, which show the degree of closeness with which duplicate assays can be made by the asbestos method, using the Stutzer tube for the extraction of the fat.

TABLE I.

T. solids by asbestos method.	T. solids by plat. dish.	Increase in percentage of t. solids by evap. in plat. dish.
12·85	13·25	0·40
14·36	14·73	0·37
15 21	15·70	0·49
12·80	13·14	0·34

First Column.—In these experiments, about 10 c.c. of milk was weighed in the tubes containing asbestos fibre, which had previously been dried in the steam cupboard.

The tubes, with the milk absorbed in the asbestos were then replaced in the steam cupboard, allowed to remain there twelve or sixteen hours (over night usually), cooled in the desiccator, and again weighed. The temperature of the cupboard during the operation of drying is between 85° C. and 90° C., a strong current of air passing through the chamber.

Second Column.—The milk, about 5 c.c., was weighed quickly into small platinum dishes. These were placed on a water-bath for four hours (the water being in brisk ebullition), cooled, and weighed. All the results are calculated from duplicate analyses.

It will be noticed from an inspection of the foregoing table that the solids obtained by drying in the platinum dishes are from 0·34 to 0·49 per cent higher than those obtained by the asbestos method. I am of opinion that the results from the former method are too high, and that the increase in the total solids may be accounted for on one or more of the following grounds:—1. By the greater evaporation of the milk while being weighed, owing to the large surface of the fluid exposed. 2. By the scum which inevitably forms not allowing the complete drying of the milk. 3. By a probable oxidation of the fat or other organic constituents of the milk.

It may be noticed here that while the milk solids in the asbestos are always perfectly white, those in the platinum dishes are more or less brown, clearly showing that some change takes place in the latter process which does not ensue by the asbestos method.

TABLE II.

Fat by exhaustion.	Fat by weight in flasks.	Increase in percentage of fat by direct weighing.
3·81	3·89	0·08
4·64	4·72	0·08
5·40	5·31	—
3·90	3·88	—
3·47	3·51	0·04
3·95	3·97	0·02
6·01	6·02	0·01
4·36	4·40	0·04
3·11	3·16	0·05
3·58	3·57	—
3·81	3·84	0·03
4·38	4·47	0·09
4·31	4·34	0·03

In the first column is shown the percentage of fat obtained by exhausting the solids in asbestos by means of the Stutzer tubes; in the second are detailed those got by extracting in Soxhlet tubes and weighing the fat in flasks. Though the results obtained are very close, those obtained by direct weighing are, in almost every instance, slightly the higher of the two. It will be seen, when considering the results of Table III., that the fat obtained by difference when using the Soxhlet is somewhat lower than when the Stutzer is employed, and hence the differences shown in the third column would most probably have been greater had Soxhlet tubes been used in this series. The increased percentage of fat may, therefore, be accounted for by the

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* *Trans. Roy. Soc. Canada*, Section III., 1890.

partial oxidation of the fat when drying in the flask on the water-bath previous to weighing. The ether used was of the best German manufacture, and left no appreciable residue on evaporation.

Table III.

Specific gravity.	Total solids, asbestos method, average of duplicates.	Fat by Soxhlet.	Fat by Stutzer.	Increase in percentage of fat by Stutzer tube.
1032·0	12·84	3·73	3·88	0·15
1033·5	14·35	4·60	4·61	0·01
1033·0	15·21	5·33	5·56	0·23
1032·1	12·77	3·85	3·97	0·12
1032·0	11·98	3·44	3·47	0·03
1033·2	13·03	3·94	3·96	0·01
1032·1	15·31	5·95	6·05	0·10
1033·4	13·71	4·33	4·35	0·02
1032·9	12·11	3·09	3·08	—
1031·0	12·20	3·58	3·58	—
1033·2	13·16	3·79	3·82	0·03
1033·8	13·89	4·35	4·34	—
1032·6	13·50	4·26	4·31	0·05

In the asbestos method, as described by Mr. Macfarlane, Soxhlet tubes were recommended to be used for the extraction of the fat. As but two—or at most three—tubes containing the milk solids can be exhausted by this method at once, I was induced to inaugurate the experiments detailed in the above Table (III.), which shows the percentages of fat obtained by exhausting the milk solids for the same length of time (four hours) in Stutzer tubes, in which from six to eight of the glass cups can readily be treated at once, thus effecting a saving of one-third the time over the Soxhlet method. The results by both processes are very close, yet it will be noticed that in nearly every instance the Stutzer tube gives a slightly higher percentage of fat, *i.e.*, the extraction of the fat is more complete by the Stutzer process. This fact may be accounted for by the more frequent washing of the solids by the ether in the Stutzer tubes, as well probably as by the slightly higher temperature of the ether in these tubes. The results by the Stutzer process are therefore, I am led to believe, the nearer to the truth of the two.

Table IV.

Total solids.	Fat.	Solids other than fat.
13·42	4·31	9·12
13·43	4·31	
12·68	3·80	8·88
12·67	3·80	
13·13	4·35	8·78
13·12	4·35	
13·54	4·20	9·35
13·57	4·22	
17·23	8·13	9·14
17·30	8·11	
15·14	6·08	9·06
15·16	6·10	
14·09	4·61	9·49
14·07	4·58	
12·24	4·03	8·22
12·27	4·04	
12·70	3·85	8·84
12·68	3·85	

Table IV. contains the results of consecutive analyses made in duplicate by the asbestos process, using the Stutzer tubes for the extraction of the fat. Where the third figure in the decimal place exceeded 5, the second decimal figure was raised.

If it be granted that the total solids and fat can be accurately determined by this method, an inspection of the above figures will clearly prove that the results are not variable, and that when duplicates are performed no large differences will have to be averaged in order to arrive at the truth. Judging from my own experience, I should say that the labour and time involved in using the asbestos method with the Stutzer tubes are about one-third less than when other processes are employed.

ADULTERATED SPIRITS OF TURPENTINE.

A Convenient Method for Detecting and for Estimating Petroleum in Spirits of Turpentine.

By SAMUEL J. HINSDALE, Fayetteville, N.C.

Put ten drops of the spirits to be examined in a (moderately concave) watch-glass, and float the glass on about a quart of water which has a temperature of about 170° F. If the spirits is pure, it will evaporate and leave the glass quite dry in seven minutes. If the spirits contains even five per cent of petroleum, it will not have completely evaporated in that time.

This experiment will prove the absence or presence of petroleum in the sample.

To estimate the *percentage* of petroleum, weigh a watch-glass and put into it ten drops of the mixture, and weigh again. Put into another glass ten drops of pure spirits of turpentine, and float both glasses on about a quart of water at about 170° F.

As soon as the pure spirits has evaporated, take off the glass which contained the mixture and weigh it. The difference between this weighing and the weight of the glass will indicate the amount of petroleum in the mixture. Knowing the weight of the ten drops, the percentage can be calculated.

A bent loop of wire is convenient to place on and remove the watch-glass from the water.

The hydrometer will detect adulteration with benzene or petroleum, but it cannot be used to estimate the amount of adulteration.

The specific gravity of pure spirits of turpentine is about 0·865.

Petroleum is the usual adulterant.

The Presence of Alcohol in Commercial Ethyl-Ether.—Th. Poleck and K. Thümmel (*Archiv. der Pharm.*).—If a clear mixture of 4·5 vols. of a saturated solution of potassium bicarbonate and 1 vol. of a saturated solution of mercuric chloride is shaken up with commercial ether, the mixture becomes turbid in ten to twenty minutes, and a white amorphous precipitate separates out. If further quantities of ether are added, all the mercury is eliminated except traces, whilst the substance which reacted upon the ether is withdrawn from the mercurial solution. The yellow or brown colour imparted to commercial ether on the addition of potassium hydroxide is occasioned by alcohol.—*Zeit. fur Anal. Chemie*, Vol. xxix., Part 6.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

March 20th, 1891.

Prof. W. E. Ayrton, F.R.S., President, in the chair.

Prof. S. U. Pickering, F.R.S., read a Paper on "*The Theory of Dissociation Into Ions and its Consequences.*"

According to this theory, electrolytes are entirely dissociated into their ions in weak solutions. This dissociation was held by Arrhenius to absorb heat, and although heat is evolved by the dissolution of hydrochloric acid, &c., it is not maintained that dissolution evolves heat, but that the heat absorbed by the decomposition of the molecule into its atoms is more than counterbalanced by the heat supposed to be evolved by the combination of the atoms with their electric charges. These actions the author considered improbable, and thought that before being accepted, the theory must give satisfactory answers to the following questions:—How can matter combine with an affection of matter to produce heat? Whence do the electric charges originate? Why does not the opposite electrification of the different atoms make them cling more firmly together, instead of dissolving the union between them; and why should an atom which possesses a strong attraction for a negative charge (such as chlorine) go to the positive electrode during electrolysis?

When a dilute solution, which is supposed to contain some gaseous molecules, is further diluted, then, according to the theory, some of the molecules are dissociated, and, if heat is absorbed, it follows that the dissociation, and therefore dissolution, of the gas must absorb heat; yet, he said, it can be shown that in some of these cases the dissolution of a gas evolves a large amount of heat.

The antagonism between the present and the old electro-chemical theory—according to which the atomic charges are identical with the free energy of an atom, and are the cause of combination, not decomposition—was commented on, as well as the disagreement between the present theory and Clausius's view that there are a few ions or atoms present in a liquid owing to accidental super-heating of some of the molecules. Reasons, however, were adduced for believing that the presence of even a few atoms in a solution to be improbable.

A communication on "*Some Points in Electrolysis*" was made by Mr. J. Swinburne.

Considering a reversible single fluid cell, the author, by a process of reasoning based on Carnot's principle and the conservation of energy, arrives at Helmholtz equation—

$$E = E_c + \theta \frac{d\,E}{d\,\theta}$$

where E is the electromotive force, E_c the part due to chemical action, and θ the absolute temperature. Writing the equation in full, using suffixes n and p to denote the negative and positive plates, it becomes—

$$E_n + E_p = E_{nc} + E_{pc} + \theta \frac{d\,E_n}{d\,\theta} + \theta \frac{d\,E_p}{d\,\theta}$$

He then shows that by having the two plates in different vessels and heating them to different temperatures, the Peltier effects represented by—

$$\theta \frac{dE_n}{d\theta} \quad \text{and} \quad \theta \frac{dE_p}{d\theta}$$

can be determined separately. Similarly those of a two fluid battery might be found by arranging the junction of the fluids in a third vessel.

After pointing out the desirability that the conditions under which all thermo-chemical data have been obtained should be clearly stated, he proceeded to show that any cell in which secondary actions occur (as, for example, if zinc oxide primarily formed by electrolysis were to dissolve in sulphuric acid), must necessarily be non-reversible. He also contended that in a secondary battery the formation of lead sulphate on both plates is the essence of the cells action, and that there is no intermediate formation of PbO.

On the subject of so-called "nascent" hydrogen or oxygen, he said that reasoning from the conservation of energy showed that neither could exist. Taking the case of persulphate of iron in dilute sulphuric acid, which is said to be reduced to protosulphate by the "nascent hydrogen" liberated on putting a piece of metal (say magnesium) into the liquid, he said a better explanation of the phenomena would be that the metal dissolves if it either reduces the metal or evolves hydrogen; and as the former requires less energy, the reduction takes place, and when no reducible salt is available, hydrogen is evolved. Evolution of hydrogen, and reduction of the per salt, are thus *alternative* and not *consecutive* actions.

Examining Dr. Lodge's views on the contact E.M.F. between metals, he remarked that if the tendency of a metal (such as zinc) to oxidise can produce an electric stress or difference of potential which prevents further combination, actual combination must charge the metal, if it be insulated. A piece of sodium, however, oxidises continuously, and therefore should become charged to an enormous potential. As this effect is not known to occur, the author suggested that the Volta effect may be due to films of water, and in support of this view adduced the fact that metals, when perfectly dry, do not combine with chlorine, and that even sodium is not attacked by dry chlorine.

In the discussion on the two papers, Prof. Pickering said the idea of nascent elements had, to a large extent, been given up by chemists, and pointed out that the fact of one reaction taking place rather than another was not merely a question of heat energy, but that a kind of chemical selection was involved.

Prof. S. P. Thompson recalled attention to the fact that the products of electrolysis depend on the E.M.F. employed in producing it, and thought the E.M.F. required to produce the various products might be taken as a measure of their affinities. He did not agree with Mr. Swinburne's method of finding the E.M.F. of a secondary battery from thermo-chemical data, for he failed to see how two similar actions going on at the two plates of a cell could add anything whatever to the E.M.F. of the cell.

The President said the question whether the potential difference between two dissimilar substances was due to oxidation or to mere contact could only be decided by direct experiments made in a vacuum, from which all traces of moisture and oxygen had been removed. Without agreeing with Dr. Lodge's view on the subject, he pointed out that the continuous oxidation of a piece of insulated sodium need not necessarily produce a great potential difference, for the combination might produce heat.

After Prof. Pickering and Mr. Swinburne had replied to the points raised, Mr. Walter Bailey took the chair, and

Prof. Perry read a note "*On the Variation of Surface-Tension with Temperature,*" by Prof. A. L. Selby, M.A.

Considering unit mass of liquid at constant volume, but variable surface (S), and temp. (t), the author expresses the gain of intrinsic energy due to changes of the variables by $dH + dW = kdt + (l + T)dS$; where dH is the heat absorbed, dW the work done on the film, k the specific heat at constant volume, l the latent heat of extension, and T the surface tension. This being a perfect differential, it is shown that $T = c - bt$, and $l = bt$, c and b being constants.

Supposing c and b to be independent of the specific volume of the liquid, it is shown that at the critical temperature $t = \frac{c}{b}$; hence, this temperature may be determined by finding the surface tension at two very different temperatures. Since, also, $l = b\,t$, the latent heat of extension is proportional to the absolute temperature.

Reasons for supposing *b* to be independent of the specific volume are given in the paper.

Mr. Blakesley described an effect of temperature on surface tension which he had observed in sensitive spirit-levels. By warming one end of the tube, even by the hand, the bubble immediately moves towards that end. This effect, which might produce considerable error in engineering operations, was, so far as he was aware, not mentioned in the text books.

Prof. Perry remarked that although the volume, temperature, and surface of the liquid had been referred to in the paper, pressure was not mentioned, and on this point he enquired whether the results arrived at were true, quite independent of the pressure.

Prof. S. P. Thompson, D.Sc., read a paper on "*Magnetic Proof-pieces and Proof Planes.*"

The distribution of magnetism over magnets has been examined in various ways by different observers, but mostly by observing the force of detachment of either rods, ellipsoids, or spheres used as proof-pieces. In all these cases it was, the author said, difficult to see exactly what was measured; for the presence of the proof-pieces altered the thing to be tested. The pull exerted must also depend on the permeability of the piece used, as well as on its shape and disposition with respect to the magnetic circuit. He had therefore investigated the subject by finding the actual distributions by means of a flat exploring coil and ballistic galvanometer, both with and without the presence of proof-pieces of various shapes and sizes. The results show that the perturbations produced by the proof-pieces are always large, in some cases the perturbed field about a point being four to six tfmes the unperturbed field. In most cases, however, the ratio of the perturbed to to the unperturbed field was constant so long as the former did not exceed 6000 C.G.S. units.

The amount of perturbation was also found to depend on the saturation of the magnet, and on whether it was a permanent or an electro-magnet. The numbers obtained in various experiments, and curves plotted from such results, were shown.

In conclusion, the author said that in using proof-pieces much depended on the accuracy of the contact, but in any case the results obtained were not very reliable. The flat exploring coil, or magnetic proof-plane, however, furnished a satisfactory method of examining magnetic distributions.

NOTICES OF BOOKS.

The Action of Water on Lead. Being an Inquiry into the Cause and Mode of the Action and its Prevention. By J. H. Garrett, M.D. London: H. K. Lewis.

The presence of lead in the water supplied to many towns is certainly a serious evil, and as it has not been by all means fully understood, Dr. Garrett's contributions to the question are exceedingly valuable. It is now clear that if a water is fairly pure it is found to act upon lead or dissolve it to a certain extent, even in the absence of an acid. The author observed that distilled waters that were neutral, or even very faintly alkaline, can act upon lead. The lead, it would seem, derives the oxygen necessary for its corrosion, not so much from the free oxygen or any other oxygenous gas existing in solution in the water, as from nitrates and nitrites present. The quantity requisite for action, at least in the absence of any alkaline-earthy carbonates, is extremely small. Its origin may be sought "in the decomposition of the organic matter which such waters invariably contain." Such nitrogenous matter may possibly be converted into nitric acid by the action of a bacillus. This question we agree with the author requires further study.

A careful examination was made of the water supplied to Mirfield by the Huddersfield Corporation. The author remarks that in a town in which the water, as delivered into the mains, is absolutely free from lead, it may become contaminated by means of leaden service pipes. This is especially the case where the water supply is intermittent. But even if constant, as it ought on sanitary grounds to be universally, the water from the service pipes may fall back into the mains in consequence of interchanging currents.

We may here ask whether the mechanical ingenuity of the age could not devise some arrangement which should render the reflux of water into the mains impossible. The author thinks that "in places like Mirfield no single inhabitant could protect himself by using an iron service pipe." But what if leaden service pipes were altogether prohibited.

The evidence collected from the author's experiments, which appear to have been well planned and carefully executed, leads to the conclusion that if the water contains any inorganic acid it is, in part at least, probably nitric acid.

The author's proposed remedy lies in the addition to the water of an alkaline carbonate, and especially carbonate of lime! This is not a welcome expedient. To have the skin, after washing, coated with a gluey film of lime, to find linen returned from the laundry in the same clammy condition, to partake of vegetables hardened instead of softened by boiling, are certainly a serious grievance. If the water supply is constant, and if the consumer takes the precaution of letting a few quarts of water run away from the tap every morning before any is used for drinking or cooking, the danger is reduced to the vanishing point.

Dr. Garrett's improvement on the ordinary method of testing for lead in water seems very feasible. He puts into a narrow test-tube half an ounce of the water and one drop of hydrochloric acid; passes into it washed H_2S, and adds half a grain barium sulphate. Shake, and set aside. Ammonium sulphide may be used instead of sulphuretted hydrogen, but in series of comparative experiments one and the same precipitant should always be used.

Dr. Garrett may be congratulated on the thoroughness and the value of his researches.

Kelly's London Medical Directory, 1891. London Kelly and Co.

We have here a work filling a vacancy which had become more and more widely felt. The compilers give the names, addresses, qualifications, and works, if any, of all qualified medical men in practice in the Metropolitan district. In addition it furnishes particulars concerning hospitals, public analysts, learned societies, medical and scientific publications, insurance companies, lunatic asylums, and examining bodies.

Turning firstly to the section on scientific societies, we note a few defects which will doubtless not reappear in next year's issue. Thus there is no mention of the Society for the Promotion of Medicine by Research, which we hope is not defunct, the South London Microscopical Society, and the South London Entomological and Natural History Society—a very numerous body. The anti-scientific societies are deservedly ignored.

Turning to the medical and scientific publications we find the names of two "weeklies" which, to our great regret, have ceased to appear.

A glance at the main body of this directory, the muster roll of practitioners will prove that the labour incurred in its compilation must have been very heavy, and we cannot feel surprised if a few mistakes have occurred. We wish the publishers the success which they have so fully merited.

Notes of a Thousand Men and Some Things they did in Art, Literature, War, Government, Science, and Industry. Arranged in Group and in Order of Time. By David K. Morris. London: Cassell and Co. (for the Author).

The idea of this work is novel, and it will, in our opinion, often prove useful. It gives in parallel columns the names of the eminent characters, the date and place of their birth, the date and place of their death, and their works, discoveries, inventions, or achievements. As a rule, living celebrities are prudently omitted. As regards the selection of the "thousand men," no objection can fairly be raised. The weak point of the work lies in its classifications. It is strange to find Gilbert White placed, not among zoologists, but among the essayists and critics. Ure, in virtue of his Dictionaries of Chemistry and of Arts and Manufactures, is made to figure among lexicographers, whilst H. Watts and A. Würtz, also the authors of Dictionaries of Chemistry, rightly rank among chemists. Perhaps the only statement which we can formally question, often as it has been repeated, is that the works of Celsus were burnt by the Caliph Omar in A.D. 640. The balance of evidence now seems to show that the Alexandrian Library was destroyed by the Bishop Cyril and his monks at an earlier date.

A reflection which must strike the reader is that scientific men and brain-workers generally are long-lived.

A Treatise on the Law and Practice relating to Letters Patent for Inventions, with an Appendix of Statutes, International Convention, Rules, Forms and Precedents, Orders, &c. By Robert Frost, B.Sc., F.C.S., Barrister-at-Law. London: Stevens and Haynes.

There are obviously two points of view from which a treatise on patent-law might be written. On the one hand, it would be possible to show what a patent-law ought to be to answer its purpose, that is to confer the maximum possible advantage on the arts, manufactures, and commerce of the nation, to examine in what respects our present system falls short of this ideal, and how it might best be amended. On the other hand, such a treatise like the work before us might simply expound the law as it stands, carefully keeping back any aspirations after its higher development. We must not imagine that the compilation of such a treatise is an easy task. In a country where the patent-law is not codified, and where its decision on any contested point can be gathered merely by the tedious and often difficult task of collating statutes and judicial decisions, how differently the statutes and precedents may be interpreted by different judges it is not necessary to show.

At the same time we must remember that tedious and costly litigation concerning patents cannot be excluded either by a codified patent-law or by a rigid preliminary examination. In proof of this we need only refer to the patent-suits in Germany, in France, and in the United States.

The author, in discussing the subject-matter of letters patent, lays down, very rationally, the principle that "an art which is to be exercised for the sole object of breaking the law, or for the sole object of producing anything designed to be used for any illegal purpose, cannot form the subject-matter of valid letters-patent." It is to be feared, however, that a patent has been granted for a fraud, in the shape of moulding worthless pastes or powders into the form of coffee-berries, or by analogy of other seeds, fruits, or berries.

We are happy to learn that "patents will not in future be granted to agents resident abroad in respect of inventions communicated to them by aliens also resident abroad."

As regards "communications from abroad" it seems very clear that patents were originally granted for such communications in order that some new art or manufacture may be introduced into the realm. At present such communications are made to have the very opposite effect, viz., of keeping new arts out. An alien communicates his invention to some agent, who then obtains a patent for it in his own name, but immediately conveys it exclusively to the alien, whose sole object in the transaction is to *prevent* the art from being worked in Britain.

It has been held, we are told, that "the prior user of an invention in a colony forms no legal bar to the granting of a patent for the same invention in this country." This is gravely to be regretted, since the principle thus involved will form a bar to the adoption of an imperial patent-law.

The question of utility is discussed at some length. Utility in law is not utility in the common sense of the term, but merely means "an invention better than the preceding knowledge of the trade as to a particular fabric." This is the more important because not a few very successful inventions, very lucrative to the patentee, are completely devoid of utility in the ordinary acceptation.

Without further extending our examination of this work, it has been the outcome of careful and prolonged study, and it cannot fail to prove extremely valuable to patent-agents as well as to counsel and solicitors engaged in patent-cases.

The Electro-Platers' Handbook: A Practical Manual for Amateurs and Young Students in Electro-Metallurgy. By G. E. Bonney. With 61 Illustrations. London: Whittaker and Co., 1891.

Like other departments of industrial art, electro-metallurgy is receiving an increased share of attention. Mr. Bonney undertakes in the present work to guide the amateur experimentalist through a field which is by no means free from difficulties. In this task he is very fairly successful.

After some preliminary matter, he classifies the metals as those of low and high cost, and again as those easily and not easily deposited. He gives a notice of the batteries most suitable for electro-deposition, and gives instructions on their management. Then follow dynamos of various kinds. The one which will ultimately survive is, he considers, a "long drum running in a single magnet type of field, which for plating must be shunt-wound." An instrument for indicating the speed of a dynamo, here described and figured, bears the barbarous name of the speedometer.

In a section on thermometers and hydrometers, the author performs the novel feat of giving a formula for recalculating degrees Baumé into degrees direct specific gravity. But as the Baumé instruments do not agree among themselves, the rule will not always work smoothly. For the respective conversion of degrees Twaddell and direct specific gravity, he gives no formula, as any reader can deduce it from an inspection of the two scales.

The remarks on cleanliness are by no means needless it is not easy to convince the student and the amateur to what a degree the cleanliness demanded in the laboratory transcends that of the best-managed household.

To nickel he scarcely does justice. If pure, *i.e.*, free from copper, arsenic, &c., its salts are scarcely more poisonous than those of iron.

The table of combining weights at the end of the book —Mr. Bonney does not say atomic weights, though the figures given are clearly meant for the latter—is not on a level with the most recent determinations. The atomic weights of platinum and indium are made equal, and both are higher than that of gold—an inveterate error which we hope to see corrected in the next edition. The work is of evident utility, and has before it a future.

CORRESPONDENCE.

PALMELLINE AND ASPERGILLINE.

To the Editor of the Chemical News.

Sir,—It appears from your paragraph (Chem. News, vol. lxiii., p. 153) that the "vegetable hematine"—the pigment of the spores of *Aspergillus niger*—from its striking analogies with the hematine of the blood, must be identical with the substance *palmelline* extracted by me from *Palmella cruento* in 1879, accounts of which were published in the Chemical News and in the *Comptes Rendus* for that year. I proved the absorption-spectrum of palmelline to be very similar, if not identical, to that of the blood. It is singular that old botanists should have named the alga in question *Chaos* "*sanguinea*," and the moderns *Palmella* "*cruenta*," since the resemblance with blood goes beyond the mere external appearance.—I am, &c.,

T. L. Phipson.

Putney, March 27, 1891.

SEWAGE PURIFICATION.

To the Editor of the Chemical News.

Sir,—My attention has been called to the last issue of your esteemed journal, in which you reply to your correspondent, W. Naylor, "We know of no method of sterilising sewage."

I take the liberty of handing you herewith our pamphlet containing copies of reports by Dr. E. Klein, F.R.S., the eminent bacteriologist, and by Mr. Cassal, F.I.C., Public Analyst, on the results of their independent and exhaustive investigations of the effect of the "Amines" process as applied to the treatment of sewage. Since both certify to the absolute sterility of the effluent, I should deem it a favour if, after perusal of the said reports, you can see your way to giving publicity in your next issue to the facts above stated, so that your correspondent may obtain correct information upon the point.—I am, &c.,

Hugo Wollheim, Managing Director.

The "Amines" Syndicate, Limited,
101, Leadenhall St., E.C.
London, April 1, 1891.

Determination of Dry Matter in Fibrous Materials.—O. Knöfler (*Papier Zeitung*).—The apparatus consists of a cylindrical water-bath in which is introduced the recipient for the samples, consisting of two concentric cylinders with bottoms. In this is suspended a wire basket containing the sample fixed to one arm of a balance. The other arm is like Westphal's balance, provided with a counterpoise to the wire basket, and graduated in 10 parts. So much of the sample is used as the large rider weighs, so that the balance is in equilibrium when it is placed at the mark 10. When the desiccation has gone on for a time the balance is again brought to an equilibrium by displacing the large rider, and putting on the smaller $\frac{1}{10}$ and 100 riders, and observing if the weight is constant. The percentage of dry matter is then read off from the position of the riders.

Determination of Paraffin, Ceresine, and Mineral Oils in Fats and Waxes.—F. M. Horn (*Zeit. Angew. Chemie*).—The sample is generally saponified, and the soap is extracted with petroleum ether. This method is not quite trustworthy in presence of mineral oils, as in this case a part of the soap dissolves in petroleum ether. The author therefore prefers to extract the dried soap with boiling chloroform in Soxhlet's apparatus.

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. cxii., No. 10, March 9, 1891.

On the Hydrated Sodium Manganates.—G. Rousseau.—If sodium manganate is heated from 300° to white redness it undergoes a series of curious metamorphoses. There is first formed the hydrate (old notation), $8MnO_2NaO,5HO$. From about 500° this product tends to become polymerised, and at 800° it changes into the hydrate, $12MnO_2NaO,4HO$. About 1000° there appears a more complex compound, $16MnO_2NaO,8HO$; then between 1200° and 1300° we return to the manganite, $8MnO_2NaO,5HO$, which was originally formed at 300°. Finally at white redness the hydrate, $12MnO_2NaO,4HO$ reappears, as if a new cycle parallel to the former was about to be produced. The author has already pointed out analogous variations in the condensation of the alkaline earthy manganites, but these compounds were anhydrous. On the other hand, the hydrated alkaline ferrites and platinates which he has discovered do not form cycles in their successive changes. The union of these two orders of phenomena in one and the same group of compounds constitutes a novel fact to which he wishes to call the attention of chemists.

On the Transformation of Sodium Pyrophosphite into an Acid Phosphite.—L. Amat.—The object of the present memoir is to trace the laws of this transformation, noting especially the influence of time and that of dilution.

On Silicibromoform.—A. Besson.—This compound is a colourless liquid which in an inert gas distils over without decomposition at 109°—111°, and does not solidify at 60°. It gives off copious fumes, and finally ignites spontaneously in contact with air. The vapour forms detonating mixtures with air. It is decomposed with violence by water and alkalies. Ammoniacal gas reacts upon silicibromoform, and if the reaction is not moderated there is a development not merely of heat but of light.

Thermic Study of Certain Alkaline Derivatives of Erythrite.—M. de Forcrand.—A thermo-chemical paper, the main portion of which does not admit of useful reproduction. The formation heats of the sodium alcoholates increase regularly with the degree of atomicity. For the potassium derivatives the corresponding numbers are higher and increase in the same manner.

On Some Ammoniacal Compounds of Mercury Cyanide.—Raoul Varet.—The compounds studied are the mercury-copper bromo-cyanide, the mercury-cadmium bromo-cyanides, the mercury-cadmium iodocyanide, the corresponding chloro-cyanide and the mercury-nickel chlorocyanide.

Fermentation of Starch by the Action of the Butyric Ferment.—A. Villiers.—The author has previously shown that if potato-starch is allowed to ferment under the action of *Bacillus amylobacter* the products are chiefly dextrines. At the same time there are formed certain carbohydrates which the author names cellulosines, and to which he assigns the composition $C_{12}H_{10}O_{10}+3HO$ and $(C_{12}H_{10}O_{10})\cdot C_4H_6O_2 10HO$. These compounds differ very decidedly from the saccharines. The latter especially does not melt at temperatures within the thermometric scale. It is not fermentible, and does not reduce the cupro-potassic solution.

Vol. cxii., No. 11, March 16, 1891.

On the Different Manifestations of the Phosphorescence of Minerals under the Influence of Light or of Heat.—H. Becquerel.—In the phosphoroscope we recognise that one and the same body may emit several different spectra; these spectra are distinguished from each other by the duration of the luminous emission. The researches which the author published some years ago on the variation of the absorption spectra and on their relations with the spectra of phosphorescence justify the conclusion that the various spectra of one and the same body are due to the presence in this body of different substances or of different compounds of the same substance. The light of the electric spark striking near bodies induces phosphorescence like the solar light, and the emission spectra are the same. Heat, in the luminous form, restores to bodies a limited quantity of energy. When this quantity is exhausted, the bodies no longer phosphoresce by heat. If the necessary energy is restored to them by the action of an electric spark or by exposure to light, they phosphoresce again when heated. The brilliant bands of the spectra emitted under the influence of heat are the same as those in the phosphoroscope, but they have different relative intensities.

The Transformations which Accompany the Carburation of Iron by the Diamond.—F. Osmond.—The author's results show that diamond in itself does not cement iron, but first undergoes in contact with the metal a molecular transformation which makes it capable of cementation. The diffusion of carbon in the iron involves as a corollary a diffusion of iron in the transformed diamond.

The Formation of Coloured Laks.—Lés Vignon.—The absorption of a basic colouring matter coincides with the existence of intense acid functions in the absorbing substance; if these decrease, the absorbent power is enfeebled and disappears.

Researches on Dispersion in Organic Compounds (Ethers).—Ph. Barbier and L. Roux.—In the series of ethers examined the specific dispersion powers increase progressively with the molecular condensation. The mean of the differences between two consecutive values of the molecular dispersive powers is approximately constant and equal to 7·5.

Influence of Extractive Matters on the Real Alcoholic Standard of Spirits.—Ch. Blarez.—This paper requires the accompanying tables.

MISCELLANEOUS.

Royal Institution.—Mr. J. Scott Keltie will, on Tuesday, April 7th, begin a course of three lectures on "The Geography of Africa, with special reference to the Exploration, Commercial Development, and Political Partition of the Continent." Professor Dewar will, on Thursday, April 9th, begin a course of six lectures on "Recent Spectroscopic Investigations," and Professor Silvanus P. Thompson will, on Saturday, April 11th, begin a course of four lectures on "The Dynamo." The Friday Evening Meetings will be resumed on April 10th, when Sir William Thomson will give a discourse on "Electric and Magnetic Screening."

Camera Club.—The 1891 Conference will be held in the Theatre of the Society of Arts on Tuesday and Wednesday, April 7th and 8th, under the presidency of Captain W. de W. Abney, C.B., D.C.L., R.E., F.R.S. Tuesday, April 7th, papers will be read from 2 p.m. to 5.30 p.m., in the Theatre: Captain W. de W. Abney, R.E., C.B., D.C.L., F.R.S., Presidential address; Mr. Lyonel Clark, C.E., "The Use of Uncorrected Lenses"; Mr. Joseph Pennell, "Photography as a Hindrance and a Help to Art"; Rev. F. C. Lambert, M.A., "Note on the Physiological Aspect of Some Problems in Art." At 8 p.m., exhibition of lantern slides in the Theatre. Wednesday, April 8th, 2 p.m., papers to be read from 2 p.m. to 5.30 p.m.: Major J. F. Nott, "Photography and Illustrated Journalism"; Mr. C. V. Boys, "An Application of Photography"; Sir H. T. Wood, subject will be announced later. 7.30 p.m., Annual Club Dinner for Members and friends at the Criterion Restaurant. The Annual Exhibition of Photographs by Members will be on view in the Club House Meeting Room, Charing Cross Road, from 10 a.m. to 4 p.m. Admission by card from any member of the club, or by ticket from the hon. sec. The exhibition will be open under these conditions for about six weeks from Tuesday, April 7th.

MEETINGS FOR THE WEEK.

Monday, 6th.—Medical, 8.30.
—— Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. (1) "The Analysis of Illuminating Gases." (2) "The Products of Checked Combustion," by Professor Vivian B. Lewes.
Tuesday, 7th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30
—— Royal Institution, 3. "The Geography of Africa," by J. Scott Keltie, F.R.G.S.
Wednesday, 8th.—Geological, 8.
—— Pharmaceutical, 8.
—— Society of Arts, 8. "The Durability of Pictures Painted with Oils and Varnishes," by A. P. Laurie.
Thursday, 9th.—Royal, 4.30.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "Recent Spectroscopic Investigations," bp Prof. Dewar, M.A., F.R.S.
—— Society of Arts, 8. "The Indian Village Community, with special reference to Modern Investigation," by B. H. Baden-Powell, C.I.E., late Bengal C.S. (Punjab).
Friday, 10th.—Astronomical, 8.
—— Royal Institution, 9. "Electric and Magnetic Screening," by Sir William Thomson, D.C.L., LL.D., Pres. R.S.
Saturday, 11th.—Royal Institution, 3. "The Dynamo," by Prof. Silvanus P. Thompson, D.Sc., B.A.

THE CHEMICAL NEWS.
Vol. LXIII., No. 1637.

VAN 'T HOFF'S LAW OF OSMOTIC PRESSURE.

By D. J. CARNEGIE.

There are few, I think, who would oppose the application of the qualification "epoch-making" to the recent work of Van 't Hoff in connection with the osmotic pressures of dilute solutions.

Although this work involves nothing of what is popularly styled scientific romance, and is of too specialised a nature to beget the general interest of the public, yet it must be admitted that, taken along with its immediate consequences, it appeared at first sight very much in the light of romance to the smaller world of scientists, whose thoughts and energies it has, notwithstanding, rolled into altogether new courses.

Before detailing this work, however, certain preliminaries are necessary to the full appreciation of the position it assumes in the province of knowledge to which it essentially belongs.

Matter exists in three states: solid, liquid, and gaseous. Up till quite recent times theoretical chemistry has had chiefly to do with matter in its gaseous condition. The deportment of gaseous matter is conditioned by very simple laws, the chief of these being (1) Boyle's law, (2) Charles's law (Gay Lussac's law), (3) Avogadros's law, and (4) Graham's law.

In his "defence of the doctrine touching the weight and spring of the air" (1662), Boyle very quaintly describes how, by means of "a tube crooked at the bottom through the instrumentality of a dextrous hand and a lamp," he discovered "not without delight and satisfaction," that the volume of a constant mass of gas varies inversely as the applied pressure; or expressed algebraically, $pv = \text{constant}$.

Then in 1787 followed Charles's law, which ultimately giving rise to the conception of an absolute zero of temperature finds its fullest enunciation in the form; the volume of a constant mass of gas at constant pressure is proportional to its absolute temperature, or $v = \text{constant} \times \text{T}$.

In 1811 Avogadro laid the foundation of modern chemistry in advancing the hypothesis that equal volumes of gases under like conditions of temperature and pressure contain equal numbers of molecules. Expressed algebraically, molecular weight = 2 × specific gravity of gas. This hypothesis (raised to the rank of a law by the Kinetic theory of gases) lies at the foundation of all the fundamental constants of chemistry—the atomic weights; and till within quite recent times has been the only method of any generality for determining molecular weights, and through these atomic weights.

Graham (1833), following up some of Döbereiner's experiments, which had their origin in a small crack in a glass gas receiver, discovered empirically that the rates of diffusion of gases through very small openings are inversely proportional to the square roots of their specific gravities; or—

$$\frac{\text{Rate of diffusion of } x}{\text{Rate of diffusion of } y} = \frac{\sqrt{\text{Specific gravity } y}}{\sqrt{\text{Specific gravity } x}}.$$

Before inquiring what laws, having a chemical bearing, pertain to matter in the liquid state, it will be well to divide liquids into the sub-classes homogeneous liquids (such as mercury, molten sulphur), and non-homogeneous liquids or solutions (such as solution of sugar in water). It is the latter sub-division with which we have to do.

In 1867, Guldberg and Waage, in enunciating their law to the effect that chemical action which takes place between substances in solution is proportional to the active masses of each of the substances participating in the reaction, laid the foundation of modern concepts regarding chemical affinity.

Quite recently, Raoult in showing that equimolecular solutions (*i.e.*, solutions consisting of quantities of substances proportional to their molecular weights, dissolved in equal quantities of solvent), have the same freezing points and vapour tensions, furnished two new methods of wide applicability for determining molecular weights—methods which can be applied where Avogadro's law fails. Expressed algebraically, Raoult's laws stand as follows:—

$$m = \frac{p \, \text{M} f^1}{(f - f^1)\,\text{P}}, \qquad m = \frac{r p}{\Delta \, \text{P}}.$$ [*]

The molecular theory of matter has found its greatest development in its application to matter in the gaseous state, that is, as the Kinetic theory of gases. Allow that heat is essentially a molecular movement, and that the pressure of a gas is due not to any specific repulsive forces indwelling in the molecules, but merely to the repeated impacts on the sides of the containing vessel of the heat-impelled molecules, then the laws of Boyle, Charles, Avogadro, and Graham, following as necessary consequences of these postulates, are raised from the low level of mere empiricisms to the higher platform of logical deductions from a theory which, involving only the most simple and probable premises, co-ordinates and explains a vast number of at first apparently disconnected facts.

The question now arises, are our theories respecting the structure and mechanism of liquids (the case of solids does not concern us in this paper), as definite as the Kinetic theory of gases, so that they, in an analogous way, confer warranty on the laws conditioning the properties of liquids? In answer we must reply that up to the present time our views regarding the constitution of homogeneous liquids are so vague as to scarcely merit the name of theories, and that the nature of non-homogeneous liquids or solutions is a burning question of to-day's theoretical chemistry, which is dividing chemist against chemist.

By no means the least result of Van 't Hoff's work on osmotic pressure is the elucidation of the nature, if not of solutions generally, at least of that important class of solutions—the dilute solutions which Raoult and others have experimentally investigated. What is this quantity—osmotic pressure? Suppose a vessel A, filled with, say, sugar solution, and immersed completely in water as in Fig. 1. Further, suppose the walls of A of such a nature that they permit the passage through them of water, but not of sugar molecules. Such walls Van 't Hoff calls *semi-permeable*. In virtue of the attraction of sugar molecules for water molecules, water will enter the vessel A, thereby increasing the pressure on its sides up to a certain limit when equilibrium is established. This equilibrium pressure in A is called osmotic pressure.

Such *semi-permeable* vessels are realised in practice as follows. The porous cell A, Fig. 2, filled with a solution of potassium ferrocyanide, is immersed in a beaker containing a solution of copper sulphate. The solutions diffusing into the walls of the cell, and meeting about half way, react, forming a precipitate, S, of insoluble copper ferrocyanide, which possesses the semi-permeable qualities alluded to.

In order to take a measure of osmotic pressure with the cell, it is washed out, filled with a solution of known strength of the substance to be investigated, and closed air-tight by cementing in the glass head piece, H, which

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[*] Where m = molecular weight to be ascertained, M = molecular weight of solvent, P = weight of solvent, p = weight of dissolved body, f^1 = vapour pressure of solution, f = ditto for solvent, Δ = lowering of freezing-point produced by dissolving p grms. of substance in P grms. of solution, and r = constant depending on solvent and determined experimentally for each solvent.

carries the manometer, M. The whole apparatus immersed in a beaker of pure water is allowed to stand till the mercury levels in the manometer cease to change. The difference in height in the levels in the two limbs gives the osmotic pressure.

Accepting this definition of osmotic pressure, Van 't Hoff asserts the existence of a very close and deep seated analogy between gases and substances in dilute solution, provided always in dealing with the analogy we make osmotic pressure in solutions as thus determined correspond to gaseous pressure.

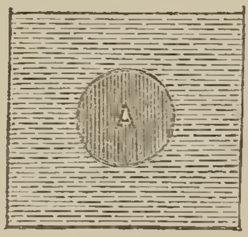

FIG. 1.

Now Boyle's law states that pressure varies inversely as volume, or what is the same thing, varies directly as concentration. If Van 't Hoff's asserted analogy be valid the osmotic pressure of a solution should vary directly as its concentration. The following measurements made by Pfeffer shows that Boyle's law *does* hold for dilute solutions, provided osmotic pressure be substituted for gaseous pressure in the enunciation of the law.

Concentration in percentages.	Osmotic pressure in m.m. of mercury.	Ratio : Pressure to Concentration.
1	535	535
2	1016	508
2·74	1518	554
4	2082	521
6	3075	513

It will be noticed that the figures in the third column in conformity with Boyle's law are approximately constant. That Charles's law also holds for dilute solutions has been proved in several ways. I select as the most interesting a physiological method of proof which we owe to De Vries. A leaf—all of such a plant as *Tradescantia discolor* (one of the plants actually used)—consists essentially of an outer cell wall, C, Fig. 3, lined by a layer of protoplasm, the primordial utricle P; the double envelope forming the boundary of the vacuole V, which is filled with cell sap.

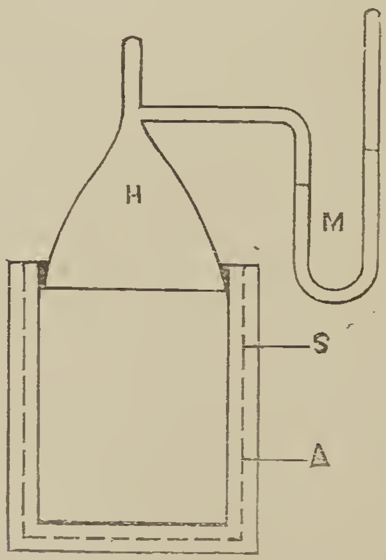

FIG. 2.

The living primordial utricle has all the properties of a semi-permeable membrane; consequently, if the cell be immersed in a solution having a greater osmotic pressure than that of the cell sap (due to its contained organic acids and acid salts), water will pass from the sap to the surrounding solution, and the cell will assume a *plasmolytic* condition. That is, the primordial utricle will leave the cell wall, and contract on its diminished sap contents, as represented in Fig. 4.

If the concentration of the surrounding solution be so arranged that its osmotic pressure is equal to that of the sap, then there will be no plasmolysis—the primordial utricle will remain in close contact with the cell wall. Of course, if two different solutions are in osmotic equilibrium with the same cell, they must be in osmotic equilibrium with each other. Taking advantage of this behaviour of vegetable cells, it has been shown that solutions of common salt, nitre, and sugar, which exert equal osmotic pressure (*i.e.*, are *isotonic*) at 0°, are isotonic also at 34°. But this is none other than an indirect admission that Charles's law holds also for dilute solutions.

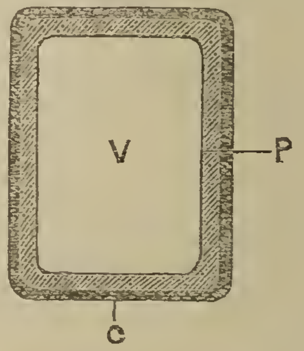

FIG. 3.

So far as I am aware, dilute solutions have not yet been investigated with respect to Graham's law. With the aid of a cylinder with semi-permeable walls fitted with a piston, we can conceive of various *reversible* processes to which these dilute solutions may be submitted. But that protean and powerful law—the second law of thermodynamics (which states that the energy at our disposal, though unchangeable in amount, is continually spproaching a dead level condition in which it will no longer be available), deals with *reversible cycles*, and Van 't Hoff has shown that by applying this second law of thermodynamics to a special reversible process carried out without change of temperature, the necessary consequence is that the osmotic pressure exerted by a dilute solution of a substance is equal to the gaseous pressure which the substance would exert under the same conditions of temperature and concentration. Hence, suppose we have x grms. of a substance dissolved in V volumes of a solvent exerting an osmotic pressure P at $t°$; then x grms. of the same substance in the gaseous state, occupying V volumes at $t°$ would exert a gaseous pressure = P.

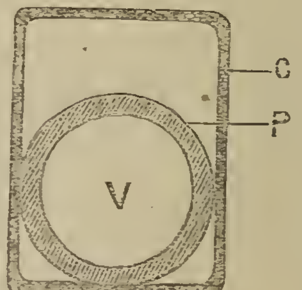

FIG. 4.

It is but a short step further to conclude that Avogadro's law holds also for dilute solutions, and that under equal osmotic pressures, and at the same temperature, equal volumes of dilute solutions contain equal numbers of dissolved molecules; and, moreover, the same numbers of molecules which would be contained in equal volumes of gases under like conditions of temperature and pressure. This is Van 't Hoff's *law of osmotic pressure*, which has been amply confirmed by experiment.

But further, assuming the truth of all that has preceded, and applying the second law of thermodynamics to other reversible processes suitably conceived,* and carried out with the cylinder of semi-permeable material; and Van 't Hoff shows that the important laws of Raoult in all their entirety are direct consequences of this analogy between gases and dilute solutions. Nay more, the equations arrived at have new information of their own, and show that the constant r in Raoult's second equation (see *ante*), which up to date has only been determinable by experiment, may be easily calculated from a knowledge of the freezing-point and heat of fusion of the solvent; the calculated results agreeing very closely with the experimentally observed results.

By similar methods of reasoning, he has lastly shown that Guldberg and Waage's law (in a slightly modified and more exact form), is a necessary consequence of his development of the conception of osmotic pressure.

Thus we see that the laws relating to dilute solutions, Boyle's law, Charles's law, Raoult's law, Avogadro's law, and Guldberg's law, are not disconnected and independent truths; just as the kinetic theory of gases coordinated the laws regulating the deportment of gases, and gave them an imprimatur which they did not before possess, so the analogy worked out by Van 't Hoff has resulted, not only in the discovery of new and unsuspected laws for non-homogeneous liquids, but also in the power to group together new and old, and to regard, from a common standpoint, laws, which having a wide applicability, we are glad to have established and confirmed by theoretical deductions.

No longer do we, in a vague blotting-paper impression way, picture to ourselves a dilute aqueous solution of a substance as consisting of various ill-defined hydrates of the dissolved body diffused through the inert excess of solvent; on the contrary, the molecules of the dissolved body retain their individuality just as they would were the body gasified instead of dissolved, with this difference, however, that in the former case the molecules would be separated from one another by the inert ether of space, while in the latter case the molecules are kept outside each other's spheres of action by the intercalated molecules of solvent which are not always inert, but demand the introduction of constants peculiar to the solvents employed into certain of the equations conditioning the properties of solutions.

In conclusion, let us glance at the fringe of the vast sheet of consequences of Van 't Hoff's analogy. Notable exceptions to Avogadro's law occur among gases. Thus the gas of ammonium chloride under certain conditions exerts a pressure double that which Avogadro's law would lead us to expect under the conditions. Such cases are, as is well known, explained satisfactorily in terms of the theory of dissociation. The question naturally arises: Is the analogy between gases and dilute solutions so perfect that the latter also afford examples of deviation from Avogadro's law, explicable in terms of dissociation?

The answer is an affirmative.

A dilute solution of potassium chloride exerts twice the osmotic pressure that theory demands; it is hence concluded that in dilute solution each molecule of KCl is dissociated into its *ions* K and Cl. So startling is this and similar conclusions, that had they not been backed up by scientists of such authority as Ostwald, van t' Hoff, and Arrhenius, I doubt whether they would have ever been granted a fair hearing.

But it must not be supposed that such conclusions rest merely on analogy. Ostwald has described a simple experiment which points to the existence of free ions in a dilute solution of potassium chloride.

Further, it has been noted that those substances which in solution do not conform to van 't Hoff's law are all electrolytes, while all non-electrolytes obey the law of osmotic pressures. Now, Clausius and Williamson, years ago, suggested that the explanation of electrolysis was to be found in a partial dissociation into their ions of those substances which are electrolisable. Modern research in defining and confirming their views has shown that the very partial dissociation which these scientists were thought bold for asserting is in reality anything else but partial. In fact, in the case of those substances which we have been in the habit of regarding as most stable (HCl, KCl, KOH, &c.), the dissociation in solution is almost, if not quite, perfect; water completely, or nearly so, separating the molecule of the dissolved substance into its ions. So intimate, indeed, is the relation between electrolysis and osmotic pressure, that the latter quantity for any substance may be fully determined from measurements of the electric conductivity of its aqueous solutions.

Accepting this view of the general existence of dissociation in solution, which has arisen out of van 't Hoff's law of osmotic pressure, many purely chemical facts, hitherto inexplicable, receive a *rationale.* We can now account for Hess's law of thermo-neutrality, which states that the mixture of two neutral salt solutions is unattended by any thermal disturbance; we can now understand why the heats of neutralisation of all strong acids is approximately constant; we can conceive of a strong acid displacing a weaker acid from combination without introducing vague views on chemical forces and chimerical attractions; we begin to see through such everyday and familiar experiences as the fact that solution of silver nitrate does not produce a precipitate of silver chloride in all solutions of chlorinated compounds; in short, the development of van 't Hoff's views leads us to look on many otherwise inexplicable and seemingly isolated phenomena as part and parcel of one vast harmonious system.

> "Where order in variety we see,
> And where, though all things differ, all agree."

Colorado College, Colorado Springs, U.S.A.

DISCUSSION ON THE THEORY OF SOLUTION.*

(Concluded from p. 159).

Professor van 't Hoff stated his conviction that we were forced on theoretical grounds, thermodynamic as well as kinetic, to admit in dilute solutions a law corresponding to that of Avogadro, differing from this only in its bearing upon "osmotic" instead of "ordinary" pressure. He insisted on the necessity of dissociation in the case of KCl as a consequence which, on this line of argument, it was impossible to escape from. On the other hand, an ordinary separation into free atoms was in evident contradiction to all we knew about them, as in the vapour of iodine and mercury. These objections become invalid when we admit a splitting up into ions, which by their enormous electrical charge ought to be widely different from what we might expect in ordinary atoms, and hence it is that Arrhenius's "electrolytic dissociation hypothesis" was at once most favourably received by the adherents of the "osmotic pressure theory." Since then both have become closely allied by the fact that the dissociated fraction, according to the last, agreed with that admitted by the first on wholly different grounds.

In reply to the objections raised by Professor Fitzgerald, it may be observed, with respect to the theoretical foundation of the osmotic pressure law, that the action on

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* For details see Translation of Van 't Hoff's paper in *Phil. Mag.*, August, 1888.

* British Association (Section B), Leeds Meeting, 1890.

a semipermeable diaphragm is due, partly to the shock of the dissolved molecules, partly to the difference of forces acting upon them, from the solvent on one side, and from the solution on the other. Now, the result of the shock is directly proportional to the concentration, whereas that of the attraction is proportional to the square: thus in very dilute solutions the second action vanishes when compared with the first, and the shock is alone the origin of pressure as it is in gases. However, he insisted on these views as more intended to popularise than to prove the laws in question. If we want to do the last on kinetic grounds, we must take everything into account—movement of the molecules of the two substances mixed, action on themselves and on each other. Now, this has been just recently done by van der Waals, and the result is a very complicated formula, simplified, however, for dilute solutions into this statement, "that the dissolved molecules act on a semi-permeable membrane with strictly the same force as they would do on an ordinary membrane in the gaseous state." So from a kinetic point of view the law of Avogadro and the "osmotic pressure" law stand on the same basis.

Mr. Pickering commits a fundamental error in supposing that the osmotic pressure theory arrives at 0·63 as the number with which we had to multiply the solvent's molecular weight in order to get the so-called "constant of depression." Such conclusion was never drawn from the theory in question; it was the formula $\frac{0{\cdot}02T^2}{W}$ that was deduced. The value 0·63 was an empirical one, introduced by Raoult. This difference has urged Professor Eykman to a very extensive experimental research, the conclusion of which was so evident that in the July number of the *Annales de Chimie et de Physique* Raoult openly accepts the value $\frac{0{\cdot}02T^2}{W}$. On p. 359 Raoult states:—"L'abaissement α du point de congélation produit par une molécule dissoute dans 100 molécules dissolvantes est, d'après M. van 't Hoff, donné par l'expression $\alpha = 0{\cdot}02\,\frac{T^2}{L}i$, dans laquelle T est la température absolue de congélation et L sa chaleur latente moléculaire de fusion." In addition, on p. 361, he says:—"L'accord entre l'expérience et la théorie est donc, sur tous les points, aussi complet qu'on peut le désirer en pareille matière." No one now defends the value 0·63, and a good deal of the objection which Mr. Pickering directs against it has no bearing on the osmotic pressure theory itself.

Mr. W. N. **Shaw** remarked that the meaning of the term solvent used by physicists when referring to water, alcohol, and the like, is somewhat widely extended when it is understood to include $100H_2SO_4$, H_2O, and the other equally complex solvents of Table I. of Mr. Pickering's paper.

An ordinary solvent could not fairly be regarded as being "inert" and "having no action whatever" when it was claimed that the solvent caused the dissociation of a large portion of the dissolved salt. The action is in fact most remarkable, and is the important point now requiring investigation and explanation. This action has been clearly illustrated by Mr. W. Coldridge (*Phil. Mag.*, May, 1890, p. 383), who has endeavoured at Cambridge to ascertain the circumstances under which stannic chloride can be brought into the dissociated or electrolytic condition. The compound is interesting, since water and alcohol produce well-known and remarkable actions upon it; moreover it is comparatively easily prepared in the pure state. It appears from the paper referred to that stannic chloride can be mixed with chloroform without receiving any conducting power. It will also absorb a considerable quantity of dry H_2S gas without chemical action, and again without becoming electrolytic; whereas the addition of a drop of water or alcohol to the non-electrolytic mixture immediately gives rise to chemical action with a deposit of tin sulphide, the liquid becoming at the same time electrolytic.

The action of water or alcohol seems to be clearly different in this case in some fundamental manner from that of H_2S or chloroform.

Mr. Shaw also drew attention to the diagram (fig. 1) in Mr. Pickering's paper, from which, if he understood it correctly, it appears that for very weak solutions the "molecular depressions" produced by certain salts are the same for solutions containing 0·08 molecule per $100H_2O$ as they are for infinitely dilute solutions.

Mr. **Pickering** remarked that there were very strong positive arguments in favour of the hydrate theory, and that his opponents had in no way controverted them. Even if they succeeded in refuting all the objections which he had raised against the physical theory, this theory could not be established till it was shown that other theories were either untenable or less satisfactory.

The freezing-points of sulphuric acid solution calculated by Arrhenius certainly showed a very striking agreement with the observed values; but, before attributing much weight to this agreement, it would be necessary to examine carefully the details of the calculations, for there are considerable sources of doubt and difficulty in applying the values for the conductivity of weak sulphuric acid solutions; but even if no exceptions could be taken to the calculations, it must be remembered that the agreement exhibited extended only up to 1 per cent solutions, or 0·4° depression, whereas, according to the values quoted above, his theory offered an equally good agreement up to 30 per cent, or 34° depression, and, according to values given elsewhere, a similar agreement extended, with certain exceptions, up to 94 per cent. It must also be remembered that according to the chemical as well as the physical theory there must be a mathematical connection between the freezing-points, conductivities, and all other properties of solutions. The freezing-point curve shows irregularities, and so also does the conductivity curve; the chemical theory explains these irregularities, whereas according to the physical theory they should not exist.

Professor van 't Hoff pointed out that according to his theory the freezing-points were influenced by the nature of the solvent; but this does not remove the objection that the nature and amount of the *dissolved substance* (even when this is a non-electrolyte) are found to influence the results. Professor van 't Hoff had misunderstood what had been said about Raoult's constant. He (Mr. Pickering) was well aware that this constant and that deduced in the osmotic pressure theory were quite different.

Professor Ostwald stated that his experiment of bringing a charged body up to a solution, dividing the latter and removing the charged body was precisely analogous to a similar operation performed on a metallic conductor instead of a solution. This is undoubtedly the case, but in both instances there is an expenditure of mechanical energy, for more work must be done to remove the charged body from the separated and now charged solution or conductor than was required to bring it up to it; energy has been expended, and as a result we get a current and a certain amount of chemical decomposition: how can this prove that the substance was decomposed to start with? All that it could prove seemed to be that a current developed by electrostatic induction produced the same results both qualitatively and quantitatively as an ordinary galvanic current—a fact which has been established long ago.

Considerable stress has been laid on the constancy of the heat of neutralisation as an argument in favour of the physical theory, but it must be remembered that this constancy has received an equally simple explanation on the hydrate theory.

At the conclusion of the discussion Dr. **Gladstone** remarked upon the satisfactory circumstance that by means of the meeting of the British Association scientific men had been brought together from the Continent and various parts of England who held diametrically opposite opinions upon the subjects discussed, but that there had ensued a *rapprochement* and mutual understanding which could not fail to render the views of both sides more accurate representations of fact.

As the meagre ten minutes allotted to each speaker in the above discussion did not give time for the expression of all that appears above, some of the statements therein contained are new to me, and I may perhaps be allowed to supplement my answer by a few further remarks.

The bone of contention between Professor Arrhenius and myself, as to whether strong solutions possess an abnormally low or high freezing-point, is easily removed, for we are using "strong" in a different sense, he meaning solutions containing 5 to 10 per cent of the dissolved substance, of which the freezing-point is generally abnormally high; I in the sense of the strongest solutions (of any easily soluble substance) from which the solvent can be frozen, and of which the freezing-point is in most known cases abnormally low, the increase in the molecular depression exhibited by them amounting to from about 6 to 45,600 per cent. Twelve instances, which Professor Arrhenius seems to have overlooked will be found in the *Phil. Mag.*, xxx., pp. 499—501. It certainly appears to be somewhat disingenuous of Professor Arrhenius to pretend that I could have been ignorant of the fact that moderately strong solutions of sulphuric acid show a smaller molecular depression than very weak ones, for it is my own observations which have established this fact, and to it I have twice especially alluded (*loc. cit.*, p. 499, and *Chem. Soc. Trans.*, 1890, p. 357). It is also remarkable that Professor Arrhenius should be so anxious to show that strong solutions have an abnormally high freezing-point, since he starts by telling us that according to the physical theory the reverse should be the case.

Professor Arrhenius accuses me of neglecting the effect of dissociation when discussing the freezing-points. In this he is quite right, for I do not believe in it; nor do I think that correcting the irregularities of one property (freezing-points) by the irregularities of another (conductivities) can be offered as a legitimate "explanation" of the irregularities in either. Moreover, these irregularities cannot be attributed to the same cause which endows a solution with the power of conducting electricity, for solutions of non-electrolytes (though as a rule they behave more regularly) show in many cases as wide a deviation both from constancy and from regularity as any of those quoted above. One of these, indeed (alcohol), is a so-called non-electrolyte. I shall have occasion to show elsewhere that the freezing-points of sulphuric acid when calculated with the help of the conductivities do not show quite such an absolute agreement with the observed values for very weak solutions, as Arrhenius's table indicates, even if we allow the alteration of Kohlrausch's conductivity value for infinite dilution from 270 to 256, or to any other number apparently selected with the object of making the agreement as good as possible. Professor Arrhenius should have extended his calculations further than he has done; he would then have found that the small negative error between 0·6 and 1 per cent, after becoming a fairly large positive one between 1 and 8 per cent, again becomes negative, and reaches the modest dimensions of 60°.

I do not think with Mr. Shaw that any exception can be taken to the monohydrate of sulphuric acid as a solvent; it is a definite crystalline substance, which separates in a pure condition when a liquid containing it is cooled, just as sulphuric acid or water itself does. Mr. Shaw's remarks about Fig. I. is due to a want of clearness on my part in describing this figure, which does not represent the molecular, but the total depression.

Professor Lodge misunderstood my criticism of Ostwald's experiment. This would form a perpetual-motion machine only if no energy has been expended in the decomposition, which is impossible, whereas if energy has been expended the experiment can prove nothing whatever. Our views on this point seem to be identical.

Professor Fitzgerald very truly remarks that the dissociation hypothesis cannot be said to be in contradiction to the conservation of the energy if sufficient hypotheses be made respecting the energy of the ions; but are not these hypotheses themselves in practical contradiction to the conservation of energy (or of matter)? They involve either the introduction of electric charges from nowhere, just when and where we please, which can combine with matter to generate just as much heat as may be convenient to the theory, or else they hypothecate a new form of atom which shall be *minus* that free energy which we must admit an ordinary isolated atom possesses, or at any rate *minus* just so much of it as will suit the theory in question.

Dr. Gladstone's remarks at the conclusion of the debate must have made many of us feel that, however useful these discussions were, they might be much more useful if they were better arranged, if the contributors had more time for preparing their papers, if they had some opportunities of communicating together respecting the arguments to be adduced, if the hour of the debate were more convenient, and if the speeches were not cut short through lack of time. In the present case it was as late as July 29th when (in the middle of a holiday and far removed from all requisite materials) I received the invitation of the organising committee to open the discussion, the paper having to be sent in by some early day in August, if it were to appear in print before the meeting. Then on the day of discussion an interesting paper was introduced just before the hour (11.30) for which the discussion had been advertised to begin, the effect of which was the proceedings did not begin till past noon, and then before one o'clock, and after the opening paper and Dr. Gladstone's paper had been read, the President, naturally preferring the discussion of sandwiches and sherry to that of hydrates and ions, left the chair, having first, however, graciously signified that subsequent speakers, several of whom had come many hundred miles to honour us as our guests, and to expound their own views, might have a whole ten minutes each in which to do the latter. Surely these things might be better managed.—SPENCER U. PICKERING.

THE RELATIONS BETWEEN ATOMIC WEIGHT AND MAGNETISM.

By LEO ERRÉRA.

IN a sealed paper committed to the care of the Belgian Academy of Sciences on February 2nd, 1878, and opened in March, 1881, I endeavoured to show that the magnetism of the elements depends periodically on their atomic weight in such a manner that the elements of Mendeleeff's odd series are dia-magnetic, and those of the even series are para-magnetic. The discrepant statements on the magnetic behaviour of simple bodies are to be found in the memoir quoted, collocated at length and inserted in Mendeleeff's well-known table. Certain exceptions were then already taken into consideration, and their possibility was to a certain extent admitted.

Independently of the author, Carnelley arrived in September, 1879, at the same conclusion.

As for the intensity of the para-magnetic and dia-magnetic powers, the author pointed out at the same time that it also was in connection with the periodic system, as it may be easily seen from the elements of the 4th, the 7th, and the 11th series. In consequence of our very imperfect knowledge of the magnitude of those forces I was unable to detect a pervading regularity in this respect. Carnelley was similarly unsuccessful.

Latterly Bachmetieff (*Journal Russian Phys. Chem.*

Soc., xxi., 4, 1889) believed that he had found a general law. He assumes that we obtain an irregularly serpentine curve, alternately ascending and descending by plotting out the atomic weights as abscissæ and the intensities of the positive or negative magnetism as ordinates. This curve would be to a great extent in conflict with the rule indicated by the author and by Carnelley. On examination it is perceived that the Russian physicist has proceeded in an arbitrary manner. Thus he asserts that K, according to Lamy (*Ann. Chim. Phys.*, Series 3, vol. li., 1859, p. 305), is dia-magnetic, whilst Lamy maintains the very opposite. Ti, Pd, Os, Pt are placed by Bachmetieff as dia-magnetic, though Faraday found them to be para-magnetic. As regards platinum, Bachmetieff certainly appeals to the statement of Kokscharoff (1867); but for this body Faraday's observation is certainly correct, since subsequent experiments by Mouton (1878) confirm its para-magnetic character. And as the metal employed by Mouton had been prepared by Stas, and declared to be pure and free from iron, it may be maintained that the para-magnetic character of platinum is fully established. This sufficiently shows the incorrectness of Bachmetieff's curve. It evidently does not agree with demonstrated facts as well as the conjectural rule proposed by Carnelley and the author.—*Berichte der Deutsch. Chem. Gesellschaft*, Vol. xxiv., No. 1, p. 88.

DETECTION AND DETERMINATION OF VERY SMALL PROPORTIONS OF ALUMINIUM IN CAST-IRON AND STEEL.

By ADOLPHE CARNOT.

The author takes a rather large quantity of the metal, for instance 10 grms., and attacks it with hydrochloric acid in a platinum capsule. The use of glass or porcelain is avoided as much as possible to prevent any accidental introduction of alumina from the apparatus.

When the metal is entirely dissolved, without allowing the solution to become peroxidised by exposure to the air, it is diluted with distilled water and put into a flask or a beaker, washing it several times by decantation, and retaining the insoluble portion—graphite, silica, &c.—upon a filter. A portion of silica may remain in solution, and must be eliminated afterwards; but this must not be done by evaporating the solution to dryness, as it contains an enormous quantity of ferrous salt.

The greater part of the free acid is neutralised with ammonia and then with sodium carbonate, and sodium thiosulphate is added. When the violet colouration has entirely disappeared and no more ferric salt in the solution, which is now completely colourless, he adds 2 or 3 c.c. of a saturated solution of sodium phosphate and about 20 c.c. of a solution of sodium acetate. The liquid is then heated and raised to a boil, which is kept up for about forty-five minutes, as long as the slightest odour of sulphurous acid is perceived.

There is formed a precipitate, generally of little bulk, consisting of aluminium phosphate mixed with sulphur, and containing a little silica and ferric phosphate. This precipitate is received on a filter and washed with a little boiling water, and then placed on a capsule of platinum and treated in heat with 10 or 15 c.c. of hydrochloric acid diluted with water.

The solution is evaporated to dryness, and the residue is kept at 100° for an hour, so that the silica may become perfectly insoluble in acids. It is then re-dissolved in a little dilute hydrochloric acid, heat being applied to redissolve all the aluminium and iron phosphate; the liquid is filtered to remove the last traces of silica, diluted with 100 c.c. of cold water, and the precipitation of the aluminium phosphate is repeated by the same method—that is, by almost complete neutralisation of the acid with sodium carbonate, the addition of thiosulphate in the cold, and subsequently of a mixture (previously dissolved) of 2 grms. acetate and 2 grms. thiosulphate, boiling for half an hour, and filtration through a small filter of paper, which has been washed with acids and leaves no ash.

The silica and the small quantity of iron which remained in the first precipitate have thus been completely eliminated from the second, which, after having been washed with boiling water, is dried, ignited, and weighed.

The aluminium phosphate thus obtained $(PO_5Al_2O_3)$ contains 22·45 per cent of aluminium. The operation requires only a few hours, and gives accurate results.—*Bull. de la Soc. Chim. de Paris*, Vol. v., No. 3, p. 139.

STUDIES ON THE EARTHS OF THE CERIUM AND YTTRIUM GROUP.*

By A. BETTENDORFF.

(Continued from p. 159).

Lanthanum ammonium nitrate is much disposed to form supersaturated aqueous solutions, from which crystals operate only on prolonged standing. It is therefore advisable, as Auer von Welsbach observed, to induce crystallisation by means of small crystals of the salt when it ensues very rapidly. After a few series of crystallisations, systematically conducted, we obtain colourless transparent lanthanum-ammonium nitrate in large crystals. If examined by daylight, both the crystals and their aqueous solution are perfectly colourless; but by gas or petroleum light they both show a rather strong rose-red colour. The solution, in fact, displays then a strong absorption spectrum of didymium. If we proceed to a further purification by separating out the greater part of the double salt by a number of successive crystallisations, removing the mother-liquor and again proceeding in the same manner with the solution of the crystals, we obtain a series of mother-liquors, first of a faint rose-colour, then yellowish-green, and lastly colourless. From the last-mentioned, pure lanthanum-ammonium nitrate separates out in large crystals, colourless both by daylight and lamplight. The concentrated solution shows no trace of absorption lines in a stratum of 0·1 m.m. in thickness. A comparative spectroscopic examination of the various mother-liquors to which the author returns below, showed that this manner of treatment effected a separation of Auer von Welsbach's neodymium and praseodymium. The ammonium double salt of the latter earth is evidently less soluble and adheres more firmly to the corresponding lanthanum salts. It is interesting that the salts when mixed in certain proportions give crystals and solutions which appear perfectly colourless by daylight, but in which neodymium may be at once recognised by gas light.

The explanation of this phenomenon, as well as of the fact that all the didymium salts and their solutions appear of a more intense rose-colour by gaslight than by daylight is to be found in the mutual action of complementary colours, and the poverty of the gas-flame in those rays of light which are absorbed by neodymium.

In his research on the decomposition of didymium into its elements, Auer von Welsbach found in the spectrum of praseodymium four absorption bands which are shown in the illustration accompanying his memoir as gradually decreasing in intensity and breadth towards the red end of the spectrum. Unfortunately they have not been reduced to wave-lengths, but by comparing the designs for didymium and its components it is easily found that the bands $\lambda 5917$ and 5871, and then $\lambda 4813$, $\lambda 4687$, $\lambda 4453$, must belong to praseodymium.

The absorption spectrum of the author's second mother-liquor showed the three bands last mentioned extremely intensified, while the groups of lines in the yellow part of the spectrum was much enfeebled with the exception of

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* From *Liebig's Annalen*.

the bands λ5815, λ5692. In the seventh mother-liquor this behaviour was more clearly visible. Of the band λ5917, which was to be the only characteristic of praseodymium in the yellow, nothing remained; the band λ5871 was faint, but λ5815—λ5723 appeared fairly intense. The spectrum of the twelfth mother-liquor had only indications of the above-named groups in the yellow; λ5765 was almost as sharp as a hair. The eighteenth mother-liquor displayed merely the bands λ4813, λ4687, λ4452.

This behaviour is seen most plainly if the mother-liquors are compared spectrophotometrically, care being taken that equal quantities of the absorbent substance are traversed by the source of light. The quantity of absorbent substance was so selected for the band λ4813, which is equally sharp on both sides that it shows the same intensity and breadth in all comparisons.

The intensity and the breadth of the absorption bands vary, as it is well known, according to the contents of the absorbent medium. They are, as Bunsen showed for the salts and solutions of didymium, equally great if the equal quantities of absorbent matter are presented to the light on its way. If we call l and l' the lengths of the strata traversed, d and d' the quantity of didymium oxide in the volume unit of the solid or liquid substance, the conditions for a comparative examination are fulfilled if $l.d=l'd'$. If in two solutions of didymium both l and d are known in one, and if the second is placed in a hollow prism, and if we compare the spectra projected above each other in a suitable manner, the thickness of the stratum l' may be so varied by displacing the prism that both spectra display, for didymium compounds of the same origin an identical appearance as concerns the number, the breadth, and the intensity of the absorption bands.

For didymium compounds of different origins this does not hold good for all bands, as Nilson and Krüss have observed in a number of cases. In their investigations they were led to the conjecture that Auer von Welsbach's neodymium and praseodymium must be mixtures of different earths. As regards the latter component of didymium this suspicion has proved correct.

For comparative spectrophotometric determinations the author uses a small hollow prism, made from a thick-sided glass tube of 0·02 m.m. internal diameter. It was melted off round at one end, and at the other drawn out and cut off like a combustion tube. The glass vessel thus prepared, about 0·09 m.m. in length, is ground off prismatically in such a manner that at the rounded end there remains in the middle only 0·001 thickness of side. Thus is formed the glass frame-work of a hollow prism which is closed by cementing on with Canada balsam two thin glass slips, such as are used for microscopic covering glasses.

The hollow prism is mounted in such a matter that it can be moved to and fro before the slit of the collimator of the spectroscope, and the thickness of the stratum traversed can be read off on a scale. A small instrument supplied by the mechanician Max Wolz, of Bonn, is eminently adapted for obtaining, in systematic fractionated precipitations or decompositions of the earths which yield absorption spectra, a speedy decision on the intensities of the several bands.

As a source of light the author uses, according to the example of Linnemann, the light of zirconia ignited in the oxy-hydrogen blowpipe. In addition to its unusual intensity this light contains a number of violet rays, so that this part of the spectrum appears brightly illuminated, and longer than with gas or petroleum light. With the best lamps the author has been able to effect sharp measurements of the absorption-bands up to λ4240, but with the zirconia light it is easy to extend the measurements as far as λ4100.

(To be continued).

Professor Corfield has been elected an Honorary Member of the Imperial Society of Medicine of Constantinople.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

March 19th, 1891.

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

Messrs. William Ramsay, Spencer Umfreville Pickering, and Edgar J. Millard were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward Arthur Barnes, 57, Delafield Road, Charlton, S.E.; Frederick Arthur Evans, Cape Colony, South Africa; Joseph Fitze, 1, New China Bazaar Street, Calcutta; Walter Herbert Joseland, 9, Campbell Grove, Oxford Road, Manchester; John Wild, 28, Hyde Road, Woodley, Stockport.

The following papers were read:—

18. "*Molecular Refraction and Dispersion of Various Substances.*" By J. H. Gladstone, Ph.D., F.R.S.

This paper contains a record of a considerable number of hitherto published observations of refractive indices that had accumulated in the author's note book, together with the optical constants calculated from them, and remarks on their bearing on chemical or physical theory.

Observations are quoted on carbon bisulphide and benzene at various temperatures which confirm the old conclusion that the specific refractive energy of a liquid is a constant not affected by temperature.

In a second series of tables the data are recorded relating to a number of carbon compounds mostly prepared by Dr. Perkin; the molecular refraction and dispersion calculated from experiment are compared with those reckoned from the values already assigned to the constituent elements. In the majority of cases the experimental and theoretical numbers are in fairly close accordance; in some cases, however, there is a discrepancy larger than is likely to be due to experimental error or impurity of substance. This, of course, points to some difference of constitution. Amongst the comments made upon these results the following may be noted:—The molecular dispersion of amylene shows the amount of increase for double-linked carbons which characterises the allyl compounds previously examined, and the allyl and diallylacetic acids in the table. The three modifications of xylene, while differing considerably in their actual indices, have almost identically the same molecular refraction and dispersion.

Safrol agrees in optical properties with what may be termed the normal value reckoning for four double-linked carbons; but anethoil, cinnamene, and butenylbenzene, though they have only the same number of double linkings, give a refraction, and especially a dispersion, far above what theory requires; thus indicating the presence of carbon in that still more refractive and dispersive condition to which the author drew attention in 1881.

Some of the results, *e.g.*, those relating to the isomeric maleic and fumaric ethers, afford fresh confirmation of the analogy between the molecular refraction and dispersion and the molecular magnetic rotation of the same substance as observed by Perkin.

The nitrogen compounds give results quite confirmatory of the two values previously assigned to that element in combination. The same remark applies to the isomeric ethylic thiocyanate and mustard oil.

The observation of stannic ethide gives a refraction equivalent for tin, 18·1, in fair accordance with that determined from its chloride; but the value of zinc in zincic ethide, 15·9, differs totally from that determined from its dissolved sults.

Observations are also quoted of the halogen compounds of silicon and titanium which tend to confirm the former refraction equivalents, and indicate that the atomic dispersion of silicon is very small, about 0·32; and that of titanium very large indeed, about 8·7.

19. "*Contributions to Our Knowledge of the Aconite Alkaloids.* Part I. *On the Crystalline Alkaloid of Aconitum Napellus.*" By Wyndham R. Dunstan and W. H. Ince, PhD. (from the Research Laboratory of the Pharmaceutical Society).

The authors have investigated the properties of a crystalline alkaloid obtained from the root of *Aconitum napellus* by extraction with amyl alcohol, as suggested by the late Mr. John Williams. For a supply of the material they are indebted to the kindness of Messrs. Howard and Sons, of Stratford.

The yellowish indistinct crystals melted at 188·4° (corr.), and by crystallisation from alcoholic solution were proved to be associated with a small quantity of a gummy amorphous base. On combustion, the original substance gave numbers agreeing fairly well with the formula $C_{33}H_{43}NO_{12}$, which is that proposed for aconitine by Wright and Luff (*Trans.*, 1879). The alkaloid was purified by repeated crystallisation from a mixture of alcohol and ether, or more readily by conversion into its bromhydride and regeneration of the alkaloid from the salt, or by regeneration from its crystalline auri-chloride. It crystallises in tabular prisms belonging to the rhombic system; the crystallography of the substance forms the subject of a separate communication from Mr. Tutton. The crystals are very slightly soluble in water and light petroleum, more soluble in ether and alcohol, most soluble in benzene and chloroform. They melt at 188·5° (corr.). Contrary to the statements of previous observers, who found aconitine to be lævo-rotatory, the authors found an alcoholic solution to be *dextro-rotatory*, $[\alpha]_D+10{\cdot}78^\circ$; the aqueous solution of the bromhydride is, however, lævo-rotatory, $[\alpha]_D-30{\cdot}47^\circ$. On analysis, the alkaloid afforded results which agreed best with the formula $C_{33}H_{45}NO_{12}$.

Two crystalline *aurichlorides* were obtained. One melting at 135·5° (corr.) ($C_{33}H_{45}NO_{12}HAuCl_4$); the other, a basic aurichloride ($C_{33}H_{45}NO_{12}AuCl_3$) melting at 129° (corr.) These compounds are obtained without difficulty, and afford trustworthy means of identifying aconitine. The alkaloid may be readily recovered from them in a pure state.

Aconitine is not appreciably affected by heating at a temperature below its melting-point, but at this temperature it is gradually converted into the uncrystallisable base aconine. Prolonged boiling in aqueous solution induces a similar change, but not to the same extent unless an alkali is present. Boiling with water acidulated with chlorhydric acid also produces decomposition of the alkaloid.

Dehydraconitine or *apo-aconitine* is a base differing from aconitine by the absence of a molecular proportion of water which was first obtained by Wright and Luff by acting on aconitine with acids. Its existence has, however, been questioned by later workers. The authors find that such a substance may be readily procured by heating aconitine with saturated aqueous tartaric acid in closed tubes, as recommended by Wright and Luff. The crystals of this substance melt at 186·5° (corr.). It forms crystalline salts, and in other respects closely resembles the parent alkaloid. The results of analyses agree well with the formula $C_{33}H_{43}NO_{11}$. Three *aurichlorides* were obtained: one ($C_{33}H_{43}NO_{11}HAuCl_4$) melts at 141° (corr.); this salt, when crystallised from aqueous alcohol, affords a hydrate ($C_{33}H_{43}NO_{11}HAuCl_4,H_2O$), m. p. 129° (corr.), isomeric with aconitine aurichloride, into which, indeed, it very readily changes. The third aurichloride is a direct compound of the alkaloid with auric chloride—

$$(C_{33}H_{43}NO_{11}AuCl_3);$$

it melts at 147·5° (corr.).

An *amorphous base* was obtained from aconitine, together with benzoic acid, by prolonged heating with water in a closed tube. It appears to be identical with the *aconine* of Wright and Luff. The same substance is formed together with a resinous substance when aconitine is heated with an alkali. Neither aconine nor its salts could be crystallised. The amorphous base after purification and its amorphous aurichloride afforded analytical data agreeing with the formulæ $C_{26}H_{41}NO_{11}$ and $C_{26}H_{41}NO_{11},HAuCl_4$ respectively.

A further study is being made of aconine, and of the question as to the existence of other alkaloids in this plant.

Discussion.

Dr. Alder Wright expressed his gratification that the authors so substantially corroborated the results brought before the Society by himself some thirteen years ago. The difference in the results obtained by various chemists he thought was largely attributable to defective methods of isolation of the active principle, whereby the true aconitine became more or less hydrolysed, or otherwise acted on, so as to be transformed into non-crystalline, and comparatively inert, substances; also to the imperfection of the methods adopted for separating the true active crystallisable alkaloid from the non-crystalline and far less active alkaloids naturally accompanying it. It was greatly to be regretted that preparations were largely sold under the name of aconitine, of which only a very small fraction actually was aconitine, the greater part consisting of relatively inert other alkaloids. It was as though a substance should be sold as morphine which almost entirely consisted of narcotine and the other less active opium bases, so that its physiological potency was only a small fraction of that of genuine morphine.

Dr. Thudichum forcibly described the uncertainty and danger attending the use of the drug "aconitine" in medical practice, owing to absence of uniformity in the products of English, French, and German manufacture. A final determination of the properties and mode of preparing the active principles of the various kinds of aconite would, he said, be a work of great value.

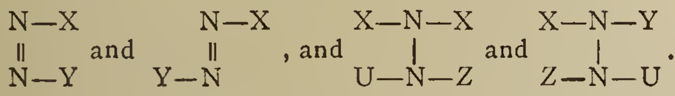
Professor Dunstan, in reply, said it was well known that the commercial aconitines varied much in toxic power, all of them being more or less impure, chiefly from the presence of amorphous alkaloid, which appeared to be non-toxic. Dr. Waller, of St. Mary's Hospital, had undertaken to investigate the physiological action of the pure alkaloid obtained in the course of this research. It was intended to fully examine the alkaloids contained in in *A. ferox and A. saponicum.*

20. "*The Crystallographical Characters of Aconitine from Aconitum Napellus.*" By A. E. Tutton, Royal College of Science, London.

The author has made a complete crystallographical examination of some fine specimens of aconitine crystals, obtained during the course of the work described in the preceding communication. Aconitine crystallises in the rhombic system. Habit: prismatic, with inclination to tabular, owing to the large development of the brachypinacoid. Ratio of axes: $a:b:c = 0{\cdot}5456:1:0{\cdot}3885$. Forms observed: $a\{100\}$, $b\{010\}$, $p\{110\}$, $p'\{120\}$, $m\{101\}$, $q\{021\}$, and $o\{121\}$. A complete table of angles is given in the memoir. There is a good cleavage parallel to $a\{100\}$. Optic axial plane is $b\{010\}$. Aconitine is a highly dispersive substance. The apparent acute angle of the optic axes in air 2E for lithium light is 47° 0′, for sodium light 56’ 10′, and for thallium light 65° 5′. Hence there is a dispersion of 18° 5′. The double refraction is positive.

21. *The Asymmetry of Nitrogen in Substituted Ammonium Compounds.*" By S. B. Schryver, B.Sc.

Although isomeric compounds in which isomerism is due to the different geometrical arrangement of radicles round the carbon atom have for several years been known, stereo-isomers—to use V. Meyer's term—in which the radicles have different arrangements round a nitrogen atom—have not up to the present been conclusively proved to exist. Hantzsch and Werner (*Ber.*, 23, *et seq.*) have sought to explain the existence of the different hydroxamic acids of Lossen and the mono- and di-benzoxime compounds of V. Meyer and Auwers (*Ber.*, 21, 784) by the hypothesis that they are stereo-isomers of nitrogen: they suppose that this element is capable of forming compounds the general types of which may be represented by the constitutional formulæ—



$$\begin{array}{l}N-X\\ \parallel\\ N-Y\end{array} \text{ and } \begin{array}{r}N-X\\ \parallel\\ Y-N\end{array} \text{, and } \begin{array}{c}X-N-X\\ |\\ U-N-Z\end{array} \text{ and } \begin{array}{c}X-N-Y\\ |\\ Z-N-U\end{array}.$$

This explanation of the isomerism is not accepted by Meyer (*Ber.*, 23, 603). Moreover, the evidence of the existence of such stereo-isomers in the case of compounds other than the hydroximes and hydroxamic acids is, up to the present, very slight and of a very doubtful nature.

If, however, the compounds of trivalent nitrogen *are* capable of forming such stereo-isomers, we should expect that in compounds of pentavalent nitrogen, where the opportunity for difference in the relative arrangements of the radicles in the molecule is greater, stereo-isomers should also, *a fortiori*, exist. To produce these has been the primary object of the author's work.

The class of compounds chosen for study was the substituted ammoniums. The tertiary amines easily combine with alkyl iodides without evolution of heat (under suitable conditions), and it is, therefore, possible to obtain well-crystallised compounds, viz., the platinichlorides, *under such conditions that isomeric changes are not likely to take place.*

The author, in conjunction with N. Collie, examined the platinichlorides obtained from the different mixed methyl and ethyl ammonium bases of the formulæ Me_3EtNOH, Me_2Et_2NOH, $MeEt_3NOH$; these were prepared both from triethylamine and also trimethylamine as a starting point. But it did not seem to make any difference in the crystalline form of the platinochlorides, whether the base was prepared from triethylamine or trimethylamine, or whether the solutions were evaporated by the aid of heat or *in vacuo.*

The author has, however, since prepared quaternary ammonium compounds, containing three different radicles:—

I. By adding methyl iodide to diethylisoamylamine.
II. By adding isoamyl iodide to diethylmethylamine.
III. By adding ethyl iodide to ethylmethylisoamylamine.

The platinichlorides of I., II., and III. gave on evaporation by means of heat needle-shaped crystals belonging to the *rhombic system.*

The platinichlorides of I. and II. on evaporation *in vacuo* gave needle-shaped crystals belonging to the *monoclinic system*, whilst III. on evaporation under the same conditions gave needles which resembled those obtained by evaporation by heat.

Further, the monoclinic needles on re-dissolving in hot water on evaporation were changed into the rhombic variety. They were also changed to the rhombic variety by adding excess of chlorhydric acid and allowing the solution to evaporate at the temperature of the atmosphere. From these results the author is led to the conclusion that *the difference in crystalline form is due to the various arrangements of the radicles ethyl, methyl, isoamyl, and chlorine around the nitrogen atom, and, therefore, that stereo-isomers are possibly capable of existence in the case of quaternary ammonium compounds.*

22. "*Acetylcarbinol* (*acetol*), $CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH$." By W. H. PERKIN, jun., Ph.D., F.R.S.

Some time since the author, in conjunction with Dr. Tingle (*Proc. Chem. Soc.*, 73, 156), succeeded in preparing acetylcarbinol by the hydrolysis of monochloracetone by means of barium carbonate. As, however, the amount obtained by this process is exceedingly small and its isolation extremely laborious, the author has been engaged for some time in endeavouring to improve the method of preparation. The following process was ultimately devised and employed with success in preparing large quantities of pure acetylcarbinol. 200 grms. of acetylcarbinyl acetate ($CH_3{\cdot}CO{\cdot}CH_2{\cdot}OC_2H_3O$), prepared by digesting monochloracetone with potassium acetate in alcoholic solution, is dissolved in 350 grms. of water heated to boiling, and freshly precipitated barium carbonate added in small quantities at a time until no further action takes place. The clear solution is distilled as rapidly as possible under reduced pressure (100 m.m.) and the distillate, which contains 20 per cent of acetylcarbinol, very carefully fractionated under ordinary pressures with the aid of a long Glinsky column. After repeated fractionation a product is obtained which contains over 90 per cent of acetylcarbinol. This is dissolved in pure ether, thoroughly dried with freshly-ignited sodium sulphate, the ether distilled off, and the residue fractionated under reduced pressure.

Acetylcarbinol boils at 120—122° under 250 m.m., and at about 147° under ordinary pressure. When cooled in a mixture of ice and chlorhydric acid it solidifies to a hard crystalline mass; its rel. den. at 15°/15° is 1·07915; its magnetic rotation 3·650.

Sodium amalgam converts acetylcarbinol quantitatively into *methylglycol*, $CH_3{\cdot}CH(OH){\cdot}CH_2OH{\cdot}$ (b.p. 188°).

23. "*The Action of Ethyl Dichloracetate on the Sodium Derivative of Ethyl Malonate.*" By ARTHUR W. BISHOP, Ph.D., and W. H. PERKIN, jun., Ph.D., F.R.S.

When a mixture of ethyl malonate (2 mols.), sodium ethylate (2 mols.), and ethyl dichloracetate (1 mol.) is digested in alcoholic solution in a reflux apparatus, interaction rapidly takes place with separation of sodium chloride. At the end of two hours, the alcohol was distilled off, the residue mixed with water, extracted with ether, and the oily residue which remains, after distilling off the ether, fractioned under reduced pressure. After repeated refractionation it was ultimately separated into two new compounds, *α-ethylic ethylenetricarboxylate*, $(CO_2Et)_2C{:}CH{\cdot}CO_2Et$, and *β-ethylic propanetricarboxylate*, $(CO_2Et)_2{:}CH{\cdot}CH(CO_2Et){:}CH(CO_2Et)_2$.

The former is a colourless peculiar-smelling oil which boils at 203—205° (100 m.m.); on hydrolysis, it yields ethylenetricarboxylic acid, and this, on heating to 180°, is decomposed quantitatively into *fumaric acid* and carbon dioxide.

The latter ethereal salt is an extremely thick oil which boils without decomposition at about 265° under a pressure of 80 m.m. On hydrolysis it is converted into a polycarboxylic acid, probably propanepentacarboxylic acid, as the substance, when heated at 180°, readily loses carbon dioxide with formation of *tricarballylic acid*,—

$$(COOH)_2{\cdot}CH{\cdot}CH(COOH){\cdot}CH(COOH)_2 = \\ = COOH{\cdot}CH_2{\cdot}CH(COOH){\cdot}CH_2COOH + 2CO_2$$

24. "*Benzoylacetic Acid and some of its Derivatives.* Part V." By W. H. PERKIN, jun., Ph.D., F.R.S., and JAMES STENHOUSE.

This research was instituted with the object of supplementing, and in some cases rectifying, the results obtained in investigations previously carried out on the same subject (compare *Trans. Chem. Soc.*, xlv., 170; xlvii., 240; xlvii., 261; xlix., 154).

Ethylic benzoylacetate contains one hydrogen atom which is readily displaced by sodium, and the resulting sodium derivative yields, on treatment with alkyl iodides, the ethereal salts of higher homologues of benzoylacetic acid, of the formula $C_6H_5{\cdot}CO{\cdot}CHR{\cdot}COOC_2H_5$.

Sodium dissolves readily in ethereal solutions of these derivatives, but, in spite of a large number of experiments, no general method has as yet been found by which di-substituted derivatives of ethylic benzoylacetate (similar to those obtained from ethylic acetoacetate) can be prepared. When treated with sodium ethylate and alkyl iodides in the usual manner, mono-substituted derivatives of ethylic benzoylacetate usually yield only traces of di-substituted ethereal salts,—

$$C_6H_5{\cdot}CO{\cdot}CRR'{\cdot}CO_2Et,$$

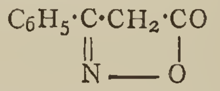
the greater portion being decomposed with formation of benzoic acid, fatty acids, &c.

By digesting ethylic methylbenzoylacetate with sodium ethylate and allyl iodide in alcoholic solution in a reflux apparatus, however, an almost quantitative yield of *ethylic allylmethylbenzoylacetate*,—

$$C_6H_5{\cdot}CO{\cdot}C(CH_3)(C_3H_5){\cdot}CO_2Et,$$

is obtained. This ethereal salt boils at 243—245° (225 m.m.); on hydrolysis it yields quantities of benzoic acid, together with a small quantity of a ketone, probably allylmethylacetophenone.

Action of Hydroxylamine on Dibenzoylacetic Acid.—Dibenzoylacetic acid and hydroxylamine readily interact in alkaline solution, with formation of a substance, $C_9H_7NO_2$, which, on examination, was found to be identical with the *phenylisoxazolon*,—



$$\begin{array}{l}C_6H_5{\cdot}C{\cdot}CH_2{\cdot}CO\\ \quad\ \| \qquad\quad\ |\\ \quad N\ \text{—}\ O\end{array},$$

obtained by Claisen (*Ber.*, xxiv., 140) by the action of hydroxylamine on ethylic benzoylacetate. When heated with phenylhydrazine at 180°, ethylic dibenzoylacetate is completely decomposed with formation of *benzoylphenylhydrazine*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5$. On reduction, dibenzoylacetic acid yields β-phenyllactic acid,—

$$C_6H_5{\cdot}CH(OH){\cdot}CH_2COOH,$$

and *dihydroxydibenzoylacetic acid*,—

$$[C_6H_5{\cdot}CH(OH)]_2{:}CH{\cdot}COOH.$$

This new acid crystallises from water in slender glistening needles which melt at 188—190°.

Ethylic methyldibenzoylacetate,—

$$(C_6H_5{\cdot}CO)_2{:}C(CH_3){\cdot}COOC_2H_5,$$

is prepared by the action of benzoyl chloride on the sodium compound of ethylic methylbenzoylacetate. It is a thick oil which is much less stable than ethylic dibenzoylacetate and is almost entirely decomposed on hydrolysis with formation of quantities of benzoic acid.

Ethylic benzylbenzoylacetate,—

$$C_6H_5{\cdot}CO{\cdot}CH(C_7H_7).COOC_2H_5,$$

prepared by heating together ethylic benzoylacetate, sodium ethylate, and benzyl chloride in alcoholic solution, is a thick light-yellow oil boiling at 265° (80 m.m.).

Benzylacetophenone, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$, is obtained by the hydrolysis of the previous compound. It crystallises from alcohol in glistening plates which melt at 70°. It is converted by hydroxylamine into the hydroxime $C_6H_5{\cdot}C(NOH){\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$, which melts at 80—81°. Reduction with sodium in moist ethereal solution converts benzylacetophenone into *diphenylpropyl alcohol*, $C_6H_5CH(OH)\ CH_2{\cdot}CH_2{\cdot}C_6H_5$, a thick colourless oil which boils at about 240° (70 m.m.).

α-Methyl-β-phenyllactic acid,—

$$C_6H_5{\cdot}CH(OH){\cdot}C(CH_3){\cdot}COOH,$$

obtained by reducing ethylic methylbenzoylacetate with sodium amalgam, melts at 95° (not at 124—125°, as previously stated, *Trans. Chem. Soc.*, xlix., 160). When heated at 280°, it is decomposed with evolution of carbon dioxide and water and formation of methylstyrolene, $C_6H_5{\cdot}CH{:}CH{\cdot}CH_3$ (b. p. 174—175°).

α-Ethyl-β phenyllactic acid,—

$$C_6H_5{\cdot}CH(OH){\cdot}CH(C_2H_5){\cdot}COOH,$$

is obtained by the reduction of ethylic ethylbenzoylacetate with sodium amalgam. It crystallises from bisulphide of carbon in needles which melt about 108°.

Ethylic furfuralbenzoylacetate,—

$$C_6H_5{\cdot}CO{\cdot}C({:}CH{\cdot}C_4H_3O){\cdot}COOC_2H_5,$$

is prepared by heating a mixture of furfural, ethyl benzoylacetate, and acetic anhydride at 180°. It crystallises from methyl alcohol in beautiful glistening prisms which melt at 68°.

25. "*Syntheses with the aid of Ethyl Pentanetetracarboxylate.*" (Preliminary Note). By W. H. PERKIN, jun., Ph.D., F.R.S., and BERTRAM PRENTICE.

Ethylic pentanetetracarboxylate (*Trans. Chem. Soc.*, li., 241) yields a disodium derivative,—

$$(COOC_2H_5)_2{:}CNa{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CNa{:}(COOC_2H_5)_2,$$

from which by the action of alkyl iodides, higher homologues may be obtained, and these, on hydrolysis and subsequent splitting off of two molecules of carbon dioxide, yield higher homologues of pimelic acid,—

$$\begin{aligned}&(COOC_2H_5)_2{:}CR\ CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CR'{:}(COOC_2H_5)_2+\\&\quad+4KOH=(COOK)_2{:}CR{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CR'(COOK)_2+\\&\qquad\qquad+4C_2H_5OH.\end{aligned}$$

$$\begin{aligned}&(COOH)_2{:}CR{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CR'{:}(COOH)_2=\\&\quad=COOH{\cdot}CHR{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHR'{\cdot}COOH+2CO_2,\end{aligned}$$

Ethylic dibenzylpentanetetracarboxylate,—

$$\begin{aligned}&(COOC_2H_5)_2{\cdot}C(C_7H_7){\cdot}\\&\qquad CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(C_7H_7)(COOC_2H_5)_2,\end{aligned}$$

prepared by the action of benzyl chloride on the disodium compound of ethyl pentanetetracarboxylate, is a solid crystalline substance which melts at 75—77°.

Dibenzylpentanetetracarboxylic acid,—

$$(COOH)_2{\cdot}C(C_7H_7){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(C_7H_7)(COOH)_2,$$

obtained by the hydrolysis of the above ethereal salt, is a colourless crystalline substance, very sparingly soluble in ether. It decomposes at 207—210° into dibenzylpimelic acid and carbon dioxide. The silver salt, $C_{23}H_{20}Ag_4O_8$, is a white powder, insoluble in water.

Dibenzylpimelic acid,—

$$COOH{\cdot}CH(C_7H_7){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(C_7H_7){\cdot}COOH,$$

crystallises from a mixture of benzene and light petroleum in well-formed glistening prisms which melt at about 117°. The *barium salt*, $C_{21}H_{22}O_4Ba+3H_2O$, is more soluble in cold than in hot water, and separates, when the cold saturated solution is heated to boiling, in colourless plates.

26. "*The Oxidation of Mannitol by Nitric Acid. α-Mannosaccharic Acid.*" By T. H. EASTERFIELD.

The recent researches of Emil Fischer and his pupils have shown that, whereas mannose is almost quantitatively converted into mannitol on reduction, dextrose yields mannitol with difficulty; hence it appears probable that dextrose and mannitol are not so directly related as has been supposed, and that as mannitol and mannose are easily converted, the one into the other, their relationship is a very close one; it therefore was to be supposed that mannitol, like mannose, would yield mannosaccharic and not saccharic acid, on oxidation with nitric acid. The author, at Professor Fischer's suggestion, has experimentally investigated this question, and his results completely confirm the correctness of the theoretical argument.

Mannosaccharic acid yields no sparingly soluble acid potassium salt; and it readily affords a double lactone.

Specific Odour of Soil.—MM. Berthelot and André. —The peculiar and not disagreeable odour given off by arable soils when recently moistened, *e.g.*, by a short shower, is well known. The authors find that the essential principle of this odour resides in a neutral organic compound of the aromatic family, and which is carried away by the vapour of water, as is the case with bodies possessing a feeble tension. Its proportion is exceedingly small, and may be regarded as some millionths.—*Comptes Rendus*, cxii., No. 12.

CORRESPONDENCE.

ATOMIC WEIGHTS.

To the Editor of the Chemical News.

Sir,—I have read with some interest the reply which my note on Atomic Weights has called forth from Mr. A. E. Johnson.

Mr. Johnson's contention—as I understand him—is, that he is quite right in retaining the erroneous weight for platinum, since the correct weight leads to an incorrect factor in calculating potash analyses, &c. This statement is, of course, in accord with Dittmar and MacArthur's results; for they point out that it is unsafe to assume that the precipitate of the double chloride consists of the theoretical PtR'_2Cl_6; and they further seem to suggest that every analyst should determine his own factor by experiments on pure salts of potassium, &c.; since, by so doing, he would get a factor certainly correct for his own mode of working. But, of course, admitting all this, I cannot admit that it is advisable to state a wrong atomic weight in a table of weights; and it appears to me that Mr. Johnson, in the next edition—which will doubtless be very soon required—of his handbook, should correct the atomic weight of platinum, and call attention in a footnote or elsewhere to the experiments of Dittmar and others on the determination of the *factor* to be taken.

With regard to the closing paragraph of Mr. Johnson's letter, I may point out that as the revised weights for the members of the platinum group now cause these elements to appear in the order which is demanded by deductions from the Periodic Law, it is pretty certain that no *considerable* readjustments of the weights will be found necessary.—I am, &c.,

F. H. P. C.

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. cxii., No. 12, March 23, 1891.

This issue puts on record the regrettable death of M. Cahours, which took place on the 17th ult. The deceased became a member of the Chemical Section in 1868, having been elected as successor to Dumas.

Action of Heat upon Carbon Monoxide.—M. Berthelot.—Carbon monoxide persists, even at the most elevated temperatures, and its gaseous density remains constant, sensibly identical with that of nitrogen up to about 4000°, according to experiments on gaseous explosive mixtures. Yet this stable compound gives signs of decomposition, with production of traces of carbon and of carbon dioxide, at much lower temperatures, such as at a bright red, according to H. Sainte-Claire Deville, and even at dull redness, according to the author's former observations. He does not accept the hypothesis that we have here a phenomenon of dissociation, since charcoal, &c., is not the true element C, but a polymer of lower or higher rank. Hence charcoal never appears as the *direct* result of decompositions effected at low temperatures. Whatever is the temperature employed, the proportion of carbon monoxide decomposed varies little, whether at 500°, or at moderate redness, or at bright red heat. But at a full or even a moderate red heat there are deposited at the extremities of the tube two distinct rings of carbon, whilst at 500—550° not the least trace of a carbonaceous deposit is to be seen. Hence the decomposition is preceded by polymerisation.

On a Reaction of Carbon Monoxide.—M. Berthelot.—This gas reduces ammoniacal silver nitrate. The reagent was prepared by adding to a dilute solution of silver nitrate dilute ammonia drop by drop so long as the precipitate formed at first re-dissolved completely. If a few bubbles of carbon monoxide are passed into this solution, it quickly turns brown, even in the cold, and at a boiling heat it gives at once a very abundant black precipitate. This reaction is a new approximation between carbon monoxide and the aldehyds.

A Contribution to the Physiology of Parasitical Plants.—A. Chatin.—The author proves that a parasite growing on plants of the *Strychnos* genus contain neither strychnine nor brucine. The mistletoe growing upon the oak does not contain the blue tannin of the latter, but exclusively a green tannin. In like manner, other parasites are shown not to absorb the peculiar principles of their hosts.

Action of Hydriodic Acid upon Silicon Chloride.—A. Besson.—Dry hydriodic acid is without action on silicon chloride at ordinary temperatures. At elevated temperatures, we obtain partial substitution products. The author obtains Si_2Cl_3I as a colourless liquid which distils at 113—114° and does not solidify at 60°. It is decomposed by water and by exposure to air and light. A second chloriodide, $Si_2Cl_2I_2$, accompanies the former in small quantities. It distils at 172°, and is also decomposed by water.

Transformation of Sodium Pyrophosphite into Phosphite. — L. Amat. — The author examines the conditions of this change, namely, the influence of dilution, of the proportion of acid and of the kind of acid. The hydrochloric and nitric acids act the most energetically, the sulphuric and the phosphorous less so, and the acetic acid least energetically of all the acids examined.

On Platinum Bromonitrites—M. Vèzes.—The series of bromonitrites includes the platonitrite, the platibromononitrite, the platibromonitrosonitrite, and the bromoplatinate.

The Disaggregation of the Neutral Salts of Amines of the Fatty Series by means of Water.—Albert Colson.—The salts of the amines capable of restoring the blue colour of litmus which have been reddened by the mineral acid with which they have been combined, are decidedly dissociated by water, even about 50°.

New Compounds of Pyridine.—Raoul Varet.—The compounds formed are the pyridine bromozincate, bromonickelate, bromocuprate, argentoiodide, and argentobromide. The argentochloride, if it exists, is not stable at the ordinary temperature. The affinities of the haloid salts of silver for pyridine decrease from the iodide to the bromide and the chloride, the inverse of what takes place with ammonia.

Theory of the Phenomena of Dyeing.—Léo Vignon.—All the phenomena of dyeing necessitate two essential conditions:—The presence of acid or basic functions in the material to be dyed; the presence of the same functions in the colouring matters. The sole exception of this rule is that of the tetrazo colouring matters, which are taken up by cotton without a mordant, in an alkaline bath, and which will require a special study. We are entitled to say that the phenomena of dyeing obtained with soluble colouring matters are of a purely chemical order, and that the rules of chemical action are sufficient for their explanation.

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.

Fancy Soaps and Perfumery.—A correspondent desires the name of the most recent work on this subject.

An Explosion.—Could any of your correspondents explain the following:—One evening, while getting my lantern ready for exhibition, I had attached the tubing to the oxygen cylinder, but found it was leaking at the coupling. I had to re-adjust this several times, and, of course, each time turning on and off the gas; the last time I turned it on, the regulator, which was of the bellows pattern, or exactly like an oxygen bag, exploded with a very loud report equal to a 4-bore gun, accompanied with a flash of light at least 15 inches in diameter. I at once turned off the gas, but in the few seconds a portion of the metal was fused. Now there was no light nearer than the gas-light in the hall 10 feet off—and we know oxygen is not inflammable of itself—nor was the hydrogen turned on; so what could have caused the explosion with combustion? No doubt pressure would have caused the collapse of the regulator, but whence the fire? Unless there was friction, the fire must have come from within.—H. D. B.

MEETINGS FOR THE WEEK.

Monday, 13th.—Medical, 8.30.
—— Society of Arts, 8. "The Decorative Treatment of Natural Foliage," by Hugh Stannus, F.R.I.B.A.
Tuesday, 14th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Royal Institution, 3. "The Geography of Africa," by J. Scott Keltie, F.R.G.S.
—— Society of Arts, 8. "Decorative Plaster Work; Stucco Work," by G. T. Robinson, F.S.A.
Wednesday, 15th.—Meteorological, 7.
—— Microscopical, 8.
—— Society of Arts, 8. "The Sources of Petroleum and Natural Gas," by Wm. Topley, G.R.S.
Thursday, 16th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Institute of Electrical Engineers, 8.
—— Chemical, 8.
—— Royal Institution, 3. "Recent Spectroscopic Investigations," by Prof. Dewar, M.A., F.R.S.
Friday, 17th.—Quekett, 8.
—— Physical, 5. (1) "On a Property of Magnetic Shunts," by Prof. S. P. Thompson. (2) "An Alternating Current Influence Machine," by James Wimshurst.
—— Royal Institution, 9. "Magnetic Rocks," by Prof. A. W. Rücker, M.A., F.R.S.
Saturday, 18th.—Royal Institution, 3. "The Dynamo," by Prof. Silvanus P. Thompson, D.Sc., B.A.

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THE CHEMICAL NEWS.

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ON THE
CAUSE OF THE ODOUR EMITTED BY THE SOIL OF A GARDEN AFTER A SUMMER SHOWER.

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

This subject, with which I was occupied more than twenty-five years ago, appears from a paragraph in the last number of the Chemical News (vol. lxiii., p. 176) to have recently attracted the attention of Professor Berthelot and M. André. I find, on referring to my old notes, which are dated 1865, that it is doubtful whether I ever published the results of these observations, and as the distinguished chemists I have just named have not quite solved the problem, I hasten to give the results I obtained so long ago.

After a considerable number of observations, I arrived at the conclusion that the odour emitted by soils and sedimentary strata after a heavy shower of rain in summer was due to the presence of organic substances closely related to the essential oils of plants, and it appeared evident to me that, during the hot dry weather, these porous surfaces absorb the fragrance emitted by thousands of flowers, and give it up again when the rain penetrates into these pores and displaces the various volatile substances imprisoned therein, which are only very slightly soluble in water. I believe that many kinds of soil possess this property, but those on which my observations were first made were the chalk soils of Picardy, in France. I found that not only chalk, but also marls, compact limetones, phosphatic rocks, and some kinds of schists and amphibolites are porous enough to possess it to such a degree as to emit a decided odour when they are strongly breathed upon.

Finding the property of which I speak very remarkable in certain chalk rocks of Picardy, I endeavoured to ascertain the nature of the substance, or substances, to which it was owed. I dissolved a very large quantity of the chalk in dilute hydrochloric acid, and passed the carbonic acid through various media, water, alcohol, weak potash solution, and dilute acid; but none of these liquids appeared to arrest the passage of the odoriferous substance. The only liquid which I found would retain it was an aqueous solution of bromine. This arrested it, and when the bromine solution was afterwards carefully evaporated at a low temperature, a yellowish product, soluble in alcohol, and having a strong odour of cedar wood, was obtained, which, from its chemical and physical properties, appeared to be very similar to, if not identical with, bromo-cedren, derived from essence of cedar.

THE VOLATILITY OF HYDROGEN SULPHATE AT THE ORDINARY TEMPERATURE OF THE AIR.

By ARTHUR COLEFAX, B.A.

In the Chemical News (vol. lxiii., p. 151) there appeared a paper by G. A. Koenig entitled "Is Sulphuric Hydrate Volatile at the Ordinary Temperature of the Air?" In this communication Mr. Koenig records an observation which has come under his notice pointing to an affirmative answer to the question his paper proposes. Some skeleton crystals of metallic iron had been placed on a watch-glass, supported on an iron triangle in an ordinary desiccator containing hydrogen sulphate, and had after nine months become coated with a white crust of anhydrous ferrous sulphate.

In the course of my work on phenuvic acid (*Jour. Chem. Soc.*, March, 1891, p. 190) I made some curious observations in connection with the neutral body obtainable from this acid by elimination of carbonic acid. Schlœsser (*Annalen*, 250, p. 223) had noticed that a portion of the white crystalline solid placed over hydrogen sulphate in a desiccator had, in twenty-four hours, become for the most part, liquid. I submit a short account of some experiments made, in the hope of gaining information as to the nature and cause of this change, which seemingly bear out Mr. Koenig's experience.

A portion of the white crystalline neutral body (phenyl methylfurfuran, according to Paal) which had remained quite unchanged in the air for three weeks, was placed in a perfectly clean desiccator over pure sulphuric acid. The substance (about ½ grm.) was in the centre of a large watch-glass, supported on a glass triangle. In four hours, the previously white crystalline neutral body had become brown and slightly moist, and in twenty-four hours was dark brown and quite moist. Other portions of the same sample of neutral body were then placed over different drying agents, withthe following results:—

Over Phosphoric Anhydride no change was observable after fourteen hours.

Over Calcium Chloride no change after the same length of time.

In order to ascertain whether the rapid change over hydrogen sulphate was due to impurities in the acid, the two following experiments were made:—

A quantity of the neutral body exposed over calcium chloride in a desiccator in which was a small vessel containing a solution of sulphur dioxide showed, even after twenty-four hours, no tendency to change.

To a solution of potassium nitrite in water, in which a small quantity of the neutral body was suspended, sufficient hydrogen sulphate was added to evolve traces of hydrogen nitrite. The experiment was made in a small glass stoppered cylinder. Even after many hours no change was noticeable.

This rapid change over sulphuric acid was not an isolated occurrence. I noticed it always when I placed any of the neutral body in a desiccator containing pure sulphuric acid. The desiccator was never exhausted; the experiments were made at the ordinary pressure.

NEW METHOD FOR THE DISCOVERY OF FAINT SPECTRAL BANDS.

Application to the Spectrum of the Hydrocarbons.

By H. DESLANDRES.

The band-spectrum attributed to the hydrocarbons or to carbon alone is furnished by the sources of light most commonly used; it is also found in the solar spectrum and constitutes to a great extent the spectrum of comets and of a certain class of stars. Its importance is therefore very great.

The author has studied this spectrum by a novel method which enables him to complete it and to add to it with certainty three new bands, *i.e.*, λ 438·19, λ 437·13, λ 436·5. These bands are not given by the combustion of the hydrocarbons, but they accompany the ordinary bands of the hydrocarbons and of cyanogen in the electric arc, and in the combustion of cyanogen. They were consequently at first, *e.g.*, by Liveing and Dewar, ascribed to this latter gas.

Now, the application of the general law of the distribution of bands which the author proposed (*Comptes Rendus*, 1887) for the spectra of bands, enables us to conclude that the bands in question belong certainly to the group of the

Spectra of the Hydrocarbons in Numbers of Vibrations.

Series I.		Series II.		Series III.		Series IV.		Series V.	
N.	Interval.	N.	In.	N.	In.	N.	In.	N.	In.
								167·94	
									14·97
								182·91	
						166·61			
							15·17		
						181·78			
				165·09					
					15·39				30·54
		163·39		180·18					
			15·64		15·67				
161·59		179·03		196·15				213·45	
	15·89		15·92		15·92		31·09		16·64
177·48		194·95		212·08		212·87		229·09	
	16·12		16·14		16·13		15·89		
193·60		211·69		228·21		228·76			

hydrocarbons. This application is summarised in the following table, which shows these three bands and the sixteen known bands of the hydrocarbons arranged in five series, in which the intervals of the bands, according to the law, increase in arithmetical proportion: the series being, moreover, superposable. The bands, expressed in the numbers of vibrations, are arranged in the five perpendicular series, so that the equal intervals of the series are on the same horizontal line. At the points of a series where a band is wanting, the interval is equal to the sum of the corresponding intervals of the other series.

According to this table, we may, with the sixteen known bands, on setting out with seven of these bands find by calculation exactly the nine others. On carrying out the calculation under the same conditions we obtain the three bands in question, which in numbers are represented by N 228·21, N 228·76, N 229·09. These three bands belong to the groups of the hydrocarbons.

We may even, by carrying out the calculation further, obtain the position of bands still more refrangible, *e.g.*, λ = 408·35 and λ = 408·17. But, according to all analogies, these bands must be very faint and lost in the very strong bands of the cyanogen group.

However this may be, by adding the three new bands the group of the hydrocarbons, considered as a whole, takes a form more systematic and regular, and approximates more closely to the band spectra of nitrogen, the only ones which have as yet been studied in a complete manner. These various spectra, as their study is carried sufficiently far, approach a common uniform type, the constancy of which is due to the similar variations of the whole numbers which govern them.

This application of the law of the distribution of bands forms a new method for the discovery of faint bands which are lost in a mixture of groups of different bands. It is the first instance of the discovery by calculation of new bands in band-spectra.—*Comptes Rendus.*

STUDIES ON THE EARTHS OF THE CERIUM AND YTTRIUM GROUP.*

By A. BETTENDORFF.

(Concluded from p. 173).

The plates of zirconia first used by Linnemann were prepared by means of strong pressure and fixed in small platinum plates. They require to be very carefully handled in order to be moderately permanent. Dr. W. Kochs, a tutor in this University, succeeded in fritting this infusible earth by a peculiar treatment, and moulding it permanently into any desired form. He found cylinders of 0·02 m.m. in length and 0·008 m.m. in diameter most convenient for illumination. I am indebted to his kindness for a number of such cylinders, which, along with the small accompanying oxyhydrogen lamp, can be obtained at a very moderate price from the mechanician Wolz, of Bonn.

As already remarked, the last mother-liquor obtained in purifying the lanthanum-ammonium nitrate—the 23rd—showed no trace of absorption lines, and the crystallisations previously separated out were perfectly pure lanthanum-ammonium nitrate. This double salt which was first obtained by Sainte-Claire Deville, and was optically and crystallographically examined by Descloizeaux, leaves on ignition perfectly white lanthanum oxide, which was dissolved in nitric acid, precipitated with pure oxalic acid, ignited again, and served for a series of determinations of equivalents, O = 15·96, S = 31·98.

1. 0·9146 grm. lanthanum oxide yielded 1·5900 grm. lanthanum sulphate.
2. 0·9395 grm. gave 1·6332 grm.
3. 0·9133 ,, 1·5877 ,,
4. 1·0651 ,, 1·8515 ,,

1. Equivalent RO = 108·14; R_2O_3 = 324·42
2. ,, = 108·15; ,, = 324·45
3. ,, = 108·15; ,, = 324·45
4. ,, = 108·16; ,, = 324·48

Hence the atomic weight of lanthanum may be calculated as R 92·19 or $\overset{\text{III}}{R}$ 138·28. P. T. Cleve in his last determinations made it $\overset{\text{III}}{R}$ 138·22.

It seemed to the author not superfluous to examine the spark spectrum of the lanthanum chloride obtained from the oxide to become certain of its identity with other oxides of lanthanum previously obtained. The monoprismatic spectroscope used for this purpose had, as I believe, been standardised according to the method first indicated by Angström and Thalèn, and subsequently used by Lecoq de Boisbaudran, G. Krüss and Nilson, by determining the position of a great number of the Fraunhofer lines as well as of the lines of the metals. The wave-lengths of these lines were taken from the measurements of Angström and Thalèn, which are given in M. Kaiser's text-book. For the production of the sparks there was used a Ruhmkorff's coil, a small Leyden jar, and a Bunsen battery of four elements. The striking distance of the sparks was 0·01 metre. The solution of lanthanum chloride was placed in a small glass tube placed vertically, and closed at both ends with corks through which a platinum wire topped with a conical carbon could be made to slide. The lower carbon cone was fixed so that its base just dipped into the solution of lanthanum. In this manner there was obtained a lanthanum spectrum of extraordinary brightness and permanence. For comparison the author gives the measurements of R. Thalèn as taken from M. Kaiser's manual.

Thalèn, who conducted his experiments with an apparatus of higher dispersion, gives also a great number of lines the values of which are intermediate between those quoted. In general the wave-lengths found agree well with Thalèn's figures, and bear witness to the accuracy of the author's spectral apparatus. Still there remain some discrepancies which need explanation. Thus among Thalèn's values, as quoted by Kaiser, the lines λ4824, λ4655, and λ4086, are printed in large figures as

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* From *Liebig's Annalen.*

	Thalèn.		Thalèn
λ6393	λ6393	λ4797	λ4796
6294	6294	4738	4739
6248	6249	4688	4687
5807	5807	4667	4668
5794	5794	4652	4655
5765	5761	4630	—
5599	5599	4604	4605
5535	5534	4558	4558
5504	5502	4522	4522
5455	5455	4430	4430
5376	3376	4384	4383
5340	5340	4354	4354
5302	5301	4330	4330
5182	5183	4295	4295
5152	5156	4286	4286
5122	5122	4238	4238
5113	5114	4196	4196
4920	4920	4152	4152
4898	4899	4123	4121
4860	4860	4084	4086
4821	4824	4077	4077
4817	—	4044	4042

main lines. The author had difficulty in finding these lines in his lanthanum preparations. But the line λ4330, which, according to P. T. Cleve, does not belong to lanthanum, is to be found in Thalèn's preparations as well as in those of the author.

BOILER DEPOSITS.*

By Professor VIVIAN B. LEWES, F.C.S., F.I.C., Associate.

Two years ago I had the honour of reading a paper before this Society on "Boiler Incrustations," in which I traced the formation of the scale, and the causes which led to the precipitation and hardening of the calcic sulphate, calcic carbonate, magnesic hydrate, and other compounds which are usually found to be present, and I pointed out that the scales formed by various kinds of water were so characteristic that one could speak with certainty as to the kind of water from which the incrustation had been formed by an analysis of the scale itself. The analyses given below may be looked upon as typical of the incrustations formed by fresh water, brackish water, and sea water respectively in marine boilers:—

Constituents.	River.	Brackish.	Sea.
Calcic carbonate	75·85	43·65	0·97
Calcic sulphate	3·68	34·78	85·53
Magnesic hydrate..	2·56	4·34	3·39
Sodic chloride	0·45	0·56	2·79
Silica	7·66	7·52	1·10
Oxides of iron and alumina .	2·96	3·44	0·32
Organic matter	3·64	1·55	trace
Moisture..	3·20	4·16	5·90
	100·00	100·00	100·00

From this it is evident we may look upon the incrustation from fresh water as consisting of impure calcic carbonate, whilst that from sea-water is impure calcic sulphate, the brackish water from the mouths of rivers yielding, as might be expected, an incrustation in which both these compounds are present in nearly equal quantities.

The importance of these differences in the deposit formed is very great, as it enables the shipowner to arrive at a conclusion as to the treatment that the boilers have received during the voyage, by examination and analysis of the scale which those boilers contained. Taking, for instance, the case of a ship which uses fresh water both for filling and make-up, it is manifest that on her return to port the scale should be very slight and should consist mainly of calcic carbonate; whilst, if the scale exceeds $\frac{1}{16}$th of an inch and shows a preponderance of calcic sulphate, it is manifest that such scale could only have been formed by sea-water, either leaking in from faulty condensers or being deliberately fed into the boilers.

The reception you were kind enough to give that paper, and the frequency with which it has been quoted since, lead me to hope that, in continuing and completing the subject, I shall be performing a not unwelcome task.

So far the deposits taken into consideration have been those formed from the impurities natural to the water itself; but with the introduction of high-pressure steam a new and highly dangerous form of deposit has added to the trouble of the marine engineer.

As early as 1878, the collapse of the furnaces of the boilers of the s.s. *Ban Righ* and a similar misadventure in the screw tug *Ich Dien*, with no apparent cause to bring about the damage, caused some attention to be paid in marine circles to the action which had taken place, and the only clue to be found was that a certain amount of oily deposit had formed on the tops of the furnaces, and experiments made by Mr. Dunlop, of Port Glasgow, led to the conclusion that this oil, which had distilled into the boiler from the lubricants used in the cylinder, was so bad a conductor of heat that its formation on the plates allowed them to get superheated, with the result that they were unable to withstand the pressure of steam existing in the boiler, and in this way brought about the collapse.

Similar cases of collapse became frequent after that date, no less than thirty vessels being disabled from this cause during the last few years.

The first case which came under my notice, in which damage to boilers had arisen from this cause, was the case of a large ocean steamer, and through the kindness of Mr. Milton, Chief Superintendent Engineer of Lloyd's, I was able to obtain samples of deposit from all parts of the boilers, and full particulars of the case.

The steamer was a large one trading between Liverpool and Boston, averaged twelve days on the voyage, and was fitted with ordinary compound engines. She had three double-ended boilers, with three plain furnaces at each end, and three combustion chambers in each boiler. The furnaces were plain in one length and connected at the back end to the tube plates, being flanged up inside the chamber, whilst the front end plate is flanged inwards on to the furnace crowns. The furnace crown was ½-in. plate, and the front bottom plate $\frac{11}{16}$ths, the working pressure being 80 lbs. The boilers are about 5½ years old, and have always been re-filled with fresh water at the end of each run, both at Boston and Liverpool; whilst, as a rule, the waste on the voyage was made up by the use of about 70 tons of fresh water, but during the last voyage sea-water was used for this purpose. Every four hours whilst under steam, 4 lbs. of soda crystals were put in the hot well, making about 2 cwt. during the run, the total capacity of the boilers being about 81 tons. For lubricating purposes about seven pints per day of valvoline were used in the cylinders.

When in port, the boilers were allowed to cool down and the water was run off, and they were swept down with stiff brushes, and were afterwards sluiced out with a hose shortly before being re-filled with fresh water. No trouble occurred with the boilers until five voyages before the final collapse, when some of the furnaces began to creep in; they were stiffened with rings and stays, and on the succeeding voyages the whole of the furnaces got out of shape, one after another. Examination of these boilers clearly showed that they had never been very heavily scaled, as in parts of the boiler where it would have been impossible to get at them to clear them out, no signs of heavy incrustation were to be found, and the

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* Read at the Thirty-second Session of the Institution of Naval Architects, March 19, 1891; the Right Hon. the Earl of Ravensworth, President, in the Chair.

absence of marks of scaling tools also showed that they had never been allowed to get very dirty. On the furnace crowns, where they had collapsed, there was only a slight white scale, not more than $\frac{1}{64}$th of an inch in thickness, whilst on the bottom of the furnaces there was a brown oily deposit $\frac{1}{16}$th of an inch in thickness, which in other parts of the boilers increased to between $\frac{1}{8}$th and $\frac{3}{16}$th of an inch. I obtained from Mr. Milton samples of the thin scale from the top furnaces, and of the deposit from various parts of the boiler, and also specimens of cut-out portions of the boiler plates, Liverpool water, valvoline, and soda crystals put into feed water, and of all these analyses were made.

The boiler plates were as good as the day they were put in, and showed no structural signs of having undergone any change, whilst the analyses of the Liverpool water and the soda crystals used showed that they could have taken no part in the action which had led to collapse.

I.—*Valvoline.*

The valvoline on analysis gave :—

Vegetable and animal oil ..	nil.
Mineral oil	100 per cent
Acids (free)	nil.
Boiling-point	371° C.
Specific gravity	0·889

II.—*Scale from Furnace.*

	From top.	From below.
Calcic sulphate	84·87	59·11
Calcic carbonate	5·90	6·07
Magnesic hydrate . ..	2·83	11·29
Iron, alumina, and silica	2·37	2·85
Organic matter and oil.	3·23	19·54
Moisture	0·80	1·14
Alkalis	nil.	nil.
	100·00	100·00

III.—*Deposit from Tubes.*

	Scale on tubes.	Deposit above scale.
Calcic sulphate	50·92	11·60
Calcic carbonate	4·18	0·82
Magnesic hydrate . ..	14·12	22·21
Iron, alumina, silica, &c.	7·47	9·14
Organic matter and oil.	21·06	50·20
Moisture	1·17	4·23
Alkalis	1·08	1·80
	100·00	100·00

IV.—*Deposit from Bottom of Boiler.*

Calcic sulphate	22·52
Calcic carbonate	nil.
Magnesic hydrate	7·09
Silica, alumina, and iron..	34·85
Organic matter and oil	27·95
Moisture	5·79
Alkalis..	1·80
	100·00

On careful examination of the organic matter and oil present in these deposits, it was found that quite one-half of it was "valvoline," in an unchanged condition, which had collected round small particles of calcic sulphate.

A consideration of these analyses, at first sight, yields no clue as to the cause of the collapse, the scale upon the furnace tops being not only free from oil, but perfectly harmless both in quantity and quality; but, on going more deeply into the question, it is evident that this scale cannot be in the condition in which it was originally formed, as the deposits from both top and bottom of tubes, from the bottom of the furnaces, and from the shell of the boiler, are all rich in oily matter; and it is impossible that, during this deposition, the furnace tops could have escaped whilst all other parts of the boiler became coated with it. Experiments, however, reveal the actions which had been at work and led to the formation of the deposit, and its absence upon the injured portions of the plates.

The pressure at which the boilers were worked was 80 lbs., corresponding to a temperature of 155° C., or 311° F., which is so far below the boiling-point of the valvoline that it was evident that it had not distilled over in the ordinary way, and experiments were made to see if it could be distilled in steam at a lower temperature. A retort containing valvoline was carefully heated over a sand-bath, its temperature being ascertained by a thermometer, and steam was then blown through it, with the result that at 248° F. or 120° C. the steam became "greasy" and the oil commenced to pass over with it.

This experiment is, I think, important, as it shows that in testing the capabilities of a lubricant, the fact that it has a boiling-point well above the temperature of the steam is no guarantee that none of it will find its way into the boiler. Having thus entered the boiler, the minute globules of oil, if in great quantity, coalesce to form an oily scum on the surface of the water, or, if present in smaller quantities, remain as separate drops; but show no tendency to sink, as, their specific gravity being 0·889, they are lighter than the water, and the difference in gravity is probably even greater at the temperature existing in the boiler.

Slowly, however, they come in contact with small particles of calcic sulphate and other solids separating from the water and sticking to them; they gradually coat the particles with a covering of oil, which in time enables the particles to cling together or to the surfaces which they come in contact with. These solid particles of calcic carbonate, calcic sulphate, &c., are heavier than the water, and as the oil becomes more and more loaded with them, a point is reached at which they have the same specific gravity as the water, and then the particles rise and fall with the convection currents which are going on in the water, and stick to any surface with which they come in contact—in this way depositing themselves, not as in common boiler incrustations, where they are chiefly on the upper surfaces, but quite as much on the under sides of the tubes as on the top, their position being regulated by whether they come in contact with the surface whilst descending or ascending.

The deposit so formed is a wonderful non-conductor of heat, and also from its oily surface tends to prevent intimate contact between itself and the water. On the crown of the furnaces this soon leads to over-heating of the plates, and the deposit begins to decompose by the heat, the lower layer in contact with the hot plates giving off various gases which blow the greasy layer, ordinarily only $\frac{1}{64}$th of an inch in thickness, up to a spongy leathery mass often $\frac{1}{8}$th of an inch thick, which, because of its porosity, is an even better non-conductor of heat than before, and the plate becomes heated to redness, and being unable to withstand the pressure of steam, collapses. During the last stages of this over-heating, however, the temperature has risen to such a point that the organic matter, oil, &c., present in the deposit burns away, or, more properly speaking, is distilled off, leaving behind, as an apparently harmless deposit, the solid particles round which it had originally formed.

Such a deposit is much more likely to be produced with boilers containing fresh or distilled water, as the low density of the liquid enables the oily matter to settle more quickly, whilst with a strongly saline solution it is very doubtful if this sinking-point would ever be reached; it is evident also that when oil has found its way into the boiler and is causing a greasy scum on the surface, the most fatal thing that can be done is to blow off the boilers without first using the scum cocks, because as the water sinks so the scum clings to the tops of the furnaces and other surfaces with which it comes in contact, and on again filling up with fresh water, it still remains there, causing rapid collapse.

A very remarkable instance of this is to be found in the case of a large vessel in the Eastern trade, in the boilers of which an oil scum had formed. The ship having to stop some days at Gibraltar, the engineer took the opportunity of blowing out his boilers, and refilling with fresh water, with the result that, before he had been ten hours under steam, the whole of the furnaces had come in.

Under some conditions the oil-coated particles coalesce and form a sort of floating pancake, which, sinking, forms a patch on the crown of the furnaces at one particular spot, and under these conditions the general result is the formation af a "pocket."

A curious fact which is worthy of attention is that in most of these oily deposits copper is to be found in considerable quantity. In an analysis of deposit from the furnace of a vessel in which a "pocket" had formed from the above mentioned cause, the scale showed, as in the case already cited, no reasonable cause for the injury at the damaged part of the boiler, whilst the deposit from the under side of the furnace tubes showed clearly the presence of large quantities of oil matters, which were partly combined with copper:—

Constituents.	Scale.	Deposit.
Calcic sulphate	90·354	1·02
Calcic carbonate	1·200	nil:
Ferric oxide	3·200	56·90
Oxide of alumina		2·30
Oxide of copper	nil.	1·90
Magnesic hydrate	2·821	1·80
Organic matter	1·600	10·46
Oil		17·84
Sand, &c.	0·825	7·78
	100·000	100·00

It is a fact that even mineral oils have a considerable solvent action upon copper and its alloys, and it is evident that the copper in the oily deposits have been obtained from the fittings of cylinder and condenser. Fortunately this copper is so well protected by oil that in most cases it is extremely unlikely to come in contact with, and deposit on, the metal of the boiler; but if it did, very serious galvanic mischief would be the result.

The next point I attempted to determine was the effect which these oily deposits had in allowing excessive heating of the plates to take place and retarding the heating of the water. A clean iron vessel was taken, and a known volume of water placed in it, and heated by a carefully regulated Bunsen flame, the water being raised to the boiling-point in ten minutes; this experiment was repeated a second time with the same result, and the vessel was then lined with a coating of deposit found in the bottom of the boilers which had collapsed, and rendered binding by admixture with a small trace more valvoline. This coating was laid on $\frac{1}{16}$th of an inch in thickness, and the former experiment repeated, the same flame being used and the same volume of water taken, with the result that it took fifteen minutes before the boiling-point was reached, showing that, even if no damage resulted to the plates from over-heating, such a deposit would cause a large increase in the fuel used.

In attempting to ascertain to what extent extra heating of the plate took place from this cause, I employed a series of substances of known igniting and melting-point, raised the water in the various vessels to the boiling-point, and then brought the clean bottom of the vessel in quick contact with the test substance, and took the results as indicating the temperature of the exterior of the plates

Clean vessel—	
Sulphur did not melt	below 115° C.=239° F.
Coated vessel—	
Sulphur melted but did not in flame	above 115° C.=239° F. below 250° C.=482° F.
Gun-cotton ignited	above 200° C.=392° F.

So that the $\frac{1}{16}$th of deposit caused with a slow heat a rise in temperature of the plate from under 115° C. or 239° F. to over 200° C. or 392° F. It is manifest, however, that the fiercer the heat the more marked will this over-heating become, and in the next series of experiments the Bunsen flame was replaced by an atmospheric blowpipe, and the temperature attained, tested in the same way as before.

Clean vessel—	
Sulphur did not melt.. ..	below 115° C.=239° F.
Coated vessel—	
Gun-cotton ignites	above 200° C.=392° F.
Tin melts	,, 228° C.=444·4° F.
Sulphur ignites	,, 250° C.=482° F.
Lead melts	,, 334° C.=633° F.
Zinc melts (just)	,, 423° C.=793·4° F.

Whilst, on replacing the atmospheric burner by an oxy-coal gas flame, I found no difficulty in fusing a hole in the bottom of the vessel, which was made of thin wrought iron plate, showing that a temperature of 1500° C.=2732° F. had been attained, and it is therefore manifest, that, with the fierce heat existing in the boiler furnaces, given an oily deposit only $\frac{1}{16}$th of an inch in thickness, the plates will readily be heated to a temperature at which they are totally unable to withstand a pressure of 80 lbs. of steam, and collapse of the furnace crowns must follow.

The great points to be sought in a good lubricating oil are that it shall be a pure mineral oil, and that its boiling-point shall be well above any temperature likely to be attained in the cylinder. Oils satisfying these requirements can readily be obtained, but users of lubricants must remember that, in order to obtain them free from any constituents of dangerously low boiling-point, expensive processes have to be resorted to, which must of necessity increase the price of the oil, and that it is useless to expect to obtain a really good lubricant at a low figure.

The great advantages of a good mineral oil cannot be too strongly insisted on, and any lubricant containing animal or vegetable oils to give it body should be unhesitatingly discarded.

The mineral oils are not fats, but hydrocarbons—compounds of carbon and hydrogen—and the portions used for lubricants are those left after the more volatile constituents have been distilled off, and they differ widely from animal and vegetable oils, which contain so-called fatty acids, which are liberated from them by the action of superheated steam, and these acids attack iron, copper, and copper alloys with the greatest readiness, forming metallic soaps, which are compounds of the fatty acids with the oxides of the metals, and so cause serious damage to both boilers and fittings.

The animal and vegetable oils, in contact with air, especially when heated, take up oxygen, and become gummy and resinous, and gradually so stiff that frequent cleaning becomes necessary—a trouble entirely avoided with mineral oils.

In dealing with the prevention of such deposits, it seems to me that the most feasible plan is to pass the feed water through a long tube filled with clean coke in pieces the size of walnuts, which would act as a scrubber, and would free the greasy water from the traces of oil, and prevent their going forward to the boiler.

I have already pointed out that the collapse of furnaces from the presence of oily deposits almost invariably takes place in boilers fed with fresh water, and that oil, when it goes into the boiler, floats, because it is specifically lighter than water, until solid particles of calcium compounds coming in contact with it and imbedding themselves in it so increase its weight, that reaching the same density as the water, it commences to circulate with the convection currents in the water, and is so drawn down, and attaches itself to tubes and furnace crowns, causing, eventually, damage.

In the case of a transatlantic liner using fresh water only, it takes at least four days' hard steaming to bring the density up to $\frac{1}{32}$nd, whilst if sea water had been used the density would have started at this and would never, after the first few days, have been much below $\frac{2}{32}$nds, and the oil would have remained as a scum, and would never have reached the furnace crowns.

In my last paper on boiler incrustations I pointed out that it was quite possible to prepare sea water in such a way as to practically prevent any serious deposit forming from it, and the same process would prevent the trouble I have now been describing to you.

In the summer of last year Mr. Biles, who is always to the front when he thinks there is a chance of improving marine engineering, kindly gave me the opportunity of trying the effect of prepared sea water upon a crane boiler at the Naval Construction Works, at Southampton, and, after a few preliminary experiments to determine the best form in which to work the "precipitator," the boiler was worked continuously for a month with water drawn from the Itchen half-an-hour before high tide, at which period analysis showed that the water was to all intents and purposes sea water, plus a fair amount of suspended mud; this, after preparation in the "precipitator," was fed into the boiler, and on opening it in the presence of Mr. Milton, Mr. W. H. Riley, R.N., Mr. Biles, Mr. Gearing, and Mr. Dusantoy, it was found perfectly clean, the surfaces looking as if they had been given the thinnest possible coat of whitewash.

The process employed was to add to the sea water a known quantity of precipitator powder, consisting chiefly of soda-ash; and, having done this in a closed vessel, to heat the mixture by blowing into it waste steam, until a pressure of from 5 to 10 lbs. was created, and under these circumstances practically all the magnesium and calcium salts separate from the water and are easily got rid of by filtering it under pressure into the hot well.

I had proposed in the first case to heat the liquid by blowing the steam through a coil in the precipitator, but practical experiments soon showed that the heating surface was not nearly enough, and so the waste steam was simply blown in, allowance being made in the precipitator for the water due to the condensation.

I also found it aided the reaction to heat the water first just to boiling-point before adding the precipitator power, as under these circumstances the deposit settled more quickly and threw less strain upon the filters.

The precipitator was 6 ft. 4 in. high and 3 ft. in diameter, and held a ton of water, and the time taken from the first running the sea water in to its delivery into the hot well was 1 hour 15 minutes, so that in practice, giving plenty of time between the makes, it would be perfectly easy to prepare 8 to 12 tons in the 24 hours with a small precipitator of the size used.

The prepared water has a density of $\frac{1}{32}$nd, and may with safety be evaporated until its density is $\frac{5}{32}$nds, the salts present not crystallising out until a density of from $\frac{6}{32}$nds to $\frac{7}{32}$nds is reached.

Professor Doremus, of the College of the City of New York, proposes to use sodic fluoride as a precipitant for the scale-forming constituents of sea water, as a smaller weight is required, and the action is more rapid and more perfect.

The great objection has up to the present time been its cost, but I am informed that this has now been so far reduced as to bring it within the scope of extended commercial use; and, should it be used on a larger scale, the price could be readily brought much lower.

Professor Doremus claims that the precipitation of the calcium and magnesium salts takes place with very great rapidity, that the sediment shows no tendency to cake or adhere to the sides of a hot vessel, and that it is less bulky than the precipitate formed by soda-ash.

In preparing sea water in the way I have proposed, every precaution must be taken to add slightly less of the precipitant than is necessary to entirely throw down the calcium and magnesium salts, as it is manifestly impossible in practice to guard against small quantities of sea water finding their way into the boiler either from leaky condensers or else being fed in by the engineer during some emergency, and, if under these conditions any excess of the precipitant were present in the boiler, a bulky precipitate would be thrown down and cause trouble, although it would not bind into a solid scale.

There is no doubt that, if Professor Doremus can so reduce the price of sodic fluoride as to enable it to be used for this purpose, it would be of great use, as the fluoride undoubtedly completes its action on the salts of magnesium and calcium more rapidly and thoroughly than the soda-ash, and it would be easier therefore to so regulate the quantity added as to remove, say, five-sixths of the injurious constituents from the sea water without allowing any precipitant to enter the boiler.

In conclusion, I will briefly recapitulate the means which seem to me best adapted for preventing the formation of the dangerous organic and oily deposits I have considered in this paper, and these are:—

I.—Filtration of condenser water through a coke column.

II.—Free use of the scum cocks.

III.—The use of water of considerable density rather than of fresh water.

IV.—The use of pure mineral oil lubricants in the smallest possible quantity.

THE PRECIPITATION OF MANGANESE AS AMMONIUM MANGANOUS PHOSPHATE.*

By ALEXANDER G. McKENNA.

In the determination of manganese in iron ores, it is customary to precipitate the manganese as dioxide, after separation from the sesquioxides by the basic acetate process, by adding bromine to the filtrate from the acetic acid precipitation. The manganese thus thrown down may be ignited and weighed as manganese proto-sesquioxide, but the results are inaccurate from two causes. Manganese dioxide when precipitated in the presence of sodium or potassium salts always carries down with it some alkali, which appears to be chemically combined with the manganese, since it cannot be removed by the most prolonged washing with water.†

This source of error can be avoided by using ammonium acetate in the basic separation, but in this case the solution must be made alkaline before manganese can be precipitated by bromine, and the separation from calcium is then rendered less sharp.

Another objection to the determination of manganese based on the ignition of the precipitated dioxide is the uncertainty of the resulting oxide, which is generally assumed to be Mn_3O_4. Pickering‡ has shown that the percentage of manganese in this oxide varied between 69·69 per cent and 75 per cent, according to the temperature of ignition and other causes.

It is now customary to re-dissolve the manganese dioxide in hydrochloric acid, and then precipitate it as ammonium manganous phosphate. The precipitate is ignited and weighed as manganese pyrophosphate. This method of determining manganese, which we owe to

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* From the *Technology Quarterly*, Vol. iii., No. 4, November, 1890.

† See Wright and Menke on Manganese Dioxide, in the *Journal of the Chemical Society* for 1880, p. 23.

‡ Chemical News, vol. xliii., p. 226.

Dr. Wolcott Gibbs, is now generally admitted to be the most accurate as well as the most easily performed of all the methods of determining manganese. It has been variously modified by many chemists, but none of these modifications seem to possess any advantages over the original process as given by Dr. Gibbs.

The following work was undertaken at the suggestion of Dr. T. M. Drown, to determine if some of the proposed changes in the details of the process were of any advantage in simplifying the method or enhancing its accuracy.

Two solutions of manganous chloride were prepared, and measured portions were taken for precipitation. In the first method, Gibbs's original directions were followed.* The precipitation was made in a platinum dish, by adding a solution of sodium hydrogen phosphate in excess. The white precipitate which formed was dissolved in hydrochloric acid, the solution heated to boiling, and ammonia added in excess. The solution was now boiled for ten minutes and allowed to stand near the boiling-point for one hour. It was filtered hot, and washed with hot water.

In the second method, Blair's† directions were followed. The solution was made acid with hydrochloric acid, an excess of sodium hydrogen phosphate added, the solution brought to boiling in a platinum dish, and ammonia added drop by drop, with constant stirring, until further addition of a drop of ammonia made no change in the silky character of the precipitate; a dozen drops more of ammonia were added, and after boiling a minute longer the solution was cooled in ice water before filtering. The wash water used was made by dissolving 10 grms. of ammonium nitrate in 100 c.c. of slightly ammoniacal water.

The chief object in view in the third method was to discover if there is any valid objection to making the precipitation in glass, and also to determine the length of time required for complete precipitation. To the solution of manganese salt in a beaker, hydrochloric acid and sodium-hydrogen phosphate were added. The solution was heated to boiling, and 20 c.c. ammonia water added. The boiling was continued three minutes, with constant stirring, which is absolutely necessary to prevent bumping. The wash water used was made by adding one volume of ammonia (sp. gr. 0·96) to three volumes of water. Following are the results obtained in this series of analyses:—

Comparison of Results Obtained by the Three Methods.

	Gibbs's original method. Grms.	Blair's method. Grms.	Precipitation in glass and washing with ammonia water. Grms.
Weight of manganese pyrophosphate obtained, first solution	0·4990 0·4996	0·4997 0·4992	0·4994 0·5007
Do., second solution..	0·0897	0·0896	0·0894

Three more determinations were made by precipitation in glass, but the precipitates did not become crystalline in three minutes, and the washings were turbid.

The manganese precipitates after ignition were examined for silica, but none was found.

This set of experiments seems to show that essentially the same results are obtained by following either Gibbs's or Blair's directions; also that glass is not attacked by the solution in three minutes' boiling, but that this time is not always sufficient to ensure the complete conversion of the precipitate to the crystalline form which is necessary before filtration.

Another series of experiments was made in the same manner, but with a different amount of manganese.

Second Series of Results.

	Gibbs's method. Grms.	Blair's method. Grms.	In glass, as before. Grms.
Weight of manganese pyrophosphate obtained	0·2415	0·2432	0·2412
	0·2427	0·2432	0·2427
	0·2408	0·2385	0·2425
	0·2432	—*	0·2387*
	0·2355*	—*	

* Not crystalline.

These results confirm those in the first series, and indicate the necessity of having the precipitate thoroughly crystalline.

The amount of manganese in the filtrates and washings of each set of these experiments was determined (except in those cases where the precipitate was not crystalline) with the following results. The total volume of the filtrate and washings was in each case about 300 c.c.

Solubility of the Precipitate.

	Gibbs's method. Washed with water. Average grm.	Blair's method. Washed with dilute ammonium nitrate. Average grm.	In glass. Washed with dilute ammonia. Average grm.
Filtrate contained metallic manganese	0·0005	0·0004	—
Washings contained metallic manganese ..	0·0005	0·0012	0·0003

In order to determine the relative values of the three wash waters under precisely the same conditions, about three times the usual amount of manganese was precipitated by Gibbs's method, and the precipitate was divided into approximately equal parts by pouring alternately on three filters. The precipitate in each filter was washed thirty times, 7 c.c. of wash water being used each time.

The following results were obtained in two experiments.—

Solubility of Precipitate. Second Series.

	In hot water. Grm.	In ammonia (1 : 4). Grm.	In ammonium nitrate. Grm.
Washings contained metallic manganese	0·0012 0·0018	0·0019 0·0016	0·0024 0·0014

These results show that, if there is any preference, it is in favour of hot water.

On washing with ammonia water, the precipitate is changed in colour to a dark gold, which change does not occur with either of the other wash waters.

Another set of nine determinations was made in glass by boiling the solution, with constant stirring, for eight minutes, or until the precipitate seen through the walls of the beaker had a peculiar silky appearance, resembling that of mercurous chloride when precipitated from a mercuric salt by stannous chloride. The precipitate was washed with hot water.

Results of Precipitation in a Beaker and Washing with Hot Water.

	Grm.	Grm.	Grm.
Weight of manganese pyrophosphate obtained	0·2450	0·2445	0·2450
	0·2445	0·2443	0·2445
	0·2440	0·2443	0·2442

No silica could be found in any of the precipitates after ignition.

In one experiment iron was present in small amount with the manganese. The precipitated phosphate had a beautiful gold colour, and on being washed with dilute ammonia dissolved gradually in the wash water, giving a brown coloured filtrate. Continued washings showed no diminution in the amount dissolved. On standing ex

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* *Am. Jour. Sci.*, [II.], vol. xliv., 216.
† "The Chemical Analysis of Iron," p. 93.

posed to the air for several hours, a brown precipitate settled out from the wash water. This would seem to indicate the formation of some double salt of manganese and iron, which is soluble in ammonia when an excess of an alkaline phosphate is not present.

(Since the above was written, there has appeared in the *School of Mines Quarterly*, Vol. xi., No. 4, a paper on the same subject, by Mr. R. C. Boyd, which confirms, in general, the results given above).

NOTICES OF BOOKS.

The Evolution of the Elements: a Sketch of a Biogenetic Foundation for Chemistry and Physics. (Die Entwickelung der Elemente: Enturf zu einer biogenetic Grundlage fur Chemie und Physik). By Gustav Wendt. Berlin: Hirschwald.

That elemental evolution—the necessary complement of our accepted interpretations of the phenomena of astrogeny and organogeny—has been for some time "in the air" is almost a truism. The old theory of some seventy odd simple bodies, all supposed primordial, independent and incapable of mutual conversion, fails to satisfy the inquirer. We crave to know how they have arisen; why their number and their mutual relations are as we find them. Attempts have been already made to answer these questions. The evidence in favour of the non-primordial character of the elements has been carefully marshalled. A principle, the survival of the most inert, has been suggested as likely to play a part similar to that of the survival of the fittest in the organic world. The author of the present memoir goes boldly forward. He contends that the chemical elements are not present in all other worlds in the same number as we find them at our feet. It is not by accident that a certain number have met together with us, another, *e.g.*, on Mars, and some few in the nebulæ. Each of the heavenly bodies has a number of elements exactly corresponding to its present stage of development. Or, as he otherwise puts it, the chemical elements are gradually formed during the evolution of the stars and planets. He raises the question whether it might be possible here upon our earth to produce the conditions for several atomic combinations of identical atoms, and thus convert elements into each other. But he does not reply in the affirmative. He suggests that the art of making gold will probably never be learnt, but perhaps some day iodine may be made out of bromine.

Herr Wendt even ventures to construct a genealogical table of the elements, and to fix their possible number. He considers that "the elements in the earth have been formed so that from the seven fundamental elements two series each of seven elements have been gradually evolved, and that further from each of the 3×7 elements a further series is derived."

The fundamental elements are hydrogen, lithium, glucinum, boron, carbon, nitrogen, and oxygen. The next seven elements, fluorine, sodium, magnesium, aluminium, silicon, phosphorus, and sulphur, form a second complete series. Herr Wendt objects to the practice of placing hydrogen alone as a quite exceptional element, and beginning the first series of the elements with lithium. He doubts the propriety of classing it as an electro-negative element. He objects to several of the details of the arrangement of the elements in the periodic system as formulated by Mendeleeff and Meyer. Thus he transfers chrome from the "oxygen" to the iron group, and proposes to fill up the vacancy in the latter group by the insertion of Websky's "idunium." The author protests against the position attributed by Lothar Meyer to copper, *i.e.*, between sodium and silver. From a consideration of its properties he transfers it to the iron group.

The vacancy between sodium and silver he assigns to Dr. Phipson's "actinium," which, hitherto, like idunium, has not been by any means generally recognised.

As regards the possible number of the elements, Herr Wendt pronounces the maximum number, $11 \times 7 + 2 = 79$, the minimum 74, and the mean about 77. Hence, it would seem that he can scarcely accept the resolution of didymium into neodymium and praseodymium, and still less the highly complex (or mixed) character of cerium and others of the rare earths, to which, indeed, he makes no reference. He considers that if the determinations of Grünwald are found trustworthy on further extension this *savant* will have rendered a morphology of the elements possible.

Whilst fully agreeing with the author as regards the genesis of the simple bodies by a process of evolution, we are not able for the present to accept his limitation of their number. This point we should prefer to leave for decision by the *à posteriori* method of spectroscopic and micro-chemical research. Nevertheless, we think that Herr Wendt's work is entitled to the most careful study of every chemist who is really concerned about a truly rational development of his science.

Mixed Metals or Metallic Alloys. By Arthur H. Hiorns, Principal of the School of Metallurgy, Birmingham and Midland Institute. London: Macmillan and Co.

The author begins his work with a historical introduction, a classification of metals, and some remarks on their general properties. We regret having once more to point out an erroneous atomic weight attributed to platinum, viz., 197·4. After a variety of other preliminary matter, mostly of a very useful character, Mr. Hiorns begins the study of alloys with the metallic compounds of copper. Here he remarks that "pure copper has never been cast in considerable quantity so as to produce a good ductile casting free from blowholes." An elaborate account is given of the effect exerted upon copper by the admixture of small quantities of other metals. An extensive table shows the properties of recognised copper-zinc alloys to the number of 144, showing their analytical composition, specific gravity, colour, tenacity, ductility, malleability, hardness, fusibility, and conductivity for heat and electricity. Under the last head many blanks remain to be filled up.

Bronzes are next discussed in a very comprehensive manner, including a table of copper-tin alloys. The proportion of phosphorus in phosphor-bronze must not exceed 4 per cent. A table published by the Phosphor-Bronze Company is appended, with the remark that the absence of the statement of the composition of the alloys robs it of its chief value. Silicon bronze is considered superior to phosphor-bronze in its electric conductivity, and has entirely replaced it for telegraphic purposes. Of the aluminium bronzes, that with 10 per cent of aluminium is considered the best.

As regards the alloys of tin and lead, the author ventures upon the hazardous statement that an alloy containing 18 per cent of lead is quite harmless in vessels for wine and vinegar! The alloys of silver and steel examined by Faraday and Stoddart do not present any practical interest. Mr. Hiorns may be congratulated upon the fact that he has produced the best manual of alloys to be met with in the English language.

Action of Chlorine upon Methylethyl Acetone.—D. Vladesco.—It may be admitted for the present that there are formed by the limited action of chlorine upon methylethyl acetone in the cold, two chlorine derivatives —methyl-α-chlorethylcetone and methyl-α-dichlorethylcetone. These derivatives are capable of giving rise to bodies with multiple functions, alcoholic and ketonic. The author proposes to continue the study of these compounds.—*Berichte der Deutsch. Chem. Gesell.*, v. No. 3.

CORRESPONDENCE.

THE FELLOWSHIP OF LEARNED SOCIETIES.

To the Editor of the Chemical News.

Sir,—I venture to ask that you will allow me to trespass on your space so far as to offer some remarks on a subject that has lately given rise to no little controversy and discussion among the Fellows of at least two leading scientific Societies, viz., the Chemical and the Linnean.

To readers of the Chemical News it is of course well known that it has, for many months past, been a subject of complaint among the Fellows of the Chemical Society that improper persons have obtained admission who have no real interest at all in science, no qualifications entitling them to the honour of Fellowship, and whose only object in joining was to obtain the powers of writing F.C.S. after their names, thereby stamping themselves among the lay world as qualified chemists; and furthermore—*turpissime dictu!*—using this assumed qualification for trading purposes. We all know that this feeling has given rise to some agitation among the Fellows, and has brought on a mild epidemic of blackballing at the ballots.

At the annual meeting Dr. Russell referred, at considerable length, to this controversy; and in a speech that, as all must admit, abounded in good feeling and conciliatory spirit, expressed his views to this effect: that the Fellowship of the Chemical Society was not, neither was it intended to be, any mark whatever of qualification; that the Institute of Chemistry was open to all who wished to obtain a diploma stamping them as competent chemists, whilst the F.C.S. signified nothing at all; that so far from being exclusive or insisting on evidence of qualification he would wish to see the Society open to all—including even mere amateurs—who might be desirous of joining, always provided that candidates were personally unimpeachable, and were not joining for the sake of obtaining an F.C.S. to be used for trade purposes. In a word, Dr. Russell—as I understand him—would make the F.C.S. as meaningless and valueless as any evidence of chemical knowledge as would be the "Fellowship" of, for instance, the Society of Arts.

Before discussing this position let me refer to the Linnean Society. Here, too, a somewhat similar complaint has been made, viz., that certain persons have obtained the Fellowship simply with the intention of advertising themselves as F.L.S. for trade purposes. It was proposed at a recent meeting of the Linnean Society to limit the number of Fellows annually elected to 30, with the object of electing only the most fit and proper persons. This proposition (which was thrown out) gave rise to a somewhat warm discussion; on the one hand it was contended—just as by Dr. Russell—that the Fellowship was in no sense a diploma, or had no academic value; that the Royal Society existed for the purpose of honouring scientific workers, and that it was very undesirable for any other Society to erect itself into a quasi degree-granting body; let the Fellowship be open to all persons who wished to join, provided always that they were personally unobjectionable. On the other hand, it was contended, *inter alia*, that the Fellowship of the Linnean *was* an honour, and should not be lightly lavished.

Having thus stated the quarrel may I—without incurring the charge of presumption—venture to express a criticism? I cannot agree with Dr. Russell and others that the Fellowship of such Societies as the Chemical and the Linnean is not an honour or qualification. I cannot admit that—always if merited—it is other than an honour; and it seems to me that it should be so granted as to mark a man as possessing a *competent knowledge* of chemistry or biology, respectively. That it should possess any of the rigid precision of a London degree I do not for a moment contend, but simply that it should be given only to those who can show that they have earnestly studied and acquired a thorough grounding in the branch of science concerned. Neither can I follow Dr. Russell's argument that the existence of the Institute of Chemistry precludes the Chemical Society from giving any status by granting its Fellowship; and this, for two reasons: firstly because the Institute of Chemistry, which was founded in order to give every competently trained chemist an opportunity of stamping himself with its diploma, has persistently stultified itself by resolutely refusing even to inquire into a candidate's knowledge unless he have required that knowledge in one particular way; and secondly, because there is no such institute of biology, or of geology, or of astronomy; and, I take it, that whatever ruling applies to the Fellowship of the Chemical Society applies equally to that of the sister societies. I conclude, therefore, that the Fellowship of any scientific society confers, and should confer, to a certain extent, a mark of qualification; and if this be denied, and it be contended that the Fellowship is quite meaningless, I would ask what in the name of common sense would be the logic of a man's writing F.C.S., or F.L.S., or F.G.S., &c., after his name? No perfectly sane person would dream of writing himself as a Fellow of the Society of Arts, or of the Numismatic Society, or of the Royal Institution, simply because in all these cases it is perfectly understood that there is no sort, kind, or condition of qualification necessary for election to the "Fellowship"; whereas it has always been understood that no one without competent scientific knowledge can obtain the Fellowship of the scientific societies.

In the next place I fully admit that the other societies should make no attempt to arrogate to themselves the functions of the Royal; the analogy and reference seem to me unfortunate and misleading, since the functions are so very different. The function of the Royal Society is to honour *original research* and *this only*, *not* to signalise merely acquired learning; whereas my contention is that the Fellowship of the other societies should mark simply *competent knowledge*—thorough studentship that is—and most emphatically *not* in any way imply original work. I think this distinction very important, since at the recent meetings of the Chemical and the Linnean several speakers were knocking their heads against this desired or disclaimed analogy to the Royal.

But if the foregoing position be admitted, now comes the difficulty that, it seems to me, might be met by acting on these lines. It is contended that for want of information the societies cannot justly confer their Fellowship in this discriminating way, and also that many students would thus be shut out from the use of the libraries, the Journal, and the meetings of the Societies. Exactly so; and my suggestion is, use your power of electing *associates*: admit them at a lower subscription and without entrance fee; give them the privilege of using the library and attending the meetings, and *emphatically forbid them from writing themselves* A.C.S. or A.L.S., &c. In a word, open the associateship, *without limit*, to all students who wished to avail themselves of the great educational advantages given by membership of these societies, and at the same time prevent them from using their privilege as a qualification. It seems to me that this would, to a very great extent, meet the difficulty under which Fellows at present lie; for in very many cases they must either blackball a candidate, which is not pleasant, or elect as a Fellow one of whose qualifications they are very sceptical. This reformed procedure would irretrievably shut out all those who at present join simply with the intention of using the Fellowship for trade purposes; for these especially are the men who can show no particular evidence of qualification, and who would therefore be required to enter as associates; and it would also meet the case of students who are desirous of using the library and so on, but are not yet sufficiently advanced in their respective studies to be qualified for the Fellowship; and here, I may say, speaking from my own recollections, that I should have highly appreciated the advantages of the associateship at a time when I should not have felt myself justified in applying for Fellowship; but although the charters of the various societies empower them thus to admit associates, the practice seems almost to remain in abeyance. For instance, the Linnean Society have definitely limited the number of Associates to twenty-five.

I wish it to be understood that I entirely disclaim any desire to make this associateship a necessary preliminary to Fellowship; on the contrary, I hold that anyone who can show that he has completely studied his subject should be elected Fellow forthwith, as at present; but whenever his claims are doubtful, let him be elected associate first. Were he a *bonâ fide* student he would accept the associateship as a preliminary step; but if he desired the Fellowship for no other reason than to proclaim himself an F.C.S., &c., he would promptly decline it. This procedure would therefore, as it appears to me, exactly meet the case by shutting out the very persons it is desired to exclude, while entailing no hardship at all on the amateurs whom Dr. Russell, in his generous catholicity, wishes to admit to the privilege of the library, the meetings, and the Journal. I may further point out that the adoption of such a course would be a very great relief to Fellows, who are often asked at present to sign certificates for candidates of whom they know nothing; they must either refuse—which is always unpleasant—or else recommend a man of whose qualification they are completely ignorant. But this difficulty would be met if they offered to recommend him for the associateship; then after a year or two's associateship the new comer, if he attended the meetings, would inevitably become known to some of the Fellows, and when he applied for his Fellowship he would have no difficulty in obtaining the signature of Fellows who did personally know him to be a fit and proper person; while, on the other hand, the unfit would quickly find their level.

I must repeat, however, that it is essential to this reform that the writing of A.C.S., &c., be strictly forbidden. Could the method here suggested be adopted, it seems to me that the difficulty would be overcome, and we might admit that the Fellowship of a scientific society was invariably what—as I contend—it should be, and is now, when deservedly conferred, a mark of qualification and *an honour*. I cannot admit that it is other than an honour, a legitimate source of pride, to be a Fellow of a Society whose roll-call is studded with the names of the leaders of science.—I am, &c.,

F. H. P. C.

P.S.—It is perpetually insisted that the evil now existent might be cured if Fellows would exercise greater care in signing candidate's certificates. Exactly: and if all men were virtuous the world would become comparatively Paradise; but neither consummation is practically probable. But if the distinction between associate and Fellow were prominently brought out, Fellows would certainly become more careful about signing recommendations for Fellowship.

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. cxii., No. 13, March 31, 1891.

New Method for the Detection of Slight Bands among the Band Spectra. Application to the Spectrum of the Hydrocarbons.—H. Deslandres.—(See p. 179).

On the Origin of the Higher Alcohols in Industrial Phlegmas.—L. Lendet.—The author finds confirmations of his hypothesis that the higher alcohols are for the chief part the products of a secondary fermentation, which, in the earlier part of the operations, is overpowered by the normal alcoholic fermentation.

On Vegetable Hematine.—Dr. T. L. Phipson.—The author concludes that the vegetable hematine described by M. Lenossier in the *Comptes Rendus* (March 2, 1891), is identical with the palmalline, of which he gave an account in the *Comptes Rendus* in 1879. He has observed that the *Palmella cruenta*, formerly known as *Chaos sanguinea*, is sometimes entirely green, and becomes of a blood-red when its vegetation is completed. It is probable that palmelline may be found in various other species of plants.

The Use of Liquefied Carbon Dioxide for the Filtration and the Rapid Sterilisation of Organic Liquids. — A. D'Arsonval. — At high pressures carbonic acid becomes an extremely powerful bactericide. If the pressure is prolonged, and the temperature raised to 40°, no living being can resist.

The Simultaneous Development of Oxygen and Carbon Dioxide among the Cactaceæ.—E. Aubert.—The fact that *Cactus opuntia* gave off oxygen in the light was observed at the beginning of the century by Saussure. Mayor, in studying the *Crassulaceæ*, found that they give off oxygen even in an atmosphere devoid of carbonic acid. The author has since found that certain species of *Cactus*, *e.g.*, *Opuntia tomentosa*, give off in the light at 35° both oxygen and carbon dioxide. In the dark oxygen is absorbed and carbon dioxide liberated. With *Mamillaria elephantideus* the reactions are the same.

Justus Liebig's Annalen der Chemie,
Vol. cclv., Part 3.

On Lactonic Acids, Lactones, and Non-saturated Acids.—R. Fittig.—This continuation includes papers by L. Liebmann, on benzaldehyd and pyrotartaric acid; by Gibson Dyson, on salicylaldehyd and succinic acid; by H. C. Brown, on salicylaldehyd and pyrotartaric acid; and by Johannes Politis, on anisaldehyd and succinic acid.

On Trinitroazoxy- and Trinitroazo-benzoles.—H. Klinger and J. Zuurdeeg.—This memoir does not admit of useful abridgment.

Communications from the Chemical Institution at Marburg.—These include a paper by Th. Zincke and C. Campbell on azimido-compounds, and a memoir by Th. Zincke and Th. Cooksey on tetrachlor-α-diketo-hydronaphthaline and its fusion products, ortho-trichloracrylbenzoic acid and phthalylchloracetic acid.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. v., No. 3.

On the Benzene Hexachlorides.—C. Friedel.—Thi paper requires the accompanying figures.

On Phenanthridine.—Amé Pictet and H. J. Ankersmit. — Phenanthridine appears in the form of long crystals, fusible at 104°. Its properties greatly resemble those of acridine. Its odour is pungent and occasions sneezing. Its salts are yellow, and their aqueous solution has a fine blue fluorescence.

Detection and Determination of very Small Proportions of Aluminium in Iron and Steel.—Adolphe Carnot.—Already inserted.

Action of Soluble Fluorides upon Diastase.—Dr. J. Effront.—Hydrofluoric acid and the fluorides exert a favourable action upon saccharification, not because they act directly upon diastase, but because they destroy the lactic and butyric ferments.

Preparation of Crystalline Calcium and Barium Fluorides.—H. Moissan.—The former salt is obtained by adding a solution of calcium chloride at $\frac{1}{100}$th to a boiling solution of potassium fluoride at $\frac{1}{200}$th. The ebullition is kept up for half-an-hour in the platinum capsule; the product is washed with abundance of water, dried in the stove, and calcined at dull redness. The barium salt is obtained by pouring a solution of 18 grms. barium chloride in 500 c.c. of water into a boiling solution of potassium fluoride at $\frac{1}{100}$th.

Researches on the Atomic Weight of Fluorine.—Henri Moissan.—The author concludes from three series of determinations that the atomic weight of fluorine is very close upon 19, probably 19·05. The determinations have been made by means of the sodium and the calcium fluorides.

Study of the Fluor-Spar of Quincié.—Henri Becquerel and Henri Moissan.—This fluor-spar contains an occluded gas. All the reactions of the mineral may be explained by the presence of a small quantity of free fluorine in the occluded gases.

New General Method for Iodising Bodies of the Aromatic Series.—M. Istrati.—The author heats the body to be iodised with iodine and sulphuric acid in a flask fitted with an ascending condenser, so as not to lose any volatile products. The author, in a series of papers, applies this method to various aromatic bodies.

Action of Iodine in Presence of Sulphuric Acid upon Calcium Phenylsulphonate.—MM. Istrati and Georgesco.

Action of Chlorine upon Benzene in Presence of Sulphuric Acid.—MM. Istrati and Petricon.

On Pentrachlorphenyl Iodide.—M. Istrati.—These three memoirs describe in detail applications of the method proposed by M. Istrati.

New Method for the Preparation of the Non-Saturated Acids of the Aromatic Series.—L. Edeleano.—In a former number of this journal (*Bull. de la Soc. Chim. de Paris*, vol. iii., p. 191), the author described a method for the preparation of cinnamic acid, and he now proceeds to show its general applicability.

New Data relating to the Action of Sulphur Chloride upon Aniline.—L. Edeleano.—The author observes that the products obtained vary not merely with temperature but with the nature of the solvents employed. He obtains a compound, $S(C_6H_4 \cdot NH_2)_2$, and a resinous matter, the nature of which has not yet been studied.

Series 3, Vol. v., No. 4.

A New Method of Formation of the Derivatives of Indazol.—Otto Witt, E. Noelting, and E. Grandmougin.—This very extensive paper contains an account of nitro-indazol, its methyl-ether, its acetylic derivative, its bromation, oxidation, and reduction. The last operation yields amido-indazol, the salts of which are next described. The memoir concludes with researches on the constitution of indazol.

Studies on the Derivatives of the Toluquindeines and the Xyloquindeines.—E. Noelting and E. Trautmann.—A very lengthy treatise incapable of useful abstraction.

On the Addition of Sulphuric Acid to Wine.—M. A. Villiers.—The author, by occasion of a circular sent out by the Minister of Justice to all the "procureurs generaux," seems too disposed to defend "plastering." He admits, however, that plastering in any case introduces into wine a proportion of potassa more considerable than that which ought to be present, and augments the weight of the extractive matters. It also increases the acidity of the wine.

On the Composition of Commercial Calcium Biphosphate in its Different Forms, and the Preparation of Crystalline Biphosphate.—G. Pointet.—The biphosphate occurs in two forms, the syrupy and the crystalline. Neither of them contains a product corresponding exactly to the formula $CaH_4(PO_4)_2$. The composition of the syrupy biphosphate is by no means uniform.

This number contains very complete biographies of G. Chancel and Eugene M. Peligot.

Journal fur Praktische Chemie.
New Series, Vol. xlii., Part 1.

On the Origin of Kyanalkines.—R. Schwaize.—This paper is a continuation of the series on the polymerisation of the nitrites. The origin of the kyanalkines from the nitrites and the sodium alcoholates depends on the nature of both these classes of bodies. Only primary alkylcyanides are capable of such a polymerisation. The reaction proceeds most favourably when the alcoholate employed contains the same alkyl, as the nitril phenolates are incapable of affecting the conversion of the cyanethyls and of the other cyanides into kyanalkines.

Remarks on the Memoir of Goldschmidt and Meissler on "Experiments for the Determination of the Constitution of Tautomerous Compounds."—Arthur Michael.—The author considers that the present task of chemistry, in view of the phenomena of Desmotropy, is to ascertain under what conditions one or the other constitution of a desmotropic body is stable, as well as the constitutional changes which such a body undergoes on the replacement of an atom of hydrogen by other atoms or radicles.

Researches from the Laboratory of the University of Freiburg.—These comprise a memoir by Ad. Claus on the constitution of naphthaline, and a paper by C. Willgerodt on the stages of reduction of the nitro-group on the reduction of nitro-azo compounds with alcoholic ammonium sulphide.

Eukairite from Argentinia.—J. Fromme.—The mineral in question contains: silver 42·71 per cent, copper 25·47, selenium 31·53; and consequently differs but little from the specimens obtained from Skrikerum in Smaland, as analysed by Berzelius and Nordonskiöld. It does not contain the trace of thallium found by the last-named chemist.

On the Stereo-chemistry of Isomeric Nitrogen Compounds.—C. Willgerodt.—A controversial paper in reply to the remarks of Hantzsch and Werner.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. v., No. 59.

New Experiments on the Question of the Fixation of Free Nitrogen.—Sir J. B. Lawes and Dr. J. H. Gilbert.—From *Proceedings of the Royal Society*.

Asbestos and its Industrial Applications.—M. Ludzki.—An account of the occurrence, varieties, properties, and industrial applications of asbestos.

Revue Générale des Sciences Pures et Appliquées.
Vol. ii., No. 3, February 15, 1891.

Modern Ideas on Thermometry.—Ch. E. Guillaume.—The author admits that metrology, of which thermometry is a branch, is not a science, but a collection of methods, eminently useful to the sciences of observation. He considers that the expansion of hydrogen furnishes the normal thermometric scale.

No. 4, February 28, 1891.

Chemical Equilibria. Part I. Chemical Mechanics, Experimental Principles.—H. L. Chatelier and G. Mouret.—The authors consider chemistry as consisting of two branches: the one, *chemical architecture*, viewing exclusively bodies of a definite chemical composition, and the other, *chemical mechanics*, discussing the intermediate states through which bodies have to pass before reaching a state of final equilibrium. (The scopes of these two branches might be more intelligible if they were named the morphology and physiology of chemistry).

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.

Joining Grease-proof Paper.—I shall be glad if any reader can inform me what material will join grease-proof paper one piece to another so firmly tbat they cannot be separated.—J. S.

MEETINGS FOR THE WEEK.

Monday, 20th.—Medical, 8.30.
—— Society of Arts, 8. "The Decorative Treatment of Natural Foliage," by Hugh Stannus, F.R.I.B.A.
—— Society of Chemical Industry, 8. "Stoneware and its Application to Chemical Apparatus," by W. P. Rix. "Tanning by Electricity," by Dr. S. Rideal and Mr. A. S. Trotter.
Tuesday, 21st.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Royal Institution, 3. "The Geography of Africa," by J. Scott Keltie, F.R.G.S.
—— Society of Arts, 4.30 "China," by Sir Thomas Wade.
Wednesday, 22nd.—Geological, 8.
—— Society of Arts, 8. "Bimetallism," by Sir Guildford Molesworth.
Thursday, 23rd.—Royal, 4.30.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "Recent Spectroscopic Investigations," by Prof. Dewar, M.A., F.R.S.
Friday, 24th.—Physical, 9. "Euphuism—past and present," by The Rev. Canon Ainger.
Saturday, 25th.—Royal Institution, 3. "The Dynamo," by Prof. Silvanus P. Thompson, D.Sc., B.A.

TO CORRESPONDENTS.

E. E. H. Thorne.—*Journal of Analytical and Applied Chemistry*, published by E. Hart, Ph.D., Easton, Pa., U.S.A. Price, 3 dols. per annum.

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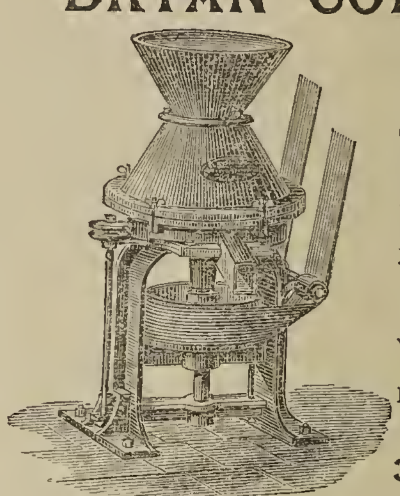

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THE CHEMICAL NEWS.

Vol. LXIII., No. 1639.

A COMPARISON OF THE METHODS FOR THE ESTIMATION OF MILK-SUGAR.

By J. KNOWLES, F.C.S., and J. ARTHUR WILSON.

The estimation of milk-sugar is, in practice, only required in the analysis of milk and milk products, especially in condensed milks, which latter may also contain cane-sugar, and it is with these this paper deals.

The physical method by the polarimeter has not received sufficient attention it undoubtedly deserves, most chemists relying for the determination on the reduction of metallic solution. It is well known that tables have been constructed for the calculation of the chief constituents of milk (proteids, sugar fat) from the total solids and specific gravity, which are said to agree well with the figures got by direct analysis. We may remark, *passim*, that this is or is not the case according to the method employed, especially as regards milk-sugar, although, for instance, the fat determinations calculated come very close to those by the Adams process, which may be regarded as our best method up to the present, and perhaps showing the actual fat contained in milk.

We have compared the following methods for the estimation of milk-sugar on the same samples of milk which were of a poor quality and high in sugar.

1. Estimation by Fehling, weighing as CuO.
2. ,, ,, Pavy Fehling, by simple dilution.
3. ,, ,, Pavy Fehling, after separation of casein.
4. ,, ,, the optical process.

We shall first describe how the experiments were conducted, and then give a table showing the differences between the processes.

Method 1.—It has been shown over and over again that to attempt to estimate milk-sugar in strongly alkaline solution is inaccurate, on account of the destructive action of alkali on milk-sugar; we have therefore taken this into account. 10 c.c. of milk is diluted and faintly acidified by acetic acid, and diluted to 100 c.c. at 60° F. 25 c.c. of the filtered solution is raised to a boil and filtered at once, the filter washed thoroughly till the filtrate measures 100—110 c.c. This is just neutralised and heated to boil, when there is added a slight but decided excess of boiling Fehling solution; boil three to four minutes. Filter, wash by decantation, and on filter dry, ignite, and weigh as CuO. We would mention that collecting the precipitate on asbestos and reduction in hydrogen gives the same results as direct ignition, but direct weighing as Cu_2O invariably gives too low results. Lastly, the reducing power of milk-sugar has been taken as $7CuO = 1$ mol. lactose.

Method 2.—In this process 10 c.c. of milk was diluted to 100 c.c., and poured into an accurate burette, with a long spit, and connected to the flask containing Pavy Fehling solution, which was briskly boiling. A preliminary test was always made, so that after boiling briskly the main bulk of milk was added, and the process finished by drops. We have not adopted the method of working in a current of gas, because we are satisfied that the above process gives the same results if properly carried out. As standard we have taken that 40 c.c. Pavy Fehling is equal to 0·02 glucose, and that 52 of the latter equal 100 of lactose.

Method 3.—This, as regards manipulation, was carried out as before. In the preparation of the milk-sugar solution 10 c.c. of milk was first acidified by acetic acid and diluted to 100, and the determination made on the filtrate. It will be noticed in all these determinations we have preferred *measured* quantities of milk for the sake of convenience. It has been urged that this is inaccurate, but we find this is not so if the milk be allowed to stand to get rid of air bubbles. The specific gravity was taken by the Westphal balance, and not till at least 24 hours had elapsed.

Method 4.—We shall describe our method of working this process minutely, because it is the one on which we are inclined to place the most reliance. In our first experiments we employed the usual method of precipitation by basic lead acetate on about 70 grms. of milk; subsequently we modified this in order to reduce the errors, and we think with some success. In the first place it is necessary to be sure that the scale of the polarimeter lying between three and seven angular degrees is correct. This can be done by means of standard solutions of pure sucrose, or still better, by the control tube of Schmidt and Haensch.

The following table assumes the normal weight of sugar for the instrument to be 26·048 grms., the weights of chemically pure sugar and the rotation are in divisions.

Division of polarimeter.	Weight per 100 c.c. of CP. sugar.
3	0·779
4	1·039
5	1·298
6	1·558
7	1·817
8	2·078
9	2·337
10	2·597
11	2·857
12	3·117
13	3·376
14	3·637
15	3·896
16	4·156
17	4·416
18	4·676
19	4·936
20	5·196

If other instrument be used, the weight corresponding to these angular degrees must be calculated. We employed, as previously stated in the first trials, the old process of precipitating by basic lead acetate on about 70 grms. of milk as follows:—About 70 c.c. of milk is weighed or measured, and 5 c.c. of basic lead acetate added (1—2), agitated thoroughly, and diluted exactly to 100 c.c. The observation was then taken at about 60° F. in a 200 m.m. tube, using an instrument of the Laurent type. The specific rotation of lactose was taken at 52·5 for the D line. The results from this process are signified in the table as A, in terms of anhydrous milk-sugar in 100 grms. of milk. The results under B were obtained by the following modified method.

50 c.c. of milk is placed in a flask, having a mark on the neck at 57 c.c., 2½ c.c. of basic lead acetate added, then 1 c.c. of mercuric nitrate, then agitate well and dilute to 57 c.c. mark. The observation is then taken in a 220 m.m. tube, which need not be provided with a vertical tube and thermometer.

The extra 2 c.c. is for the space occupied by albuminous precipitate formed by the lead acetate and mercuric nitrate. The results are calculated as anhydrous sugar in 100 grms. of milk, adopting as before the No. 52·5 as the specific rotation for the D line.

Table showing the Results given by Different Methods of Analysis.

	Fehling, gravimetric	Pavy Fehling, simple dilution.	Pavy Fehling, after separation of casein.	Optical A.	Method B.
1		4·45	4·49	4·78	4·69
2	4·63	4·71	4·78	5·03	4·92
3	4·76	4·82	—	5·17	5·10

It will be seen that the results are somewhat lower, which I attribute to the more perfect precipitation of the albumenoid, and also to the less error incurred by using 50 grms. of milk without dilution.

It will be seen that there is considerable difference between the methods, the differences between gravimetric and optical method being about 0·30 per cent, whilst there is a fairly close agreement between gravimetric and volumetric method by Pavy Fehling. The latter method is the very rapid one, and accurate if properly carried out. We have not examined the process of Ritthausen by separation of fat and casein by copper sulphate and alkali, believing that it will give no better results than separation by acetic acid and boiling. In the analysis of condensed milks sweetened by cane-sugar it suffices to take the optical activity by the above method, then to take the reducing power and deduct the activity due to lactose, when the remainder is that due to added cane-sugar. Other methods are those of the citric acid inversion process, and lastly, the admirable method of Kjeldahl with invertase.

Tottington, April, 1891.

NEW PROCESS FOR THE ESTIMATION OF SULPHUR IN COAL, &c.

By THOMAS NEILSON.

The estimation of sulphur in coal and coke is one which is of special importance, not only to the iron and steel works' chemist, but others also, and, therefore, any process which is at once reliable, and at the same time expeditious, will commend itself to all chemists.

With this object in view I will endeavour to give the results of a few of several experiments made in order to test, and make a careful comparison of, a process which I have found to fulfil those conditions of reliance and expedition.

The sample employed was of hard Durham coke, and in each experiment, which was accompanied by a blank one, I used 1 grm. of the sample. Without further premise, I give the results with an explanation below.

	1.	2.	Average.
A. Lime (HCl sol.)	0·76	0·76	0·76
B. Lime (H_2O sol.)	0·51	0·53	0·52
C. Magnesia (HCl sol.) . ..	0·58	0·58	0·58
D. Magnesia (H_2O sol.) . ..	0·55	0·52	0·53
E. Fusion ($KNO_3+Na_2CO_3$)	0·51	0·53	0·52
F. $Na_2CO_3+MnCO_3$	0·76 0·78	0·78 0·77	0·77

A. 1 grm. of the sample mixed with 2 grms. $CaCO_3$ and put into a flat platinum dish, and then kept at a low red heat for about one hour, when complete oxidation of sulphur in the coal or coke is accomplished. The platinum dish is then placed in a beaker and covered with water; boil, and add 2 c.c. of bromine water in order to prevent any sulphur escaping complete oxidation; then add 10 c.c. HCl, boil and filter, and precipitate with $BaCl_2$ in the usual manner.

B. Exactly as in A, except that the digestion is continued for a longer period and then filtered, omitting solution in HCl; then adding 2 c.c. bromine water, acidify with HCl and precipitate with $BaCl_2$.

C. In the same way as at A, using MgO instead of $CaCO_3$.

D. In the same way as at B, using MgO instead of $CaCO_3$.

E. 1 grm. coke fused with 11 grms. KNO_3 and 4·5 grms. Na_2CO_3; then digest in boiling water, adding again 2 c.c. of bromine water, then 20 c.c. of HCl; evaporate to dryness and take up with 5 c.c. HCl and water, and precipitate with $BaCl_2$.

F. This last process, which so far as I know is an entirely new process, I perform in the following manner:—1 grm. of coke is mixed with 2 grms. of Na_2CO_3 and 0·5 grm. of $MnCO_3$, and the whole placed in a flat platinum dish and kept at a low red heat (allowing only the bottom to be red) for one hour; after this time all the sulphur and carbon will have been oxidised. The mixture is now fused, then cooled and placed in a beaker with water, or in a basin, and 20 c.c. HCl added; remove platinum dish, and evaporate to dryness and take up with 5 c.c. HCl and water, then filter and precipitate SO_3 in the usual manner. I have found that it is not necessary to evaporate to dryness, but for safety it is advisable. With other samples equally satisfactory results were obtained. It is necessary in this process to make a blank experiment, which should be performed for the same length of time, and, if possible, at the same time when the experiment is made in a muffle furnace.

Laboratory, Distington Iron Works,
Near Whitehaven.

NOTE ON THE

SOLUTION OF CALCIUM CARBONATE IN CARBONATED WATER.

By Rev. A. IRVING, B.A., D.Sc.,
Senior Science Master in Wellington College, Berks.

Some little time ago the writer was led to investigate in a general way the evidence which temperature changes might afford as to the existence of a definite chemical compound of the nature of a bicarbonate, when fresh-precipitated $CaCO_3$ is dissolved in excess of CO_2 in water. For this purpose lime-water of full strength was used. The CO_2 was prepared in the usual way by the reaction of dilute HCl upon lumps of marble; but to prevent the error which might otherwise arise from some of the heat liberated in the reaction being carried over into the lime-water, the very slow current of CO_2 was made to pass first through a column of about 8 inches of distilled cold water. The temperature of this, as indicated by one of Hicks's thermometers, was 10·7° C.

The temperature of the lime-water, which was contained in an ordinary foot-jar, was at the commencement of the passage of the gas 10·2° C. As the CO_2 passed and the $CaCO_3$ precipitate increased, the temperature gradually rose, heat being evolved by the combination $CaO+CO_2=CaCO_3$.

The rise of temperature, however, did not cease when the precipitate began to dissolve, the maximum precipitation appearing to be attained in about ten minutes with a temperature 11° C. At the end of twenty-five minutes, the heavy powdery precipitate had well-nigh disappeared, the thermometer immersed in the water in which it had been suspended reading 11·6° C. From this point no further solution appeared to take place, the thermometer reaching 11·7° C. and remaining stationary, while the gas was passed for another 20 minutes. When these facts are plotted out on a diagram along with intermediate temperatures noted, they are seen to form a curve, the gradient of which rises rather rapidly during the precipitation stage, then, as solution sets in, becomes less and less, and finally *nil*.

It would appear from these results that there is heat evolved (i.) in the *precipitation stage*, representing the excess of that produced in the reaction $CaO+CO_2=CaCO_3$ over and above that required for the separation of the water-molecule from the $Ca(OH)_2$; (ii.) in the *solution stage*, which we may attribute perhaps to the formation of the hydrogen acid, H_2CO_3, rather than a bicarbonate.

Here another fact of interest was observed. The experiment was continued for about twelve hours the next day, but without completing the solution of the precipitated $CaCO_3$.

A few days later, CO_2 (washed as above) was passed through a fresh portion of lime-water for twenty-four hours, and the same failure to effect complete solution was the result. The undissolved portion of the precipitate was filtered off quickly with the aid of an ordinary vacuum arrangement for quick-filtering, and dried (1) in the air, (2) in an air-bath at 50° C. This, on examination with a low power under the microscope, was seen to be distinctly crystallised in the rhombohedral form of Iceland-spar.

A little later a third sample of lime water was similarly treated, the CO_2 being passed at intervals for several days. On filtering quickly, the following results were obtained:—

(*a*) Residue on filter (dried at 120° C.).. =0·075 grm.
(*b*) Residue obtained on evaporating the filtrate down and drying at 120° C... =0·033 ,,

The percentages of the whole precipitate deduced from these numbers being (*a*) 69·4 and (*b*) 30·6; that is to say, about two-thirds of the precipitate remained undissolved by excess of CO_2 under ordinary atmospheric pressure.

A similar treatment of baryta-water gave very much more surprising results, the percentage of $BaCO_3$ dissolved in excess of CO_2 being only 8·7.

The arrangement adopted in the above trials was then supplemented by a column of water about 15 inches deep, through which the excess of CO_2 was made to pass, in escaping from the flask (in this case) which held the lime-water acted upon. In this way the whole apparatus became charged with nearly pure CO_2, acting at above a full atmospheric pressure. Under these conditions, the gas being passed intermittently, while the lime-water was in continuous contact with it for a fortnight, the lime-water certainly became somewhat clearer, but nothing like complete transparency was obtained. A like failure to obtain a clear solution resulted from passing a large excess of CO_2, produced by direct combustion of C in oxygen, through lime-water of full strength.

Now when we meet in the text-books with such statements as the following—"If more gas is passed through, the precipitate dissolves," "The white precipitate at first formed gradually disappears, and the liquid again becomes transparent," "If you continue to pass CO_2, the solution finally becomes clear," "When all the precipitate has re-dissolved, the liquid is quite transparent," and so on, those who are engaged in using chemical science as an educational instrument, are surely justified in protesting against such unprecise and therefore misleading and confusing statements.

It is not, however, in the language merely that the want of precision appears to creep in; it shows itself in the rough and inaccurate demonstration, with which many writers of elementary text-books seem to be satisfied. The discrepancy between the actual facts, as stated above, and the statements quoted may arise from one of two causes (leaving out of account the mere compiler who mistakes a paraphrase of passages from another writer for original work): either (1), the lime-water used must have been very poor stuff, or (2) the neglect of washing the CO_2 from the trace of HCl which comes over in a rapid stream of the CO_2 has led to false results. Probably the latter is the more frequent source of error, since in all the experiments described above silver nitrate precipitated AgCl from the wash-water after acidifying with HNO_3.

Slovenliness of statement in text-books and slovenliness of experiment are both calculated to detract from the high educational value of any experimental science. It is the greatest error possible to fancy we can "simplify" by sacrificing accuracy and precision.

Royal Institution.—Dr. E. E. Klein, F.R.S. (Lecturer on Physiology at St. Bartholomew's Hospital), will, on Tuesday next (April 28), begin a course of three lectures on "Bacteria: their Nature and Functions" (the Tyndall Lectures), and Mr. H. Graham Harris, M.Inst.C.E., will, on Saturday (May 9), begin a course of three lectures on "The Artificial Production of Cold."

A QUICK METHOD FOR THE SEPARATION OF CADMIUM FROM COPPER.

By H. N. WARREN, Research Analyst.

The precipitation of copper as cupric dioxide by means of Fehling's tartrate solution in order to estimate thereby the various sugars, is to all a well-known commercial test, yet few, if any, appear to have adopted this—*vice versâ*, thus employing glucose as a reagent in order to estimate copper; the majority of opinions being that the separation of that metal may be only partially complete, or is incomplete unless a certain amount of cupric salt remains in solution. This, however, is without foundation, in so much that the author has succeeded in effecting a complete separation of copper from cadmium by a slight alteration of process.

The alloys under examination have comprised chiefly alloys of zinc, copper, cadmium; the alloy being brought into solution by the aid of nitric acid, diluted to 100 c.c., and a convenient quantity withdrawn, corresponding to an equivalent in grms. taken. The solution is now diluted and an excess of Rochelle salt added, together with a sufficiency of sodic hydrate. The whole is then heated to boiling, which should appear perfectly clear and free from any precipitate. To the boiling solution is now added, in quantities of not more than 4 c.c. at a time, a dilute solution of glucose, the solution being further boiled upon each addition. The cuprous oxide which is thus precipitated should possess a pure scarlet tint, is filtered, washed free from impurities, and decomposed by ignition in a porcelain crucible, cooling, and re-igniting with a few drops of strong HNO_3, weighing the so treated precipitate as CuO.

The filtrate, which now contains the whole of the cadmium and zinc, is acidified and warmed, a current of SH_2 being passed through the same until saturated; the precipitated cadmium sulphide thus formed being collected, washed, and dissolved in a small quantity of HNO_3, being afterwards re-precipitated as carbonate by the addition of sodic carbonate.

The second filtrate, containing the zinc, is again rendered alkaline and precipitated as zinc sulphide by the addition of ammonium sulphide, the precipitate dissolved in HCl, and re-precipitated as in the former instance. With slight precautions, perfectly reliable estimations may be thus brought about; the copper being so completely separated as to produce no colouration upon the addition of a solution of K_4FeCy_6 to the zinc and cadmium filtrate.

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MORDANTS IN DYEING AND THE THEORY OF MENDELEEFF.

By M. PRUD'HOMME.

The mordants employed for fixing colouring matters upon vegetable fibres are metallic oxides, such as those of aluminium, chromium, iron, and tin, to mention those only which are in the most general use. The oxides intimately combined with the fibre retain or attract the colouring matter, with which they form lakes of different tones. For instance, with alizarin and the oxides of the above metals we obtain red, garnet, violet, and orange.

When studying from this point of view the oxides and their reciprocal influence in mixtures, the author succeeded in detecting relations between the shades obtained as functions of their atomic weights. More precisely these shades undergo continuous variations, which are very distinct if we adopt Mendeleeff's classification of the elements in natural groups and periodic series.

The principal bodies studied are:—Li, B, Na, Mg, Al, Si, P, Cl, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Z, As, Br, Sr, Mo, Ag, Cd, Sn, Sb, I, Ba, Di, Ce, La, W, Hg, Pb, Bi, U.

He has not been able to study Be, Ga, Ti, In, and Tl for want of material.

The results of numerous experiments made under the most varied conditions may thus be formulated:—

1. In each of Mendeleeff's groups, if we consider the terms of the periods of the even or odd rank, there is a continuous variation in a determined direction from blue to red, or from red to blue. This is the phenomenon presented respectively by Mg, Zn, Cd, and by Ca, Sr, Ba.

It has been found that for the triplets, such as Mg, Zn, Cd —Ca, Sr, Ba—K, Pb, Cs, the increase of the wave length of the corresponding rays is proportional to the increase of the atomic weight. The metallic oxides have therefore the property of communicating to their combinations with colouring matters luminous vibrations related to those of their metals.

2. In each period from the first to the fourth group, there is a progression towards the red. From the fifth to the eighth there is a movement from red towards blue.

This law is easily verified for the periods 3, 5, and 11.

3. The Group IV. does not represent a maximum, properly speaking, as the shades corresponding to it (in the periods of the odd rank) contain an excess of yellow.

With alizarin Sn gives a decided orange, Cd and Sb reds, Pb a reddish orange, Hg and Bi shades much more red.

In the 4th period the orange term does not belong to the Group IV., but recedes to Group V., where it is represented by vanadium with a distinctness which is emphasized by the vicinity of chrome, manganese, and iron, the compounds of which with alizarin are respectively garnet-red, violet-red, and violet. This period IV., like the 6th and the 10th, contains more terms than the others, and it is not surprising that the orange element is transferred more towards the right of the table.

Tin, the central term of the system, with an atomic weight 118, equal approximately to half that of uranium (240), ought to be, and is in fact, the especial representative of the yellow and orange tones. This is a fact which the practice of dyeing has established long ago.

The author remarks that the sulphides of Cd, Zn, Sn, Sb, Te (bodies belonging to the 7th period) are all yellow or orange.

Besides the method of producing shades on the fibre we may employ that of lakes, which consists in precipitating the oxides from their saline solutions by means of an alkali or an alkaline salt (borate, silicate, phosphate) in presence of a soluble colouring matter, such as alizarin or alizarin blue, &c. There is often between the results obtained upon the fibre and those of which the lakes are the manifestation a total inversion, *i.e.*, the bluest term becomes the reddest, and inversely.

The alizarin violets with iron, on the addition of Mg, Zn, Cd, vary from red to blue; but with Ca, Sr, Ba, from a blue to a red.

Solutions of the salts of Mg, Zn, Cd, to which is added an ammoniacal solution of alizarin, yield a blue lake for Mg, a yellowish red for Zn, and a violet for Cd. With solutions of the salts of Ca, Sr, Ba the reddish lake is that of Ca, and the most blue that of Ba.

The influence of bases is shown by the mere presence of their salts: solutions of the sulphates of Li, Na, and K yield, with an ammoniacal solution of alizarin, shades passing from violet to red. We may admit that the base of the salt is divided between the acid and the alizarin—a body having an acid function. The influence of the bases is not less decisive.

It is not the same with that of the acids, though it seems that differences may be shown between the shades of the solutions of KCl, KBr, and KI.

The action of Cl, Br, and I (analogues of Mg, Zn, Cd) is distinctly felt in the series of colouring-matters derived from fluoresceine (eosine, primerose, Magdala red, &c.). These are tetrachlorides, tetrabromides, and tetraiodides of fluoresceine or bodies containing at once Cl and Br, Cl and I, Br and I. Their tones differ decidedly. In this case the fluoresceine nucleus may be considered as the mordant, and Cl, Br, I as the colouring matter.

The author does not pass in review each group or each period. He observes that in the groups the law of progression continues itself to the last term. P, As, Sb, Bi accentuate the passage from blue to red. In the Group VI. it is the same. Cr gives with alizarin a garnet red, which is transformed in passing by Mo and W, and changes at last with U into a violet, the bluest obtained with a single oxide.—*Comptes Rendus*, cxii., p. 236.

ON A NEW METHOD OF SEPARATING IRON FROM COBALT AND NICKEL.

By G. A. LE ROY.

It is known that one of the best methods for the determination of cobalt or nickel consists in electrolysing the solution of these metals, which may be alkaline or neutral, or even slightly acid.

It is known that in this electrolytic determination, manganese, mixed with cobalt or nickel, does not interfere, since it is deposited at the positive pole in the form of a hydrated peroxide without carrying cobalt down with it. It is not the same with iron, which must first be separated by one of the ordinary methods of precipitation. But the methods for the separation of iron from cobalt or nickel are long and tedious, as the process has to be repeated several times.

The author has sought for a method which will permit of the separation of iron by the galvanic current.

The metals cobalt or nickel, manganese and iron (in the maximum degree of oxidation) must be in a sulphuric solution. To the liquid is added a quantity, as small as possible, of a non-volatile organic acid (by preference the citric). There is then added a large excess of a strong solution of ammonium sulphate rendered very decidedly ammoniacal. Under these conditions, ferric oxide is not precipitated in presence of citric acid.

Into the ammoniacal solution of the metallic sulphates there are introduced the platinum electrodes of any electrolytic apparatus. The current of two Bunsen or Poggendorff elements (= 300 c.c. of detonating gas per hour) is then allowed to act. The manganese is deposited at the + pole, the nickel or cobalt is deposited along with the iron at the − pole.

After the deposition of the metals is completed, the current is interrupted. The negative electrode is removed, washed rapidly with boiling distilled water, and placed in a concentrated solution of pure ammonium sulphate supersaturated with caustic ammonia, and it is then connected with the + pole of the battery. Into the ammoniacal solution there is then introduced a second platinum electrode, previously tared, which is then connected with the − pole. The current is then again allowed to act (= 100 c.c. of detonating gas per hour). The electrode, on which the Co, Ni, and Fe are deposited, takes the part of the solvent electrode; the metals are oxidised by the influence of the current; but, whilst the cobalt and nickel dissolve in the ammoniacal liquor and are deposited in the metallic state on the negative electrode, the iron, transformed into ferric hydroxide, insoluble in the ammoniacal liquid, remains partly on the negative electrode and floats partly on the solution. The precipitate of ferric hydroxide formed under these conditions does not carry down with it any appreciable traces of cobalt or nickel, and these metals are entirely deposited at the negative pole.—*Comptes Rendus*, cxii., p. 722.

SEPARATION OF TIN AND TITANIUM.

By H. HAAS.

The author, in an Inaugural Dissertation, proposes a new method founded on the well-known fact that tin oxide is reduced to metal by ignition in a current of hydrogen, whilst this is not the case with titanic acid. The latter, indeed, is reduced partially or entirely to a lower stage of oxidation, for the white or yellow colour of the titanic acid is converted into a grey verging upon violet; but this lower stage of oxidation is again converted into titanic acid on boiling in dilute hydrochloric acid.

After both oxides have been ignited in a current of hydrogen the metallic tin is dissolved by treatment with hydrochloric acid in heat, and the tin is thrown down from this solution by means of sulphuretted hydrogen after the excess of acid has been partially neutralised.

In the insoluble residue the titanic acid is determined by Levy's process. The residue is fused with potassium bisulphate, the melt is taken up in water, acidifying the solution if necessary, and the liquid is neutralised with potassa or ammonia. After 0·5 per cent of the volume of undiluted sulphuric acid has been added it is boiled for six hours to precipitate the titanic acid, adding more water to compensate for the loss of oxidation. This method is not applicable in presence of ferric salts.

In their absence, according to the experiments of Haas, it gives satisfactory results. The solution of the melt with potassium bisulphate requires much time; hence the author prefers to melt with potassium carbonate, which admits more rapidly of a clear and complete solution of the melt, if instead of dilute sulphuric acid the undiluted acid is cautiously and gradually added.

In the separation of tin oxide and titanic acid the author proceeds as follows:—

As the reduction of tin oxide in a Rose's crucible or in a porcelain boat is but incomplete, the mixture of tin oxide and titanic acid is placed directly in a dry tube of the most infusible glass, and ignited for about fifteen minutes in a current of hydrogen over a common Bunsen burner. After being allowed to cool thoroughly in a current of hydrogen the grey mass is rinsed with water into a beaker, and if a small portion adheres to the side of the tube it is dissolved away by touching with dilute hydrochloric acid, and subsequent rinsing with water. About 30 c.c. of hydrochloric acid at 20 per cent are then added, and the liquid is kept for half an hour at a gentle boil. When cold it is filtered, and the residue is washed with hot water.

The filtrate is neutralised, slightly acidified, and treated with a current of sulphuretted hydrogen. After standing for some time in a warm place the precipitated tin sulphide is collected on a filter, washed with water, to which a little ammonium acetate has been added, and dried. After the precipitate has been cautiously separated from the filter and the latter incinerated, the tin sulphide and the ash of the filter are again reduced by gentle ignition in a glass tube in a current of hydrogen.

The reduced tin is washed with water and a little dilute nitric acid into a capacious porcelain crucible, mixed with about 10 c.c. dilute nitric acid; evaporated to dryness on the water-bath; the residue is again taken up with nitric acid and hot water, and the tin oxide is determined in the ordinary manner.

According to the author, the washed and dried tin sulphide may also be easily determined by igniting the precipitate along with the ash of the filter in a weighed reduction tube in a current of hydrogen and weighing it as metal. It is less advisable, especially if the quantity is large, to use asbestos filters, and to reduce the tin sulphide collected upon these, as the filtration is exceedingly tedious.

In treating the residue of the reduced mass (titanic acid) with hydrochloric acid it is burnt along with the filter and melted in a platinum crucible with 10 parts of potassium carbonate. The melt is moistened with about 200 c.c. of water and concentrated sulphuric acid drop by drop until the acid potassium titanate dissolves. The clear or perhaps slightly opalescent solution is neutralised with sodium carbonate, 2 grms. of concentrated sulphuric acid are added, the solution is made up to 400 c.c. with water, and boiled for six hours, replacing the water as it evaporates. On account of the unavoidable "bumping" it is boiled in a capacious well-glazed porcelain pan, which may be conveniently covered with a large clock-glass or an inverted funnel.

After the titanic acid which separates out has been filtered off and washed with hot water, the filtrate is measured, mixed with so much concentrated sulphuric acid that the liquid may contain ½ per cent concentrated sulphuric acid, and again heated to a boil; a separation rarely takes place. The titanic acid collected upon the filter is weighed as such after drying and ignition.

The results communicated by the author show that the separation of tin and titanium can be accurately effected in this manner:—

To make the method applicable in the case of ores containing silicates the silica must first be removed, which is readily effected by evaporating down with hydrofluoric acid, when tin and titanium remain in the residue.

The separation of iron from titanic acid is less easy. As already mentioned, ferric salts must not be present in Lévy's method. The proposal to prevent the precipitation of the iron when separating the titanic acid (by reducing the ferric salt to the ferrous state) does not always succeed. Haas, therefore, proceeds as follows:—

Titanic acid in presence of a ferric salt is separated exactly according to Lévy's instructions. The separated ferriferous titanic acid is filtered off, ignited in a glass tube in a current of hydrogen, which is kept up until the product is cold. The reduced grey mass is then rinsed into a small beaker, boiled for half an hour with hydrochloric acid at 20 per cent; the white residue is collected upon a filter, washed, and weighed as pure titanic acid.

In determining tin and titanium in a mineral, 5 to 10 grms. of the substance, finely ground and sifted, are placed in a platinum capsule or a roomy platinum capsule upon the water-bath, and opened up with dilute sulphuric acid (1 : 10) and hydrofluoric acid, so that the silica is completely volatilised, and the residual compounds are converted into sulphates. The absence of hydrofluoric acid is ascertained by a further addition of sulphuric acid, evaporation on the water-bath, and heating the residue over the open flame. Neither hydrofluoric nor silicic acid must be present in the residue. Water is then added, the whole is heated for some time, and the contents of the vessel in which the sample was opened up (without filtering off the residues) are rinsed into a spacious porcelain pan, and, as indicated above, boiled in presence of ½ per cent of concentrated sulphuric acid for six hours after dilution to 400 c.c. It is then cooled, filtered, washed out with hot water, examining if a further deposit is produced in the filtrate on boiling again in presence of ½ per cent sulphuric acid. If a precipitate appears it is collected like the former. The precipitates, which contain all the tin and the titanium, are placed in a porcelain crucible, the filters are burnt cautiously, the whole ignited gently for some time with access of air; the contents of thecrucible are rinsed upon a filter, and washed with hot water.

After the residue has been dried and again gently ignited in a porcelain crucible, it is placed in a dry tube of sparingly soluble glass, and ignited in a current of hydrogen for a quarter to half hour.

The reduced mass is then, as above directed, treated with hydrochloric acid; the undissolved residue is again submitted to reduction and treated as before. The tin is determined in the combined filtrates in the manner above described.

The residue left after the second treatment with hydrochloric acid is fused in a platinum crucible with 6 to 10 parts of potassium carbonate until everything is dissolved, proceeding exactly as above described.

If the titanic acid seems to contain a trace of iron it is again reduced in a current of hydrogen, and the iron is dissolved out with hydrochloric acid.—*Zeitschrift f. Anal. Chemie.*

THE PROPER STANDARD FOR THE ATOMIC WEIGHTS.[*]

By F. P. VENABLE.

Among the important questions attracting the attention of chemists to-day is that of the proper standard to be adopted for the atomic weights. It is a question whose settlement cannot be much longer postponed without injury. It must be settled by careful consideration on the part of associations and individuals, and then by general usage—a sort of majority vote. I therefore venture to bring the question in its present status to the attention of this body of chemists, asking a careful, thoughtful discussion and consideration of it.

Two elements lay claim to the position of standard for all other atomic weights, hydrogen and oxygen. Hydrogen is called by Meyer and Seubert the Dalton Gmelin unit, and oxygen the Wollaston-Berzelius unit. The contention is an old one then, and first one then the other has been forced to give way in the struggle. For a long time oxygen was the accepted standard of the only approximately accurate atomic weights—those of Berzelius. It was then displaced by hydrogen, and this element has so fixed itself in the literature that it cannot well be in turn displaced as the unit. But I would make a careful distinction between unit and standard. To make a radical change now would be inconvenient and difficult, and should be done only under stress of absolute need. When one considers the difficulty and tediousness of becoming accustomed to new numbers, and the decrease in value and intelligibility of all the literature in the old notation that would follow a change of unit, one can properly realise the cost of such a change.

We are closing a century's labour, however, and a century's history, and it is important that we should come to some agreement on this point, and so be in a position to confer some degree of constancy upon our so-called constants. As it stands now, each revision or re-determination is calculated by two standards, and the individual chemist is left to choose between them at his own sweet will. There is no necessity for this, and it is a blot upon our science. Other sciences, notably electricity, are getting their standards in order, their loins girt, as it were, for the race of the twentieth century We must settle this question, as well as others, if we would move freely in the grand onward march.

The best settlement comes, as is so often the case, in the way of a kind of compromise. Let oxygen be the standard, and hydrogen practically the unit. This reduces the changes to the least possible, and tables arranged on this basis have been in use a long time. In fact, it was only with the idea of securing greater accuracy that this arrangement was ever changed. The use of $O = 15{\cdot}96$ as a factor for calculation appeared about the time of the first appearance of Meyer's work on the "Modern Theories of Chemistry," and is mainly due to his instrumentality. The pursuit of accuracy in that direction has proved an *ignis fatuus*, and the necessity for something more fixed becomes every day more and more apparent.

The extent of this need impressed me greatly while studying the various re-calculations of the atomic weights as made by our own Prof. Clarke, Meyer and Seubert, Sebelien and Ostwald, and lead to an article on the subject first published by the Elisha Mitchell Scientific Society, and afterwards by the Chemical News and the *Journal of Analytical Chemistry* (vol. iii., p. 48). This seems to have been the first article published in the discussion, but to Dr. Brauner, of Prague, belongs the credit of arousing the discussion which was carried on in the *Berichte* of the German Chemical Society during 1889, and which was participated in by Ostwald, Meyer and Seubert, and Brauner.[*] Meyer and Seubert alone opposed the adoption of $O = 16$ as the standard.

Without dwelling separately on these articles, or the arguments adduced on one side and the other, I shall content myself with trying to state clearly the reasons for adopting $O = 16$ as the standard. Were it a mere matter of sentiment, of securing a larger number of integers in the table of atomic weights, or something of that kind, I think all will agree with me that the change would be mere folly. Such men as Ostwald and Brauner would not waste time quibbling over anything so insignificant. There must be and is something deeper, and it is strange to me that Meyer and Seubert seem unable to see the true point of contention.

The facts of the case are as follows:—Hydrogen, as having the least atomic weight, seems at first sight the most appropriate unit for measuring the others. It admits of all being represented by numbers greater than unity, and none of them of such inconvenient size as in the Berzelius table with $O = 100$. If we could determine the ratio of the other elements to hydrogen directly, that is, if their atomic weights were determined by means of hydrogen, and hence were directly dependent upon this as unit, there would be nothing further for us to desire. Unfortunately, very few such direct ratios can be secured. Only three or four have been determined.

Under these circumstances, two things are possible. First find the ratio between hydrogen and oxygen, then, using this as a factor, calculate the other atomic weights. Could we find this ratio absolutely, there would be no objection to this method, but it is impossible to eliminate or allow for personal and experimental errors. The ratio found can at best be but an approximation. Evidently, by using an approximation to calculate other approximations, we get further and further from the truth. As Ostwald has said, we are introducing totally uncalled for and unnecessary errors, and he is right in styling it, in this stage of our science, a barbarism. As Brauner has pointed out, these errors can easily amount to several integers, in the higher atomic weights.

It is not for lack of skilled workers to undertake the determination of this ratio. Much excellent work has been done upon it, and especially in the last two or three years. Ostwald has summed these up, and says there is an error of at least 0·3 per cent which has not been removed by recent workers. Brauner agrees with him that the variations are irreconcilable, and though Meyer and Seubert think the ratio can vary but little from that assumed by them as justifiable by the best determination, it is manifestly a point on which the best authorities differ and hence one of uncertainty.

Why should we then make use of the number 15·96 if it is not fixed by incontrovertible, unerring, universally accepted experiments? It makes the matter no whit better for Meyer and Seubert to profess their willingness to re-calculate their table should a change in the number 15·96 prove necessary. It is merely a confession of the insecurity of their own position. We do not wish any re-calculation. We wish a standard by which the calculations can be made once and for all, one that will give us the least possible error, and is itself independent of other calculations. The present use of the double stan-

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[*] A Paper read before the American Association for the Advancement of Science.

[*] See *Chem. Zeit.* 1890, No. 13, where Dittmar says: "Ich wage zu hoffen, dass diejenigen Chemiker, welche seither, nachdem sie die Ueberzeugung gewonnen hatten dass O : H kleiner ist als 16, darauf bestanden haben, dass H = 1 als einheit für die Atomgewichte festgehalten werden müsse, diese absurde Praxis aufgeben und den 16 Theil des Atomgewichtes des Sauerstoffs als einheit adoptiren werden."

dard 15·96 and 16 seems puerile and leads to all manner of inaccuracies.

The second possibility is to use oxygen as the standard.

The question reduces itself, then, really to this :—Shall we use O = 15·96, or O = 16? For oxygen must be used from very necessity. If O = 15·96 is not the absolute ratio or is not generally accepted as such then the reason for its use ceases.

It is not necessary to bring forward arguments as to the relative convenience of the two, nor as to their effect upon the periodic law. Such arguments have little weight or significance when it is seen that the question lies between O = 15·96 and O = 16, and that hydrogen can never be the actual standard or factor from purely chemical reasons. Nor yet is there much in any argument from analogy with other standards and units. Such only lead us away from the one all-important consideration—the avoidance of unnecessary errors.

I have said that the present proposition could be looked upon in the light of a compromise. If oxygen takes the place of hydrogen as standard, what falls to the share of the latter element? If oxygen were made 100, as in the Berzelius table, or 10 or 1, as have been proposed, then the present numbers, as referred to hydrogen, would be entirely changed and lost sight of. The plan is to change them as little as possible, giving oxygen the number 16, which was once regarded as the ratio between it and hydrogen, and, according to the views of some, may still be it. Then the number for hydrogen will vary very little from unity, and the whole table is nearly based upon it as the unit. This number will change from time to time with new determinations, but such changes will involve no others. Oxygen, the standard, will then be fixed, and our task lies in the accurate determination of the others by it.

Meyer and Seubert cling to the idea that if oxygen be adopted it must be taken equal to unity, maintaining that O = 16 is neither flesh nor fowl, and by no means a unit. It is true that the standard or basis of a series of physical constants has in the past usually been taken equal to unity, but I cannot conceive the power of this habit to be sufficiently strong to force us into inconveniences or inaccuracies. That it is not regarded as a binding rule has been shown by the choice of some recent standards, especially in the new science of electricity.

The atomic weights are but relative numbers. To be in any respect constants, they must be relative to but one single element. With but few exceptions, the ratio to oxygen can be determined. In revision of atomic weights, then, this should receive the chief attention, and the oxygen ratio should be most carefully and directly determined.

Where the intermediation of another element is made use of (even though this be one which "may be counted among those of which the atomic weights are already known with the nearest approach to exactness," as Dr. Mallet recommends), it must be borne in mind that the result is subject to a certain error, which is generally multiplied several times and hence cannot give concordant results with the direct oxygen ratio, and less stress must be placed upon it. If the well-determined ratio H : O is subject to an error of 0·3 per cent, how much greater is the error in the case of ratios less well known? —*Journal of Analytical Chemistry.*

The Methods for Determining the Melting Points of Organic Substances.—H. Landolt (*Berlin Akad.*).—The following methods were tested :—1. Fusion and congelation of large quantities of the substance in which a thermometer is plunged. 2. Heating the substance in capillary tubes of different forms. 3. The electric method.

ON THE
ATOMIC WEIGHT OF OXYGEN.*

By E. H. KEISER.

In a recent paper† on this subject, Mr. W. A. Noyes makes a statement which is not in accordance with the facts, and which, as it may be misleading to some, deserves to be corrected. Mr. Noyes states that he has pointed out a source of error in my determinations of the atomic weight of oxygen. I desire to call attention to the fact that Mr. Noyes has merely pointed out what he *supposes* to be a source of error in my determinations, which is quite different from having pointed out a source of error. Moreover, Mr. Noyes' supposition is not well founded, and is not in accordance with the results of experiments.

The point in question is this :—It was found as the result of direct experiments that the hydrogen which was driven out of the palladium tube contained a trace of moisture; this moisture was collected in a phosphorus pentoxide tube, and its weight was subtracted from the apparent weight of hydrogen. Mr. Noyes thinks that there could not have been moisture present in the hydrogen, and that the increase in weight of the pentoxide tube should not have been deducted from the apparent weight of hydrogen. But I had found by direct experiment that moisture was present, and was, therefore, obliged to insert a weighed phosphorus pentoxide tube. Mr. Noyes thinks that the moisture came from the gases that were subsequently passed through the tube, but, as I have clearly stated in my paper, these gases were thoroughly dried by passing through concentrated sulphuric acid and over phosphorus pentoxide before entering the tube in question, so that this supposition is also without foundation.

The fact remains that the atomic weight of oxygen as determined by the combustion of weighed amounts of hydrogen, the hydrogen being obtained from palladium hydrogen, is 15·95, and not a lower value, as Mr. Noyes thinks he has shown it to be. Nor can I agree with his statement that it is almost certain that the true atomic weight of oxygen is not greater than 15·90. Before coming to such a conclusion, it is well to remember that all recent determinations of this atomic weight, like the older ones of Dumas, and Erdmann, and Marchand, have been determinations of the composition of water *by difference*, that is, only two of the three quantities have been determined directly. In all the determinations it is assumed that the hydrogen or oxygen which is weighed is really all present in the weighed quantity of water, or, that the hydrogen and oxygen which have been weighed have combined completely with one another. In other words, no *complete syntheses* of water have yet been recorded. The words *complete syntheses* are here used in the sense in which they were used by Stas in his researches on the atomic weights of silver, chlorine, &c. To make a complete synthesis of water it is necessary to weigh separately the hydrogen, the oxygen, and the water formed by the union of the weighed amounts of hydrogen and oxygen. It seems to me that it is too early to come to any conclusion as to the true value of the relation between hydrogen and oxygen until this relation shall have been determined by the complete gravimetric synthesis of water.

I have recently made determinations of the atomic weight of oxygen by a method which permits of the separate weighing of the hydrogen, the oxygen, and the water. In brief, the method is as follows :—A glass vessel containing spongy palladium and provided with a three-way stop-cock is exhausted with an air-pump, and as perfect a vacuum obtained as is possible with a mercury-

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* From the *American Chemical Journal*, Vol. xiii., No. 4

† *Journal of Analytical and Applied Chemistry*, v., 36; *Ber. d Chem. Ges.*, xxiv., 238.

pump, and the weight of the empty vessel determined. Pure hydrogen from hot palladium is passed over phosphorus pentoxide and into the exhausted vessel. After the spongy palladium is saturated with the gas, the vessel is again exhausted, and the increase in weight after again weighing is the weight of hydrogen occluded. Pure oxygen is now admitted to the palladium hydrogen until present in excess; the hydrogen is completely converted into water at low temperatures. The weight of oxygen admitted is determined by again weighing the vessel. Now a weighed phosphorus pentoxide U-tube is attached to the palladium vessel, and the excess of oxygen, together with any nitrogen if it was present in the oxygen, is removed by the air-pump. The loss in weight of the palladium vessel and the pentoxide tube (both weighed together) gives the excess of oxygen. The water is thereupon completely transferred from the palladium to the pentoxide tube, and the increase in weight of the latter gives the weight of water formed. The weights of the hydrogen, oxygen, and water are thus determined separately and by direct weighings. Two weighings are involved in the determination of the hydrogen, two weighings also give the weight of water, and from three weighings the weight of oxygen is obtained. Thus far I have made three determinations, and in each one the sum of the weights of hydrogen and oxygen agrees with the weight of water found to within 0·2 of a milligrm., and the weight of the palladium tube at the end of the determination was found to be the same as at the beginning. The three results agree quite closely with one another, and give for the atomic weight of oxygen almost exactly the whole number, 16. After a larger number of determinations have been made, I shall publish the details of the method and of each separate determination.

I shall not here enter into a critical discussion of the method used by Mr. Noyes. It might lead to a controversy and a waste of time. It would, however, not be difficult for any thoughtful reader of his paper to see where inaccuracies might perhaps have crept into the work, and several sources of error have already been shown by Mr. G. S. Johnson (Chem. News, lix., 272) to exist in the method, which, it seems to me, have not been completely disproved by Mr. Noyes. Nor is it possible to regard the use of sticks of caustic potash for the purification of hydrogen as unobjectionable. The sticks, as Mr. Noyes states, gradually dissolved in the water carried over. But sticks of potash contain air, and when they dissolve the air is set free, and thus the hydrogen is rendered impure.

THE ELECTROLYSIS OF THE METALLIC SULPHOCYANIDES.[*]

By LEE K. FRANKEL.

In a paper published by Dr. Smith and the author, in the Franklin Institute *Journal* for August, 1889, the statement is made that manganese, when deposited from a solution containing an excess of potassium sulphocyanide, separates as a greyish white compact deposit on the negative pole, differing in this respect from solutions of the nitrate or the sulphate, from which manganese is deposited as oxide. Furthermore, it is stated that nickel, cobalt, iron, and several other metals separate very rapidly from cold sulphocyanide solutions under the influence of a weak current. In the following paper, the above experiments have been repeated, and the action of the current has been tried on various other metallic sulphocyanides. The results obtained have been, for the most part, of a negative order, but are here appended, as they illustrate some new facts in electro-chemical analysis.

Decomposition of Alkaline Sulphocyanides.—If a concentrated aqueous solution of potassium or ammonium sulphocyanides (300 grms. in 1 litre) is subjected to the action of a weak current (1·5 c.c. OH gas per minute), the solution at first remains clear. After from one to two hours it gradually becomes turbid, and an odour of hydrocyanic acid is readily perceptible. If the current is allowed to run for twelve hours, the turbidity constantly increases until at length the solution is filled with a lemon-yellow amorphous deposit. According to Bunge (*Ber.*, iii., 297), who investigated the action of the current on potassium sulphocyanide, and to Lidow (*Ber.*, xvii., ref. 252), who obtained similar results with ammonium sulphocyanide, this yellow deposit is pseudosulphocyanogen.

If, however, the solution, while being electrolysed, is heated on a water-bath, there is evolved along with the pseudosulphocyanogen an unbearable sickening odour, due in all probability to the formation of organic sulphur compounds. In dilute sulphocyanide solutions, however, the formation of the lemon-yellow compound takes place in but small quantities, and only after the lapse of considerable time, so that if the current be sufficiently weak and the solution sufficiently dilute, no turbidity whatever occurs in the solution. It was anticipated that this behaviour of the dilute solution could be utilised for the electrolytic deposition of the metals, but the other products of decomposition exerted such an influence on the solution that in but very few cases were quantitative results obtained. These are given below as they were found.

Mercury.—Mercury can be completely deposited from solutions of potassium or ammonium sulphocyanide. The metal separates very rapidly from the respective solutions, and resembles the deposit obtained in the electrolysis of the double cyanide of mercury and potassium, in that it never possesses a drop-like appearance, but is dense and coherent.

In the first determination a slight turbidity occurred, due to the larger quantity of ammonium sulphocyanide. The filtrates from all the four determinations gave the blood-red colour with ferric chloride, but did not darken on the addition of ammonium sulphide. The deposits were washed, first with cold, then with hot water, and eventually dried on the edge of a warm iron plate.

	Mercury present. Grm.	Ammonium sulphocyanide. Grms.	Time. Hours.	Current OH gas per minute. C.c.	Dilution. C.c.	Mercury found. Grm.
1.	0·2292	1·5	16	1·	75	0·2289
2.	0·2292	0·9	16	1·4	75	0·2285
3.	0·2292	0·9	16	0·65	75	0·2295
4.	0·2292	1·2	16	0·65	75	0·2294

Gold.—Like mercury, gold can be completely deposited from a solution of ammonium sulphocyanide. The metal separates as a compact firmly-adherent deposit, which can readily be washed with either hot or cold water. The conditions under which the deposits were obtained are as follows:—

1. To a solution of gold chloride containing 0·0185 grm. of gold, 1·5 grms. of ammonium sulphocyanide were added, along with 150 of water. A current of 1 c.c. OH gas per minute was allowed to act for six hours, at the end of which time the metal was completely deposited. The gold found weighed 0·0183 grm.

2. The conditions in this determination were like the above, excepting that the gold chloride solution contained 0·1443 grm. of gold, and that the current was allowed to act for sixteen hours. The resultant gold weighed 0·1439 grm.

Cadmium.—If ammonium sulphocyanide is added to a solution of cadmium sulphate, the solution remains clear. If this solution be now subjected to the action of the current, the cadmium immediately deposits as metal, but in a very spongy form. This sponginess is frequently of such an extent that the deposit spreads in a continuous layer

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[*] Read at the Meeting of the Chemical Section of he Franklin Institute, January 20, 1891.

from the negative to the positive pole, and readily detaches itself when washed. Various conditions of current and solution were tried in order to remedy this result, the current used varying from 0·25 c.c. to 2·2 c.c. OH gas per minute, and the amount of ammonium sulphocyanide from 0·3 grm. to 6 grms. in solutions diluted from 50 to 200 c.c. In all cases, however, the cadmium deposited in a spongy form, and the method had to be abandoned.

Palladium, Nickel, Cobalt, and Zinc.—In the electrolysis of neutral solutions of these four metals in the presence of ammonium sulphocyanide, similar reactions took place. In each instance, the metal began to deposit immediately with currents ranging from 1 to 2 c.c. OH gas per minute, in solutions averaging 1 grm. of ammonium sulphocyanide. In the case of the nickel and the cobalt, the metals deposited in a compact metallic form, and frequently could be separated as a thin film from the sides of the platinum dish. With all four metals, however, the deposition continued only to a certain point, after which a reverse action took place, and the coatings gradually dissolved. In the case of the zinc, after permitting the current to act for twenty-four hours, every portion of the grey metallic deposit obtained in the earlier stage of the operation had gone into solution. The probable cause for this singular action lies in the fact that in the decomposition of the alkaline sulphocyanides there is formed an estimable amount of alkaline cyanide which, in the experiments above referred to, could be easily recognised by its odour. The addition of ammonia to the solution from time to time during the passing of the current gave no beneficial results, and all attempts to deposit the metals completely, with the strength of current used, proved futile.

Iron and Manganese.—The continuation of the investigation, previously reported, on these metals led to no satisfactory results. As has been stated, the metals can be deposited from solutions of their sulphocyanides, but not completely, and the tendency to oxidise is so great that films of the oxides form on the edges of the solutions, even during the action of the current. As soon as the solutions are poured off, and the surfaces of the metals are exposed to the air, these films of oxide rapidly spread over the entire deposits, and exclude any possibility of the estimation of iron or manganese by this method.

Arsenic.—Varying quantities of ammonium sulphocyanide were added to solutions of sodium arsenate and of sodium arsenite made alkaline with sodium hydrate. In no case was there the faintest deposition of metal.

Lead.—It has already been shown that when a solution of lead nitrate is subjected to the action of the electric current, the lead will deposit as peroxide on the positive pole. If, now, ammonium sulphocyanide be added to the solution, while the current is passing the lead will deport itself similarly to the manganese, in that the peroxide of lead gradually dissolves off the anode, while the metal deposits on the cathode. This deposition of metal will continue until no more lead can be detected in the filtrate, but, while the greater portion of the lead has separated as metal on the negative pole, a white coating will now be found on the positive pole, which after solution in acids gives a reaction with hydrogen sulphide for lead. This coating on the anode prevents any quantitative estimation of lead in an ammonium sulphocyanide solution. The metal as deposited from such a solution has a grey metallic appearance, is but loosely adherent to the dish, and easily becomes covered with a yellow film of oxide.

Antimony, Bismuth, and Tin.—To the hydrochloric acid solutions of these metals, ammonia was added until precipitates formed; varying quantities of ammonium sulphocyanide were then added to the respective solutions, followed by hydrochloric acid, until the precipitates just dissolved. All three metals deposit rapidly from such solutions, the tin, however, but incompletely. The filtrate from the bismuth gave no reaction for the metal, but the deposit was so spongy that it could not be handled. The antimony deposit detached itself so readily from the sides of the dish on which it separated that no effort was made to discover if quantitative results could be obtained.

Pseudosulphocyanogen.—In a paper on the preparation of a new yellow dye colour, H. O. Miller (*Ber.*, xviii., ref. 676) states that the impure compounds, which he designates "Kanarin," is obtained by the action of hydrochloric acid and potassium chlorate on potassium sulphocyanide. The resulting yellow substance dissolves in potassium hydrate solution, from which alcohol deposits the potassium salt. If the latter is filtered off and dissolved in water, hydrochloric acid re-precipitates the dye-stuff. As noted above, Lidow (*Ber.*, xvii., ref. 252) asserts that the yellow amorphous compound obtained in the electrolysis of ammonium sulphocyanide is pseudosulphocyanogen, the yield being greatest at 50° C., and, furthermore, states that kanarin and pseudosulphocyanogen are identical.

In a still later paper, W. Markonikow (*Ber.*, xvii., ref. 279) denies that kanarin and pseudosulphocyanogen are identical bodies. In proof of this, he states that if pseudosulphocyanogen is dissolved in an equal volume of potassium hydrate diluted with twenty parts of water, it is converted into potassium sulphocyanide and potassium cyanate, while if kanarin undergoes a similar treatment, the potassium salt is obtained, which, as above stated, can be precipitated by alcohol. To prove the correctness or fallacy of these statements, the following experiments were made:—

A solution of ammonium sulphocyanide, containing 300 grms. of the salt dissolved in a litre of water, was electrolysed with a current generating 2 c.c. OH gas per minute for forty-eight hours. The yellow compound, which had separated, was filtered off and washed with hot water, until the washings no longer gave the blood-red colouration with a solution of ferric chloride, and dried at 100° C. The resulting lemon-yellow compound dissolved readily in concentrated sulphuric acid, but without any evolution of sulphur dioxide, a reaction which Markonikow gives as distinctive for kanarin. The yellow substance dissolves in potassium hydrate, more readily on heating, to a yellow solution. A portion of this solution, after acidifying with dilute nitric acid, and the addition of ferric chloride, gave not the faintest reaction for potassium sulphocyanide. To the remainder of the solution, alcohol was added. The turbidity that formed, gradually settled to the bottom of the liquid in oily drops. These were separated from the supernatant liquid by means of a separatory funnel, dissolved in water, and from this solution the lemon-yellow compound thrown out by means of hydrochloric acid. If these reactions are indicative, kanarin and pseudosulphocyanogen are identical, but the compound obtained in the electrolysis of ammonium sulphocyanide is not pseudosulphocyanogen.

The action of potassium chlorate and hydrochloric acid on ammonium sulphocyanide was also tried, the results being similar to these obtained by Miller and Markonikow with potassium sulphocyanide. The compound thus obtained has a reddish yellow colour, dissolves in potassium hydrate, the resulting solution giving a reaction for potassium sulphocyanide, and forming the potassium salt with alcohol, showing that the original substance is impure. The potassium salt, dissolved in water and treated with hydrochloric acid, now gives a lemon-yellow precipitate resembling in colour that obtained by the electrolysis of the ammonium sulphocyanide.

The author reserves for a future communication the investigation of the composition of these compounds, and in conclusion, wishes to extend his thanks to Dr. Edgar F. Smith, under whose supervision, and at whose instance, the above work was undertaken.

A New Evaporation Calorimeter.—F. Neesen.—The heat is here measured by the increase of volume which liquids undergo on passing into the gaseous state. *Zeitschrift fur Anal. Chemie*, xxix., 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. cxii., No. 14, April 6, 1891.

Preparation and Properties of Boron Teriodide.—Henri Moissan.—The author has obtained this compound by three methods, preferably by causing gaseous hydriodic acid to react upon the amorphous boron of Deville and Wœhler. It is obtained in colourless crystals, very sensitive to the action of light. It is very hygroscopic and is decomposed by the moisture which it attracts from the air. It melts at 43°, boils at 210°, without decomposition and without giving off vapours of iodine. At a red heat it burns with a flame strongly coloured with the vapour of iodine. The specific gravity of the compound in the liquid state is 3·3 at 50°. It is very soluble in carbon disulphide and tetrachloride, and in benzene. It is less soluble in phosphorus and arsenic terchlorides and in many organic liquids. A current of 50 volts does not traverse the liquid teriodide when the electrodes are placed at the relative distance of 1 m.m. In contact with water it is at once decomposed into boric and hydriodic acids, but no iodine is liberated. It does not react with hydrogen at a cherry-red heat. If heated in oxygen it burns readily with a luminous flame, yielding iodine and boric anhydride. Melted sulphur attacks it energetically, and on contact with phosphorus in the cold there takes place a violent incandescence. With silicon it does not react. With sodium there is no action at 50°, and it may even be distilled over the alkaline metal, but at a red heat there is reaction with incandescence. Magnesium is attacked with incandescence at 500°, but aluminium not at all. Silver has no action upon the melted compound at 500°.

On a New Oxygen Compound of Molybdenum.—E. Péchard.—The addition of a few drops of oxygenated water to the solution of an alkaline molybdate produces an orange colouration which remains even if the mixture is boiled. The yellow molybdenum hydrate, $MoO_3,2HO$, though insoluble in water and acids, dissolves rapidly in oxygenated water in a gentle heat, yielding a yellow liquid. The coloured liquids thus obtained by the action of oxygenated water upon the alkaline molybdates or upon molybdic hydrate do not possess the characteristic property of molybdic liquids of giving a precipitate of ammonium phosphomolybdate in an acid solution. Oxygenated water acts also upon the alkaline tungstates. Ammonium paratungstate, sparingly soluble in water, dissolves rapidly in oxygenated water, forming a pale yellow solution. From the reactions observed the author infers the existence of a super-oxygenated acid of molybdenum, Mo_2O_7Ag, which he is now examining.

A New Method of Separating Iron from Cobalt and Nickel.—G. A. Le Roy.—(See p. 194).

On Dyssymmetry and the Creation of Rotatory Power in the Alcoholic Derivatives of Ammonium Chloride.—J. A. Le Bel.—If in ammonium chloride we substitute four alcoholic radicles sufficiently elevated in the series, the molecule seems to attain an invariable geometrical form, which is shown experimentally by the existence of several isomers and appearance of the rotatory power when these four radicles are distinct. The derivatives containing two equal radicles seem to take the form of an inactive isomer which cannot be split up.

On the Nitro-Derivatives of Dimethylated Orthoanisidine. — E. Grimaux and L. Lefèvre. — These researches prove that in the action of nitric acid upon dimethylated orthoanisidine the group $N(CH_3)_2$ affects the position of the NO_2 groups, which may take an *ortho-* or a *para-* position like the nitro-derivatives of dimethylaniline.

On the Pyrogenous Transformation of the Camphosulpho-phenols into Homologues of Ordinary Phenol.—P. Cazeneuve.—The passage of the phenols of the camphonic series into the aromatic series, strictly so-called, although effected in a pyrogenous reaction seems to have a real interest. The large proportions of the phenols obtained, about 25 per cent, points to a relatively simple mode of decomposition.

On Terebenthene.—Raoul Varet.—Aluminium chloride polymerises essential oil of turpentine, with simultaneous formation of cymene and other hydrocarbons.

On Ethyl Malonate and Double Ethyl Potassium Malonate.—G. Massol.—This paper does not admit of useful abstraction.

On the Micro-Organisms found on Ripe Grapes, and on their Development during Fermentation.—V. Martinand and M. Reitsch.—The microbia capable of development in an acid medium (which alone are of importance in vinification) exist in very various numbers on the surface of grapes. The moulds and the germs of *Saccharomyces apiculatus* are much more plentiful than *S. ellipsoideus*; the bacilli which produce acids and the mycoderms are not rare. The spontaneous fermentation of grapes is generally produced during the first 48 hours by *S. apiculatus*, which afterwards give place to *S. ellipsoideus*, however, without entirely disappearing. The bacteria and the mycoderms are met with not only at the outset of fermentation, but even in the lyes which renders it probable that in many cases the origin of the diseases of wines should be sought for on the skins of the grapes rather than in any subsequent contamination by the air or by the vessels.

Contributions to the Study of the Theory of Bleaching by the Air.—A. and P. Buisine.—The destruction of colouring matters is not due, as it has been hitherto supposed, simply to ozone. This body, like oxygen, whether pure or atmospheric, does not become active, *i.e.*, capable of effecting this decolouration, except in presence of the rays of the sun. The addition of a small quantity of tallow to bees'-wax facilitates the oxidation of the colouring matter. It disappears completely during the process.

Zeitschrift fur Analytische Chemie.
Vol. xxix., Part 4.

The Rise of the Freezing-Point in Mercurial Thermometers made of Jena Normal Glass.—F. Allihn.—The author's results are:—The rise of the freezing-point after prolonged exposure to ordinary temperatures amounted in the thermometers examined to a mean of 0·04° after four years. On prolonged heating to temperatures near 300°, the behaviour of the normal Jena glass is about twice as favourable as the ordinary thermometer-glass from Thuringia. For work at high temperatures the exclusive use of thermometers of Jena glass is strongly to be recommended. They should, previous to graduation, have been heated to 300° for 30 hours.

Determination of Metallic Aluminium in the Aluminium of Commerce.—G. Klemp.—Already inserted.

Determination of Moisture in Superphosphates.—Julius Stoklasa.—Already inserted.

The Examination of Water.—Dr. F. Dickmann.—The question was to ascertain whether a well had been polluted by drainage from gas-works. The substances generally sought for in such cases are ammonium salts, carbon monoxide, sulphocyanides, and cyanides, the three last being most characteristic and most readily detected. On evaporating ½ litre of the water in order to determine the residue, the author perceived a striking, pleasantly aromatic odour, which became more distinct on treatment with dilute hydrochloric acid. A colleague confirmed the accuracy of the perception. The author added to dry residue a few c.c. distilled water, and an equal quantity of concentrated sulphuric acid. It was not necessary to add a nitrate, as the water was rich in nitric acid. The well-known blue colour at once appeared, not extending through the entire liquid, but passing in narrow stripes from certain points to the margin. The presence of diphenylamine in the water was thus proved.

A Contribution to the Determination of the Hardness of Natural Waters by means of Soap-Lye.—E. L. Neugebaur.—The chief novelty of this process consists in the use of a special burette to which the author has given the unhappy name "titanometer," but which does not refer to titanium but to τιτανος, the Greek word for lime.

Detection of Bile Constituents in Urine.—Dr. Adolf Jolles.—This paper will be inserted in full, if possible.

On the Determination of Foreign Crude Phosphates in Basic Iron Slags.—L. Blum.—Already inserted.

The Determination of Sulphur in Inorganic Sulphides.—L. Blum.—A claim of priority. The method of opening up pyrites in a current of oxygen put forward by Jannasch in the *Journal für Praktische Chemie*, 1889, was described by A. Sour in 1873 in the *Zeitschrift für Anal. Chemie* (xii., 32).

On the Coefficients of Refraction of Saline Solutions.—B. Walter finds that salts may be divided into a number of groups which have different molecular refractive powers. Within a group the refractive power of a solution depends only on the number of the saline molecules present in the solution whether they belong to one or more salts if the latter only are members of the same group. There is also reference to two papers on the same subject in the *Comptes Rendus*.

The Volatility of Hydrochloric Acid.—R. B. Warder.—From the *American Chemical Journal*.

The Acceleration of Incineration in Platinum Crucibles.—H. von Jüptner (*Chemiker Zeitung*).—This paper requires the accompanying figure.

The Production of a Vacuum in an Exsiccator.—B. Franke (*Chem. Industrie*).—This paper also cannot be made intelligible without the figure.

The Acceleration of Filtration.—R. A. Fessenden.—From the CHEMICAL NEWS.

On Thermometer.—L. Cailletet.—From the *Comptes Rendus*.

A Gas-Balance with a Compensator.—A. Siegert and W. Durr.

A Dilatometer.—O. Knöfler (*Annalen der Physik*).

Automatic Arrangement for Turning Off Gas when the Flame Strikes Back (*Chemiker Zeitung*).—Le Roy W. McCay.—If the flame strikes back it burns a string, and the cock is closed by the release of a spring.

Mercurial Air-Pump without a Cock.—F. Neesen (*Zeit. fur Instrumentenkunde*).—No particulars are here given.

A Simple Water Blast.—M. Börner (*Zeit. Angew. Chemie*).—An improvement on that of Beutell.

Diffusion of Gases through Flexible Tubing.—F. J. Smith.—From the CHEMICAL NEWS.

The Introduction of Two Gas-tubes into Narrow-necked Flasks.—O. Kleinstück (*Chemiker Zeitung*).—The author passes into a cork, with a single perforation, a tube with an escape-tube melted on at right angles, and introduces another tube through the latter.

Drying Apparatus for the Determination of Fats in Cattle Foods which contain Drying Oils.—O. Förster (*Land. Versuchsstationen*).—This paper requires the three accompanying couples of figures.

The Use of Hydrofluoric Acid.—E. Hart.—From the *Journ. of Anal. Chem.*

The Use of Magnesium as a Reagent.—H. N. Warren.—From the CHEMICAL NEWS.

Standardising a Silver Solution with Potassium Chromate as Indicator.—H. Alt (*Chem. Zeit.*).—The author uses barium chloride instead of hydrochloric acid. The barium is then removed by the addition of zinc sulphate.

Preparation of a Solution of a Ferric Salt of Known Strength.—W. French.—From the CHEMICAL NEWS.

The Methods for Obtaining Chlorine.—P. Klason (*Swenskkemisk Tidsskrift* and *Chemiker Zeitung*).—From manganese and hydrochloric acid, the best proportions, the yield obtained is 75—80 per cent of the theoretical quantity. From sodium chloride (11 parts), manganese peroxide (90 per cent), 5 parts, and sulphuric acid 14 parts the yield is 90 parts. From manganese, hydrochloric and sulphuric acids only 65 per cent. The preparation from chloride of lime and hydrochloric acid was also examined. It is not necessary to mould the chloride of lime, but this method is inferior in point of economy to the use of manganese.

Preparation and Preservation of Hydrogen Sulphides.—C. Kreuz (*Oesterreich Apotheker Vereins*).—The author fills vessels holding 150—200 c.c. with distilled water, which has been freed from air by boiling, cools rapidly, and saturates with sulphuretted hydrogen from an apparatus which has been in action for some time. The corks are cut off level and sealed with paraffin or sealing-wax.

Preservation of Sulphuretted Hydrogen Water.—A. J. Shilton.—From the CHEMICAL NEWS.

Separation of Barium, Strontium, and Calcium.—A. Russmann.—(An Inaugural Dissertation).

Separation of Aluminium and Zirconium.—J. Thomas Davis, jun.—From the *American Chemical Journal*.

A Reagent for Aromatic Bodies with a Hydroxyl Group at the Benzol Nucleus.—P. C. Plugge (*Archiv. der Pharmacie*).—The author recommends mercuric or mercurous nitrate containing nitrous acid. It produces a red colouration with the substances in question. He finds that benzol derivatives free from hydroxyl do not give this reaction, or not until they have been converted into hydroxyliferous derivatives.

Detection and Determination of Nitrogen in Organic Bodies.—E. Donath (*Monatshefte fur Chemie*).—This paper has been noticed some time ago. Donath maintains that on oxidising nitrogenous organic matter with potassium permanganate in an alkaline solution the nitrogen is converted into nitric or nitrous acid.

The Application of Kjeldahl's Method in Hygienic Researches.—B. Proskauer and M. Zülzer.—The authors use a decomposition mixture of 800 c.c. concentrated sulphuric acid, 200 c.c. fuming sulphuric acid, and 100 grms. phosphoric anhydride. From 0·5—1·5 grm. of the sample are taken for analysis, and digested with 20 c.c. of the acid mixture, with the addition of 1 grm. mercury and 0·5 grm. anhydrous copper sulphate, until the liquid is nearly colourless. The ordinary subsequent oxidation is by adding minute crystals of permanganate. A solution of Congo-red, 1 grm. per litre, is used an an indicator.

Detection of Paraffin in Bees'-Wax.—H. Hager (*Pharm. Central Halle*).—The author's method depends on the sublimation of paraffin. The process cannot be made quantitative.

Separation of Barium and Strontium.—R. Fresenius.—The author sums up the results of a prolonged investigation as follows:—1. Barium chromate is not soluble in water containing acetic acid, if so much ammonium chromate is present that the liquid contains only alkaline acetate and bichromate. 2. Barium chromate dried at 110° is not anhydrous (as formerly assumed), but contains about 0·5 per cent of moisture. 3. Barium chromate is not decomposed on gentle ignition, and if adhering to a filter it may be weighed without loss by cautiously incinerating the filter and gently igniting the residue. 4. The determination of barium by precipitation with ammonium chromate gives results which are perfectly satisfactory. 5. The complete separation of barium from strontium by a single precipitation of the former as a chromate is not successful under any circumstances. The most favourable results obtained in this manner depend on the accidental compensation of errors of a conflicting nature. 6. A complete separation of barium and strontium, and an absolutely satisfactory result in the determination of both bases can be obtained only by a twice repeated precipitation of the barium in an acetate solution with an excess of ammonium chromate; the strontium can then be thrown down first as strontium carbonate, which is then purified by conversion into the sulphate.

Band-Spectra in the Electric Arc of Carbon.—H. Kayser and C. Runge.—No particulars are given.

MEETINGS FOR THE WEEK.

Monday, 27th.—Medical, 8.30.
—— Society of Arts, 8. "The Decorative Treatment of Natural Foliage," by Hugh Stannus, F.R.I.B.A.
Tuesday, 28th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Royal Institution, 3. "Bacteria: their Nature and Functions," by Edward E. Klein.
Wednesday, 29th.—Society of Arts, 8. "The Use of Petroleum in Prime Motors," by Prof. William Robinson.
Thursday, 30th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "Recent Spectroscopic Investigations," by Prof. Dewar, M.A., F.R.S.
—— Society of Arts, 4.30 "The Perrier Irrigation Project, Madras Presidency," by Col. J. O. Hasted, R.E.
Friday, May 1st.—Royal Institution, 9. "Hawks and Hawking," by James Edmund Harting.
—— Royal Institution, 5. Annual Meeting.
—— Geologists' Association, 8.
—— Quekett, 8.
Saturday, 2nd.—Royal Institution, 3. "The Dynamo," by Prof. Silvanus P. Thompson, D.Sc., B.A.

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NOTICE IS HEREBY GIVEN that Horace Koechlin, of Loerrach, in the German Empire, has applied for leave to amend the Specification of the Letters Patent No. 4899 of 1881, granted to John Imray, for "Improvements in the manufacture of colouring-matters."

Particulars of the proposed amendment were set forth in the Illustrated Official Journal (Patents) issued on the 15th April, 1891.

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,
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THE CHEMICAL NEWS.

Vol. LXIII., No. 1640.

COMMERCIAL VALUATION OF CREAM OF TARTAR SUBSTITUTES.

By CHARLES A. CATLIN, Providence, R.I.

Few questions are more perplexing to the analyst than the commercial valuation of cream of tartar substitutes, and more especially of those containing acid phosphate preparations.

The ordinary methods of titration with standard alkali, either directly or indirectly employed, fail to give the proper data, even with the phenolphthalein indicator, as may be readily shown on taking the sample and bicarbonate of soda in the proportions thus indicated and boiling up together in water, when it will be found that the reaction is incomplete, a greater or less proportion of the carbonic acid failing of evolution, the amount varying in the same sample with the quantity of water employed, the temperature to which the mixture is submitted, and the length of time through which it endures.

Other things aside, the value of a baking acid is, of course, in its power of evolving carbonic gas from alkaline bicarbonate when in admixture therewith under the conditions in which it performs its office in the bread making process; and since, as we have seen varying conditions have decided influence upon such reaction, it is apparent that no method of valuation can have real utility that does not take into account and, as far as possible, initiate the actual baking process in these essentials.

To inform myself more exactly, I made many careful observations of the steps pursued by a cook of the best home-spun order, in preparation of baking-powder biscuit dough and subsequent baking of the same. I found that she was using about 504 grms. of flour (Haxall brand) for the quart, as leavening for which two heaping teaspoonfuls of a popular brand of baking-powder, weighing together about 17 grms., and for moistening, 386 grms. of either milk or water, or about 23 c.c. of liquid for each grm. of baking-powder employed.

The range of temperature and the length of exposure thereto were noted as follows:—When the dough was ready for baking, a thermometer was inserted so that the bulb might be held as near as possible at the centre of the biscuit or loaf, and the whole placed in the already-heated oven by the cook in the usual manner, the range of the temperature being observed through a peephole, and record made thereof at stated times.

Averaging a series of accordant results thus obtained, I found the oven at the outset to have a temperature of about 380° F., and that the temperature of the interior of the dough passed through the following range:—

After 1 minute's exposure in the oven	95° F.
,, 3 ,, ,, ,, ...	130° ,,
,, 4 ,, ,, ,, ...	150° ,,
,, 5 ,, ,, ,, ...	160° ,,
,, 7 ,, ,, ,, ...	205° ,,
,, 10 ,, ,, ,, ...	205° ,,
,, 12 ,, ,, ,, ...	210° ,,
,, 13 ,, ,, ,, ...	212° ,,
,, 15 ,, ,, ,, ...	212° ,,
,, 17 ,, ,, ,, ...	217° ,,

After thirteen minutes' exposure, the cook pronounced the biscuit "done," but for the sake of the experiment, the heating was continued when, after fifteen minutes, the crust had become far too brown to be palatable, while at the end of seventeen, actual burning had well commenced. From the above it is apparent, then, that in the actual baking process the temperature of the dough is raised gradually, through a lapse of about thirteen minutes, to a temperature of not more than 212° F., and for a successful issue, this should not endure for more than one minute, if indeed it should be allowed to continue for that length of time.

Consideration of these conditions of the actual baking process has led me to adopt the following method for determining the value of cream of tartar substitutes generally, and more especially of those having so-called acid phosphate as the active agent:—

The first step is to determine the neutralising power of the sample by titration with caustic alkali, using phenolphthalein as the indicator. To do this, weigh one grm. into a 300 c.c. titrating flask, run in upon it 100 c.c. of water, add 1 c.c. of phenolphthalein solution (1 grm. in 250 c.c. equal parts alcohol and water), agitate a few minutes to effect complete solution or dissemination of the sample, and then titrate with normal caustic alkali to light pink colouration. The amount of solution used to effect this is noted, a further addition is made in excess, and the whole is brought to a rapid boil and kept there for a few minutes. If now the pink colour has faded out, a further addition of alkali is made, and another moment's boiling allowed, and so on till a permanent pink colour is obtained, noting of course the alkali used. It is my custom to make these additions a cubic centimetre at a time, and in most cases I find the first excess of 1 c.c. sufficient. While the solution is still hot, add in c.c. quantities normal sulphuric acid, and then titrate back to light pink with the normal alkali. If normal solutions are used, the statement will then be:—Total alkali, less acid added, equal neutralising power of 1 grm. of sample. From this calculate equivalent bicarbonate of soda.

As there is found to be no definite ratio between the neutralising capacity of these preparations and their gas evolving power when in admixture with alkaline bicarbonate under the conditions of the baking process, and since this alone is the measure of their efficiency, their valuation should depend upon their determination of this quality. To arrive at this, weigh into a perfectly dry flask one grm. of the sample and also the exact equivalent of pure bicarbonate of soda as indicated by the titrating process. Perfectly bicarbonated soda is scarcely to be found, but it may be obtained very nearly by precipitation from a strong solution of pure mono carbonate supersaturated with carbonic acid, drying the salt with bibulous paper as far as possible, then powdering, and finally drying over oil of vitriol, under a bell glass, in the ordinary manner. Thus prepared, it is hardly necessary to make allowance for the slight trace of monocarbonate which seems to be all but unavoidable. Its carbonic acid strength should be carefully determined, however, for accurate work. The flask, fitted with the usual stoppered funnel and exit tube, into which has been weighed the charge of sample and its equivalent bicarbonate, is attached to a carbonic acid absorption apparatus of any of the well known types.

Personally I much prefer the soda-lime tubes to the potash bulb, but this is a matter of individual experience.

In the actual baking process, we found that 23 grms. of water were employed for each grm. of baking-powder used. A large part of this water must have been practically inert in bringing about reaction between the constituents of the powder, being absorbed by the flour. Just what that loss of water would be we have not the means of determining, but certainly not more than half the water employed can be considered as exerting solvent action upon the powder. I would therefore recommend that not more than 20 c.c. be used for each grm. of acid sample and its soda bicarbonate equivalent. A very much larger amount would so alter the conditions of reaction that unreliable results would be the consequence. A very much smaller amount would be impracticable to use. In the flask, after attaching the absorption apparatus, introduce therefore through the funnel tube 20 c.c. of water, and disseminate the powder through it by careful agitation of the whole. We have seen in our observation of the baking of the biscuit, that in the matter of temperature, 212° F. is never exceeded within the dough in proper manipulation, and that limit should never be allowed to endure for more than one minute at the longest. As a matter of fact, I believe that when the temperature reaches 200° F., or even a much lower point, the dough has attained such a consistency that further evolution of gas is rather an injury than an advantage. However this may be, it is certain that gas evolved beyond the limit of a temperature of 212° F., enduring for one minute, is of no practical value. The contents of the flask is therefore gradually raised to the boiling-point, and as we have observed in the baking process, maintained at that temperature not longer than one minute, then aspirate the flask and note the increased weight of the absorption tubes, which gives us then the amount of carbonic acid evolved under the baking conditions, and is consequently the correct measure of strength of the sample for the purpose for which it is designed. Knowing the carbonic acid contents of the bicarbonate of soda used, the results obtained as above may be readily checked by again attaching the absorption tubes to the flask and running in through the stoppered funnel a few c.c. of dilute sulphuric acid, whereby the remaining carbonic acid will be evolved. Aspirating the apparatus again, the total increase in weight of the absorption tubes above the first weighing should correspond with the calculated amount of carbonic acid in the bicarbonate of soda used.

This last step suggests a more rapid method of procedure :—

Find the neutralising power of the sample as before, then into the flask of the carbonic acid apparatus weigh one grm. and its equivalent bicarbonate of soda, add the 20 c.c. of water, bring the whole to a boil, and keep it at that temperature not longer than one minute, the flask being detached from the absorption tubes meanwhile, blow out the flask to remove all of the carbonic acid thus evolved, then attach to the absorption apparatus and determine the carbonic acid still remaining unevolved by adding the dilute sulphuric acid, &c., as before. The carbonic acid thus obtained, deducted from the total calculated carbonic acid of the bicarbonate of soda employed, gives the gas-evolving power of the sample under the conditions of the baking process.

For a convenient statement of results I would suggest taking the carbonic acid equivalent of one grm. of pure bitartrate of potassium, *i.e*, 0·2340 grm., and expressing results in thousandths of that standard, obtained by removing decimal point, adding three 0 to the amount of carbonic acid carried to tenths m.grms., and dividing by 2340.—*Journal of Analytical Chemistry*, iv., Part 4.

ON U. GAYON'S ALDEHYD REACTION.

By H. BORNTRÄGER.

For the detection of aldehyd with spirit U. Gayon (*Comptes Rendus*) proposes a solution of magenta which has been previously decolourised by the addition of a little hydrochloric acid and much sodium bisulphite. The writer has used this reaction for about two years, and concludes from his experience that it is fundamentally useless for the purpose in question, from the following reasons :—

The solution is in a short time turned red again by atmospheric air, in consequence of the presence of ozone, hydrogen peroxide, nitrous acid, &c. (possibly by oxygen alone); a phenomenon which may be observed on the stopper of the bottle, since the bisulphite (the decolourising agent) is converted into bisulphate when the colour of magenta reappears. This change occurs immediately in presence of aldehyd or of oxidising agents such as chlorine and the nitrogen oxides.

On the other hand, the magenta colour is at once destroyed by acetyl, which is present in every spirit which has not been well rectified, especially in Russian samples; so that if little aldehyd and much acetal be present, the above reaction will take place very feebly or not at all.

The reaction, therefore, can only show whether the spirit contains appreciable quantities of oxidising agents or not.

We might therefore, as in the case of spring-water, speak of "oxidisability."

This reaction, though very sensitive, is quite unfit for a quantitative determination. The only certain reactions hitherto known for aldehyd, when moderately diluted, are its power of reducing ammoniacal solutions of silver and ammoniacal permanganate, which, unfortunately, hold good only if the aldehyd is present in sufficient quantity.

All other reactions are untrustworthy, as they indicate a variety of substances.

The author is hitherto not aware of any certain reaction for detecting traces of aldehyd in spirit.—*Zeit. Anal. Chemie.*, xxx., p. 208.

THE DETERMINATION OF MANGANESE IN IRON AND STEEL.

By L. BLUM.

L. Rürup recently made known (*Chemiker Zeitung*) a method for the determination of manganese in iron and steel, said to be a modification of the Volhard process, calculated to economise time.

Six grms. of the material are weighed out, placed in a litre flask, after being dissolved and oxidised, neutralised, mixed with sodium sulphate, filled up to to the mark, and filtered through two folded filters. Of the filtrate, 500 c.c. are placed in a one-litre Erlenmeyer flask, mixed with zinc oxide, heated, and titrated with permanganate.

In an editorial remark in the *Chemiker Zeitung*, attention is called to the differences which arise from neglecting the volume of the precipitate of basic ferric sulphate. The author now points out two other defects in the method calculated to affect the accuracy of the results.

According to Volhard, the exact conversion of a manganous salt into a hydrated manganese peroxide by the action of permanganate ensues only if another strongly basic oxide is present in solution. For this purpose he found zinc oxide the most suitable. Meinecke further showed that considerable quantities of zinc sulphate—25 to 30 grms.—must be present in order to effect the intended purpose. As in Rürup's modification its presence is excluded, the precipitate formed on titration will always contain manganous compounds, thus rendering the consumption of permanganate too small.

A further defect, which tells in the same direction, lies in the presence of free zinc oxide. On this point Meinecke has made careful investigations, and has ascertained that a deficient consumption of permanganate, and consequently reduced result, is in direct connection with the presence of undissolved zinc oxide.

These facts speak decisively against the adoption of Rürup's modification, especially as in Volhard's method, as used in metallurgical laboratories, a determination of manganese can be conveniently completed in three-quarters to one hour.—*Zeit. Anal. Chemie*, vol. xxx., p. 210.

COLOURED REACTIONS OF THE AROMATIC AMINES.

By C. H. LAUTH.

The author has recently shown that on treating dimethylaniline acetate with lead peroxide we obtain a fine and very intense green. This reaction, if applied to other aromatic amines, gives in a great number of cases very

	In presence of H_2O.	In presence of alcohol.
Aniline	Fugitive violet-red, then red-brown.	As with water.
Monomethylaniline	Blue-green, then violet, blue, and finally olive.	Violet, red-violet, olive.
Dimethylaniline	Orange, grass-green, olive green, grey.	Orange-green.
Monoethylaniline	Blue-green, blue, violet, olive.	Violet, violet-black, olive.
Diethylaniline	Bright orange, yellow.	Greenish yellow.
Benzylaniline	Red-brown, reddish violet, grey.	Yellowish grey, green.
Methylbenzylaniline	Orange, greenish yellow, greyish green.	Bright green, blue-green-violet.
Ethylbenzylaniline	Orange.	Olive, bright green-olive.
Diphenylamine	Violet grey, not intense.	Bright green, olive.
Methyldiphenylamine	Magenta, violet-brown.	Violet-brown.
Paratoluidine	Blood-red, brown-red.	Bright blood-red.
Orthotoluidine	Dragon-green, violet.	Red-violet, brown-violet, orchil.
Dimethylparatoluidine	Green-brown, dirty yellow.	Green-brown, dirty yellow.
Dimethylorthotoluidine	Bright orange-red, orange-brown.	Green-brown olive.
Xylidines	Violet-blue, grey-black.	Very red-violet, orchil.
,, meta α		
,, ,, β		
,, mixture of ortho and para		
Paraphenyldiamine	Bright blue-green, brown.	As with water.
Metaphenylenediamine	Brown.	Brown.
Dimethylated paraphenylenediamine	Magenta, violet-blue, violet-black.	As with water.
,, metaphenylenediamine	Slight yellowish brown.	Yellow-brown.
Toluenediamine (from binitro)	Bright red-brown.	As with water.
Naphthylamine α	Slight violet-blue.	As with water.
,, β	Slight yellow-brown.	Slight red-brown.
Dimethylnaphthylamine α	Bright madder red, dull white.	Madder red.
Benzidine	Intense pure blue, violet, red.	Yellow, with a blue precipitate.
Tetramethylbenzidine	In presence of excess of acid, grass-green with an orange cast.	Grass-green.
Dimethylated ortho-anisidine	Violet magenta, dirty violet.	Green-grey, olive.
,, meta-anisidine	Yellowish brown.	Yellow-brown.

distinct colourations, and, as a trace of the product is sufficient for their development, they may serve to characterise such bases when present only in very small quantities.

The author puts in a watch-glass a drop of the amine in question or, if solid, a corresponding quantity of the crystals. He adds 10 drops of a solution containg 3 vols. of acetic acid at 8° and 7 vols. of water. The base generally dissolves under these conditions, though a perfect solution is not required, as the coloured reactions are more distinct with an excess of the base than with an excess of the acid. It is well to make simultaneously a blank experiment with an alcoholic solution of acetic acid at the same degree of dilution. Certain bases are, in fact, insoluble in aqueous acetic acid, and, on the other hand, we sometimes obtain in presence of alcohol different colourations due to the action of its oxidation products, especially aldehyd. On the slopes of the watch-glass he spreads out some particles of "pure oxide" (lead peroxide?), then, inclining the glass a little, the acetic solution is brought in contact with them. The accompanying Table gives the most characteristic colours and their changes.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending March 31st, 1891.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

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

London, April 7th, 1891.

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

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

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

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

Of the 168 samples examined, the whole were found to be clear, bright, and well filtered, excepting 3, which were recorded as "very slightly turbid."

We observed at the conclusion of our previous Report that towards the end of the month of February, the water furnished alike by the several Companies had all but recovered its habitual character, and freedom from turbidity and colour. That this improvement was well sustained throughout the succeeding month of March is shown by a comparison of the Thames-supply results afforded during the month of March with the mean results obtained during the six months, July to December, 1890, distinguished as this period was by the exceptionally high character of the water supply generally:—

Thames-derived Supplies.

		July—Dec., 1890.	March, 1891.
Ratio of brown to blue tint	Means	13·5 : 20	14·1 : 20
Oxygen required for oxidation	,,	0·049	0·049
Organic carbon per 100,000	,,	0·144	0·146
,, ,, ,,	Maxima	0·170	0·209

The maximum proportion of organic carbon, namely 0·209 part in 100,000 parts of the water, corresponding roughly to about three-eighths of a grain of organic matter per gallon, was met with in a single sample only, the two next highest results amounting to but 0·162 part and 0·161 part respectively in 100,000 parts of the water.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

CONCERNING THE PENTAGLUCOSES.*

By W. E. STONE.

The two isomeric sugar-like bodies, arabinose and xylose, with the common formula $C_5H_{10}O_5$, corresponding in many characteristics to the true glucoses and in others quite distinct from the latter, may be referred to collectively as *pentaglucoses*. This term expresses the relation between these compounds and the true, or hexaglucoses, and has already become established by some degree of use† (*Ber. d. Chem. Ges.*, xxi., 2151; xxii., 1046; xxiii., 137, 1751; *Ann. Chem.* (Liebig), ccxlix., 227; ccliv., 304; *Am. Chem. Jour.*, xii., 435, &c.).

The two bodies just mentioned are the only members of this group thus far observed. Of these, arabinose has been known for more than twenty years, but was regarded until within a short time as a true glucose; while xylose is a recent discovery (Koch, *Pharm. Ztschr. f. Russland*, xxv., 619, &c.), and has also been shown by Tollens and his pupils to be a pentaglucose (Tollens and Meyer, *Ber. d. Chem. Ges.*, xxi., 647; Tollens and Wheeler, *Ann. Chem.* (Liebig), ccliv., 304).

The pentaglucoses are strictly sugar-like bodies, crystallinic, sweet, reducing Fehling's solution, and dextrorotatory. In some respects, however, they differ decidedly from the true glucoses. They are not subject to alcoholic fermentation, as has been previously proven for arabinose (*Ann. Chem.* (Liebig), ccxlix., 257), and as I am now able to announce for xylose. As a distinctive and specific reaction, the pentaglucoses produce large quantities of furfurol when subjected to the action of strong acids, and in this way are sharply separated from the true glucoses, which, under similar conditions, yield levulinic acid (*Ber. d. Chem. Ges.*, xxi., 2150; *Ann. Chem.* (Liebig), ccxlix., 227). By perfected methods the amount of furfurol thus obtained amounts to nearly fifty per cent when pure arabinose or xylose is used (*Ber. d. Chem. Ges.*, xxiii., 1751).

The pentaglucoses have not been observed as occurring in nature, but are obtained by hydrolysis of certain plant constituents. These mother-substances are found either normally as a part of the cellular tissues of the plant, or in some notable examples as abnormal gum-like secretions. So far as is known, the substances occurring under either of the above conditions are identical, although at the present time we have no means of distinguishing between those substances which will yield arabinose from those which will yield xylose.

Arabinose has been prepared from the cellular tissues of the sugar beet (*Ibid.*, i., 58, 108), from gum arabic (*Ibid.*, vi., 612), gum tragacanth (Sachsse u. Martin, "Phytochemische Untersuchungen"), cherry gum (*Ibid.*), and from wheat bran (*Ann. Chem.* (Liebig), ccxlix., 239; also *Ber. d. Chem. Ges.*, xxiii., 3110). Xylose has been obtained from woods of different species and jute (*Ann. Chem.* (Liebig), ccliv., 304), and from straw (*Ber. d. Chem. Ges.*, xxiii., 137). From brewers' grains, *i.e.*, from the outer seed coats of barley, both arabinose and xylose have been prepared (*Ann. Chem.* (Liebig), ccxlix., 243), while from peach gum arabinose and galactose were obtained (*Am. Chem. Jour.*, xii., 435), and gum arabic also would seem to contain the mother-substances of arabinose and galactose.

The nature of this substance, or these substances, from which the pentaglucoses are derived is not well understood. They are of a gummy nature and may be spoken of comprehensively as *gums*, a term clearly applicable in some cases but less so in others. In normal woody tissues, for instance, it is difficult to locate any material of the nature of gums, but by means of alkalies an amorphous substance may be extracted which is insoluble in water, alcohol, and ether, and which by the action of acids may be converted into one or other of the pentaglucoses. This substance has been variously designated as metapectic acid, arabin, wood gum, &c. Tollens and Allen have pointed out that the occurrence of this gummy material *in situ* corresponds closely to the lignin reaction with hydrochloric acid and phloroglucin (E. W. Allen, "Inaugural Dissertation," Göttingen, 1890). Moreover, E. Schulze has lately shown that preparations of cellulose, which, according to all appearances, were pure, still gave the lignin reaction and yielded an appreciable amount of furfurol (*Ber. d. Chem. Ges.*, xxiii., 2579), indicating that these substances are most intimately connected with the ultimate cellular tissue, from which they are separated with difficulty. Wherever these gums occur, they may be recognised by the furfurol reaction which characterises the pentaglucoses. In this reaction, the pentaglucoses are doubtless formed as an intermediate product, and themselves eventually yield furfurol. The furfurol test may therefore be applied to any crude material as a means of detecting the presence therein of these gums, which by proper treatment yield the pentaglucoses. Indeed, the search for, and ultimate preparation of, arabinose and xylose from several of the materials mentioned has been based upon the results of a preliminary furfurol test.

The continuation of my studies beyond this point, as described later, will perhaps increase the interest and importance attached to this group of bodies.

A.—*Occurrence of the Pentaglucoses.*

The reliability of the furfurol reaction as indicative of the presence of the pentaglucoses, or the gums from which they are derived, having been established, and having led to the preparation of arabinose and xylose from several unexpected sources, the question naturally followed: how frequently do these bodies occur in vegetable products, or how widely diffused may they be in nature? Strictly speaking, only the gums are found under these conditions; but since they are little known except in their derivatives, the pentaglucoses, to which they seem to stand in direct relation, we may regard the former as representing the occurrence of the latter. If occurring commonly, they still find no recognition in our present analytical methods, towards which their reactions are those of the normal carbohydrates and glucoses. In the case of foods, results thus obtained may give rise to erroneous estimates of the values of certain materials, since we have no ground for assuming that the two classes are of equal or even similar nutritive value.

I have therefore examined a considerable variety of vegetable materials, including different parts and products of plants, for the purpose of detecting the presence of these gums as indicated by the production of furfurol when treated with strong acids. The list of materials might be greatly extended, but it suffices, perhaps, to show that these bodies are much more widely and abundantly distributed than is ordinarily supposed.

The method of making these tests is practically the same as that used in the original study of the reaction. It allows of a comparison of the amounts of furfurol produced from different sources under fairly constant conditions. The results, however, are not absolutely quantitative, failing to yield the highest possible amount of furfurol in comparison with the method proposed by

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* Contributions from the Chemical Laboratory of Purdue University. From the *American Chemical Journal*, Vol. xiii., No. 2.

† E. Fischer proposes a numerical nomenclature for the different series of sugars so notably extended by his syntheses, according to which this group are called the "*pentoses*." This is perhaps preferable to the term here used, and may find adoption eventually.

Tollens and Günther (*Ber. d. Chem. Ges.*, xxiii., 1751). Having commenced these studies, however, some time since, I have preferred to retain the original method, for the sake of comparison between earlier and later results. This method is as follows:—

2—5 grms. of the finely powdered air-dried material are placed in a flask of 200—300 c.c. capacity, with 50 c.c. of sulphuric acid of 1·254 specific gravity. The flask is then placed in a paraffin bath and connected with a condenser; through a second opening in the stopper, connection is made with a reservoir from which water is allowed to drop into the flask with just sufficient rapidity to replace the loss by distillation and thus maintain a constant concentration of the acid. The bath is heated to 125—135° C. The first action of the acid is to convert the gums into pentaglucoses, followed at once by the decomposition of the latter, probably in this way,—

$$C_5H_{10}O_5 = C_5H_4O_2 + 3H_2O.$$

The furfurol thus formed is distilled over and collected. This distillation is continued so long as there is evidence of the presence of furfurol in the distillate. This evidence is furnished by a reaction which is very delicate, and which consists in allowing a drop of the distillate to fall on a strip of filter paper moistened with aniline acetate. So sensitive is this reaction that one part of furfurol in one hundred thousand parts of water produces instantly an intense red colour upon the paper. In more concentrated solutions this colour becomes darker and eventually reddish brown.

Usually eight to ten hours are required to complete the distillation, and the distillate amounts to 200—300 c.c. The furfurol contained therein is next concentrated, by fractional distillation, to a volume of 3—6 c.c., in which it may in part appear in the form of light yellow oily drops. Upon the addition of dilute ammonia, a precipitate of furfuramide is formed, which is collected, dried over sulphuric acid, weighed, and the relation of its weight to that of the original material calculated in percentages. The following results therefore express the amount of *furfuramide* obtained from the various materials. But 1 grm. of furfuramide theoretically requires for its production 1·6875 grms. of a pentaglucose, and practically, under the conditions described, rather more. Hence the percentages given may be multiplied by the above factor (1·6785), and will then indicate *less than the actual amount* of pentaglucoses present. From about forty substances examined, thirty-one yielded appreciable amounts of furfuramide (see Table).

	Per cent of furfuramide.
Hungarian grass	3·34
Timothy hay	1·18
Cornstover, I.	2·89
,, II.	1·48
Maize ensilage	0·91
Clover hay	1·55
Clover ensilage..	0·40
Wheat straw	4·16
Oat straw	2·29
Malt sprouts	1·82
Brewers' grains..	7·20
Corn bran, I.	0·84
,, II.	1·80
Linseed meal	1·20
Corn and cob meal	0·59
Corn cobs	8·16
Oatmeal	0·40
Beet pulp	3·59
Cotton-seed hulls	3·66
Pulp of strawberries..	1·95
Dung of cattle fed on maize ensilage ..	2·88
,, ,, corn stover.. ..	3·94
Gum arabic..	5·46
Cherry gum	8·14
Gum tragacanth	8·08
Peach gum..	4·84
White lupine seeds	0·95
Yellow ,, ,, ...	1·69
Coats of orange seeds	1·35
Orange peel	0·69
Watermelon seeds	2·70

The following materials yielded no perceptible quantities of furfuramide, but all gave strong qualitative reactions for furfurol, and it is hardly too much to expect that with a better method of distillation these also might yield furfurol in noticeable amounts:—

Dried strawberries,
Cotton-seed cake,
Corn meal,
Dried sweet potato,
Kernels of orange seeds,
Raw coffee,
Buckwheat,
Beans.

Under the stated conditions, these results, indicating that in more than three-fourths of these materials, taken at random, there exist the equivalents of from 1 to 12, or more, per cent of pentaglucoses, plainly prove the common and abundant occurrence of the latter. It is evident, therefore, that among the vegetable products usually classed as carbohydrates the pentaglucoses, or the gums giving rise to them, play an important part.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 25th, 1891.

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

The President delivered an address, of which the following is an abstract:—

The number of Fellows is 1786, of whom 32 are honorary foreign members. One foreign member, Dr. Heinrich Will, and 17 Fellows have died during the year:—Dr. M. Bechler, W. Blythe, H. B. Brady, F.R.S., C. I. Burton, W. Lant Carpenter, T. Carnelley, J. B. Hutcheson, J. A. Hill, Robert MacCalmont, E. C. Nicholson, T. R. Ogilvie, C. P. Phillips, H. Poland, H. Smith, W. C. Stevens, F. O. Landell, and H. H. Walker.

The following 13 Fellows have withdrawn:—A. Bain, E. N. Butt, J. Barker, R. Carruthers, W. H. Glazier, J. Hall, A. E. Johnson, E. A. Parnell, W. E. Porter, W. R. Ruffell, J. Stokes, A. Taylor and R. C. Tresider.

28 Fellows have been removed from the list on account of arrears:—B. Akroyd, H. J. Alford, P. H. Cathcart, F. W. Dupré, A. F. Darnon, H. Eccles, W. T. Elliott, J. W. Ellis, M. P. Gossett, E. Ernest Graves, T. F. Garwin, T. Hart, W. H. Hyatt, F. H. Lowe, H. A. B. Leipner, T. Muskett, F. Nettlefold, C. O'Keefe, L. Peckitt, G. F. Rodwell, V. P. Richards, A. H. F. Ruppell, A. E. Simpson, W. F. K. Stock, C. A. Smith, P. C. Thomas, Dr. W. H. Wilson, and W. A. Wren.

114 Fellows have been elected during the year, being 31 fewer than last year.

The financial state of the Society is not quite so satisfactory, said the President, as it has been for some years past, the receipts from subscriptions being £177 less than last year. This falling off is to be accounted for partly by the accidental circumstance that there were 11 fewer life compositions than last year, but chiefly by the fact that no fewer than 26 candidates had been blackballed.

The same number of papers, viz. 72, have been printed in the *Trans. Chem. Soc.* as last year, but they occupy no fewer than 1051 pages, instead of 772 pages in the previous year. There has been a considerable increase in the number of abstracts, 2341 appearing this year and occupying 1527 pages, whereas last year the number was 2131, which occupied 1252 pages. Hence the cost of the Journal has been greater this year by £413.

All the new and valuable works on chemistry have been added to the Library as they were published.

The time had again come round for the award of the Longstaff medal, given every third year to the Fellow of the Society who, in the opinion of the Council, had done the most to promote chemical science by research. This instruction was not always easy to carry out; but the unanimous decision arrived at on this occasion to award the medal to Professor Japp would certainly, he thought, be regarded by the Fellows generally as eminently satisfactory. All who followed the higher development of organic chemistry knew how valuable were the carefully thought-out papers which Professor Japp had communicated to the Society. It was a matter of regret that he was unavoidably prevented attending the meeting to receive the medal in person.

The great event of the year had undoubtedly been the celebration of the Jubilee on February 24th and 25th; it was the intention of the Council to issue in a separate form a full account of the proceedings on these occasions. With reference to the reception held at Goldsmith's Hall on the evening of the 24th by the President and Council, the Goldsmiths' Company had not only lent their Hall for the occasion, but with that liberality for which the great City Companies were so noted, "recognising that the occasion was of quite an exceptional character," had expressed their wish to relieve the Society from the expense attending the preparation and use of the Hall.

The suggestion made in his previous address that a subject catalogue of the Journal from its commencement might be published as a fit memorial of the Jubilee had, he thought rightly, been abandoned, as it appeared that the labour and expense involved would be greater than the result would justify.

It seemed appropriate to the occasion to briefly chronicle the changes which had occurred in the constitution and government of the Society since its foundation. Little or no alteration of bye-laws or plan of working the Society occurred during the early years. In 1852 the number of Vice-Presidents, which was then four, was increased by adding all past Presidents; but it was not until 1866 that any other change worth recording took place. In that year a new form of nomination paper was introduced, and this seems to be the first indication of any feeling having arisen that undesirable people were seeking and obtaining admission into the Society: this question had from time to time caused more discussion among the Fellows than any other relating to the government of the Society.

As chemistry became of more public importance, a very natural impression gained ground that, since all the more distinguished chemists of the day belonged to the Society, therefore every Fellow must be a thorough chemist. This misconception on the part of the public had had a most mischievous effect. In 1867 the matter was very fully discussed, and was ultimately referred by the Council to a committee consisting of Mr. Crookes, Dr. Miller, Dr. Odling, Mr. Wanklyn, and Dr. Williamson. The report of this committee was adopted and sent to all the Fellows, and it stated the case so fully that it appeared well to republish it on the present occasion. This committee decided not to recommend "any alteration in the bye-law relating to the election of Fellows which would have the effect of confining the Fellowship of the Society to strictly scientific men." But with a view to increase the security against the election of undesirable candidates, they recommended that the number of signatures attached to a certificate be five instead of three, three instead of one to be from personal knowledge. The recommendations were adopted, and appear to have met the requirements of the case, as the agitation ceased.

In 1877 another similar outbreak took place, but on this occasion the feeling that it was practically impossible for the Society to insist on all its Fellows being trained and competent chemists became so strong that ultimately it was decided to found the present Institute of Chemistry.

Now, after the lapse of 14 years, a discussion is again raised, but the collateral circumstances are very different, as, through the existence of the Institute, all who desire to be stamped as educated chemists have the opportunity of obtaining such recognition. It was, however, necessary to arrive at a clear understanding as to who we desire to attract, and who we desire to exclude from our Society. Speaking for himself, said the President, he should wish to see the entrance made easy for all who have any real interest in our science, even if they be only amateur chemists, provided that socially there be no objection to their admission; he would entirely abandon the idea that amount of chemical knowledge is to determine the suitability of a candidate.

It was practically impossible by any hard-and-fast rules to exclude undesirable persons, and the history of the Society went to show that the only effective method was for the Fellows themselves to realise that it rested with them to recommend only proper persons.

What had been the history of the Society during the past 14 years as showing whether the means at disposal had been effective in securing the prosperity of the Society? Without a shadow of doubt the Society never stood so high both in the scientific and external world as at the present time; his experience during the past two years had shown him how widely the Society was known, and in how favourable a light it is regarded at home and abroad.

If the feeling be cultivated and generally acknowledged that the body of Fellows expect and require that all should act honestly and honourably towards one another, there will be very few improper persons gaining admission. On learning that any Fellow is acting in any way wrongly or dishonourably towards the Society, the first thing in future will be to ascertain, by reference to the *Proc. Chem. Soc.*, who are the five Fellows who certified that the said Fellow was a proper person to join the Society. Nothing is more powerful than public opinion, and if it be felt that such a spirit should guide all elections, far more good will accrue to the Society than any law can effect which can be invented or enforced.

Dr. GILBERT proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed; the motion was seconded by Mr. CARTEIGHE. Both speakers referred in most appreciative terms to Dr. Russell's services to the Society, especially on the occasion of the Jubilee celebration. Dr. TEED supported the motion, which was carried by acclamation. The President having acknowledged the vote,

Professor THORPE, the Treasurer, gave an account of the financial position of the Society. The receipts from Fellows had been £3459 16*s*.; from sale of the Journal £383 9*s*. 4*d*.; and by dividends on invested capital £363 0*s*. 6*d*. The expenses on account of the Journal had been £2724 0*s*. 10*d*.; on account of the Library £300 18*s*. 9*d*.; on account of the *Proceedings* £183 7*s*. 10*d*.—the total expenditure being £3790 4*s*. 9*d*. The balance at the bank was £1798 17*s*. 7*d*.; and £600 had been invested in Metropolitan Board of Works 3½ per cent stock.

Professor ATTFIELD proposed that the thanks of the Fellows be tendered to the Treasurer. Dr. ATKINSON, in seconding the vote, lamented the loss of income during the year, and referred to the smaller expenditure out of the Research Fund, and the excessive balance at the bank.

Dr. STEVENSON advocated a larger expenditure on the Library. Mr. FRISWELL followed Dr. Atkinson in lamenting the diminution in income and its cause, and also referred to the disproportion borne by the life composition fee to the annual subscription. Mr. Cassall asked that increased facilities of using the Library might be granted to Fellows.

The President said that every effort was made by the Library Committee to obtain books, and that if Dr. Stevenson and others who complained of deficiencies would point out what was required, the Library Committee would most certainly pay the utmost attention to their recommendations. The Library would be open at any reasonable and rational time. [Dr. Thorne subsequently stated that the statistics of attendance on evenings other than those when meetings took place in the buildings, were such as to indicate that there was no great desire to use the Library in the evenings]. It so happened that a considerable sum had been voted out of the Research Fund at a time just outside the financial year, so that actually the expenditure was greater than appeared.

The Treasurer, in acknowledging the vote of thanks, said that the large balance would very soon disappear, as a number of heavy payments had to be made. He took occasion to gratefully acknowledge the service which Mr. Tutton had rendered him in keeping the Society's accounts, and finally proposed that thanks be given to the Auditors, Messrs. H. Crompton, R. H. Davies, and B. Dyer. This proposal was seconded by Dr. Collie and adopted. Mr. Dyer having replied,

Professor Ramsay moved a vote of thanks to the Officers and Council, which was seconded by Mr. Friswell, and acknowledged by Dr. Armstrong.

Mr. Warington finally proposed that thanks be tendered to the Editor, Sub-Editor, Abstractors, and Librarian. Dr. Clowes seconded the motion. Mr. Groves and Dr. Thorne replied.

Scrutators having been appointed, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session:—

President: Dr. A. Crum Brown, F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, K.C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: G. Carey Foster, F.R.S.; W. N. Hartley, F.R.S.; John Pattinson; J. Emerson Reynolds, M.D., F.R.S.; William A. Tilden, F.R.S.; Robert Warington, F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar, Thomson, F.R.S.E.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council: E. Atkinson, Ph.D.; Henry Bassett; Norman Collie, Ph.D.; John Ferguson, M.A.; E. Kinch; M. M. P. Muir; F. J. M. Page; W. H. Perkin, jun., F.R.S.; S. U. Pickering, M.A.; Boverton Redwood; Thomas Purdie, B.Sc.; John A. Voelcker, Ph.D.

The meeting then proceeded to consider the alterations in the bye-laws proposed by the Council. The first alteration having been read to the meeting,

Mr. Lloyd asked the President what would be his ruling with reference to any new proposal made at the meeting to alter the bye-laws.

The President said that he could not allow any proposal to alter the bye-laws of which notice had not previously been given to the Fellows to be put at that meeting. Although there was no express provision to that effect either in the charter or bye-laws, it was manifestly inexpedient to adopt any other course, and such ruling would be in accordance with the practice of the Society hitherto.

Mr. Lloyd stated that the movement in which he and others had taken part had for its object to exclude those who were personally objectionable, and to effect this they desired to place the nomination of Fellows in the hands of the Council. He therefore moved as an amendment that the whole subject of the alterations in bye-laws be postponed.

The President having ruled this amendment out of order, after a few remarks from other speakers, a vote was taken, and the following alteration in the bye-laws was carried, there being only five dissentients:—

"That in the case of candidates resident abroad unable to obtain the before-mentioned number [five] of signatures, the Council shall have power to accept a certificate signed from personal knowledge by one Fellow of the Society, and to recommend its presentation for ballot."

Subsequently the following were also put to the meeting and carried all but unanimously:—

2. That the following notice be printed at the head of the Form of Recommendation:—

"The attention of the candidate in whose favour this certificate is made out is specially directed to the fact that, if elected, he will be required to sign the following obligation prior to his admission into the Society:—

"Obligation.—I, the undersigned, do hereby engage that I will endeavour to promote the interests and welfare of the Chemical Society, that I will observe its laws, and to the utmost of my power maintain its dignity, as long as I shall continue a Fellow thereof.

3. That Bye law XII. be altered so that it read as follows:—

"An Annual General Meeting of the Society shall be held on the 30th day of March, or on some day in March near that time, and at such an hour as the Council may determine, for the election of Officers, &c."

April 2nd, 1891.

William Crookes, F.R.S., Vice-President, in the Chair.

Certificates were read for the first time in favour of T. St. John Belbin, 12, Bolton Mansions, South Kensington; James Lane Notter, Leigh Grange, Woolstone, Southampton; Frederick Tetley, 3, Mannville Terrace, Horton Road, Bradford.

The following papers were read:—

1. "*Citraconfluorescein.*" By J. T. Hewitt, B.A., B.Sc.

With the object of further comparing citraconic with maleic anhydride, the latter having been shown by Lunge and Burckhardt to be capable of yielding a fluorescein, the author has submitted citraconic anhydride to the action of resorcinol in presence of sulphuric acid, and finds that, like maleic anhydride, it yields the corresponding fluorescein. Citraconfluorescein is readily soluble in alcohol and glacial acetic acid, and fairly soluble in water; the aqueous solution is of a yellowish-brown colour, and exhibits a green fluorescence less vivid than that of ordinary fluorescein.

2. "*Ethylic Thiacetacetate.*" By C. T. Sprague, B.Sc., Ph.D.

The author describes a series of experiments made with the object of determining the constitution of the ethylic thiacetacetate which Hübner obtained by the action of sulphur monochloride, S_2Cl_2, on ethylic acetacetate, and which, after his death, was studied by Buchka. The same substance has since been prepared by Deliole by the action of sulphur dichloride, SCl_2, on ethylic acetacetate; by Schönbrodt by the action of sulphur on the copper derivative of ethylic acetacetate; and by Michaelis and Phillips from thionyl chloride and ethylic acetacetate. Buchka proposed the formula $S(CH{\cdot}Ac{\cdot}CO_2Et)_2$, but an alternative formula $S(O{\cdot}C{:}CH{\cdot}CO_2Et)_2$, was suggested by Deliole.

After describing the preparation of the substance, the author discusses the discrepant statements made by different observers as to its melting-point. He then describes at length the products of the interaction of hydrazines and ethylic thiacetacetate, and shows that it behaves towards phenylhydrazine, &c., in the same manner as ethylic acetacetate: in the first instance, a pyrazolone sulphide is formed from 2 mols. of the hydrazine and 1 of the thiacetate; the sulphides are in the next instance converted by further action of the hydrazine into pyrazolone disulphides and bisphenylmethylpyrazolone or the homologous substances; and, finally, the pyrazolone disulphides and the hydrazine interact to form hydrogen sulphide and hydrazones of the pyrazole series. The results afford further proof of the correctness of Buchka's formula.

3. "*The Function of Chlorine in Acid Chlorides as Exemplified by Sulphuryl Chloride.*" By Henry E. Armstrong.

A large number of experiments carried out during recent years in the author's laboratory show that sulphuryl chloride, SO_2Cl_3, acts on benzenoid compounds, if at all, uniformly in the remarkable manner first pointed out in the case of phenol by Dubois in 1867 (*Zeit. f. Chemie*, p. 705), and in several other cases by subsequent observers, *simply as a chlorinating agent*. Sulphuryl chloride is in many respects a remarkable compound: it is very easily produced by the direct union of sulphur dioxide and chlorine in presence of a catalyst, such as camphor, charcoal, or acetic acid, but little heat being evolved in its formation; it is a highly mobile liquid, of low boiling-point, and it is acted on with extreme slowness by water and alkaline solutions. It is, in fact, a surprisingly inert substance possessed of properties by no means such as are usually regarded as characteristic of acid chlorides. The author questions whether, after all, the chlorine in acid chlorides is possessed of special activity. Probably our ideas on the subject are based too much on the consideration of the properties of the most familiar of acid chlorides, acetic or acetyl chloride; benzoic chloride, it is well known, is a far less active substance, and many other acid chlorides are but slowly attacked by water. It would appear that in sulphuryl chloride the chlorine is but loosely held, and that it is easily withdrawn by a compound having an affinity for chlorine—naphthalene, for example. On slightly warming a mixture of this hydrocarbon and sulphuryl chloride, SO_2 is at once evolved, and the naphthalene is rapidly converted into tetrachloride. The SO_2 radicle in the chloride being all but destitute of "residual affinity," the compound has but little tendency to act as a whole. The view that the activity of acid chlorides is conditioned by the oxygen rather than the chlorine is strongly supported by Wagner and Saytzeff's observations, and the later ones of Pawlow (*Annalen*, 188, 104), on the action of zinc organometallic compounds on acid chlorides, which, there can be little doubt, attack the oxygen and not the chlorine:—

$$R{\cdot}COCl+ZnMe_2=R{\cdot}CMeCl(O{\cdot}ZnMe).$$

Perhaps also the activity even of so powerful an agent as chlorosulphonic acid, SO_3HCl, should be ascribed less to the chlorine than to the oxygenated radicle; this view is borne out by the fact that the analogous compound SO_3EtCl is a very inert substance. Both these compounds act, in the main, as sulphonating agents, and may perhaps be regarded as mere forms of SO_3. It would almost seem that on very slight provocation they become resolved into SO_3, and either HCl or EtCl, and that in the case of SO_3HCl the formation of acid chloride (sulphochloride), which is so frequently observed, is effected indirectly by the conjoint action of hydrogen chloride and SO_3, an interaction taking place analogous to that by which acetic chloride is formed by the conjoint action of hydrogen chloride and phosphoric anhydride on acetic acid.

Pyrosulphuryl chloride, $S_2O_5Cl_2$, which is an extremely active substance, although not rapidly acted on by water, also acts as a chlorinating agent, behaving much as if it consisted of SO_3 and SO_2Cl_2; in some cases it gives rise to the formation of a very large proportion of sulphochloride, which probably is a direct product of its action. There is no reason to suppose, however, that even in this chloride the chlorine is specially active.

A detailed description will be given later on of a long series of observations on the action of the various sulphuryl compounds above referred to.

4. "*The Action of Nitric Acid on the Ligno-celluloses.*" By C. F. Cross and E. J. Bevan.

Dilute nitric acid attacks the ligno-celluloses when heated with them at 60°. The products are in the first instance a bright yellow derivative of the fibre substance (lignone) and nitrous acid. By the further interaction of these, a characteristic decomposition is determined, large quantities of nitrous oxide (N_2O) being evolved together with carbonic anhydride, only a small proportion of nitric oxide being formed. A sensible quantity of hydrogen cyanide is also produced, the proportion being increased by increase of temperature.

These observations point to the entrance of the NOH residue into the lignone molecule and its interaction with nitrous acid, according to the equation—

$$\overset{|}{\underset{|}{C}}{:}NOH+NOH{\cdot}O=N_2O+H_2O+\overset{|}{\underset{|}{C}}O,$$

the final being the displacement of 2H by O. The action is probably general for compounds containing the NOH residue—hydroximes and nitrolic acids—and the authors suggest that attention should be paid to the gaseous products formed by the interaction of nitric acid and carbon compounds as calculated to elucidate their mechanism.

The investigation, of which this is a preliminary note, is proceeding.

The Chairman, Mr. Crookes, gave a short verbal account of observations which he had made on the volatilisation of metals *in vacuo* under the influence of an electric discharge.

PHYSICAL SOCIETY.

April 17th, 1891.

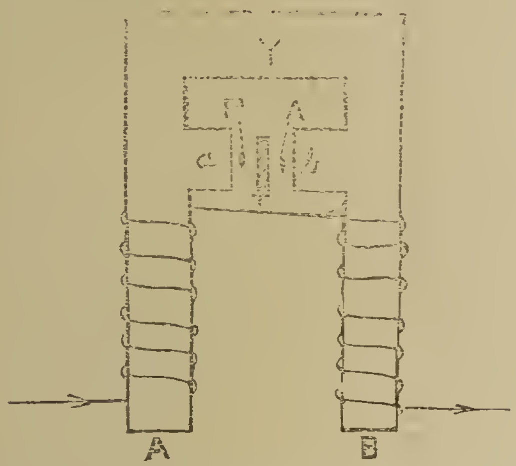
Prof. W. E. Ayrton, F.R.S., President, in the chair.

The following communications were read:—

"*On a Property of Magnetic Shunts.*" By Prof. S. P. Thompson, D.Sc.

After referring to a few instances in which magnetic shunts are employed, as, for example, the ordinary magnetic medical coil and Trotter's constant current dynamo, he said that the particular property he wished to speak of was the time taken for such a shunt to lose its magnetism as compared with the other branch of the magnetic circuit. If these times were very different, unsuspected results might be produced, and these might be regarded as being due to a kind of magnetic time-constants. Short pieces, as was well known, demagnetise much more rapidly than long ones, particularly if the latter form, or be part of, a closed magnetic circuit. Hence, in alternators, such as Kingdon's Keeper Dynamo, in which both magnets and armature are stationary, it was important that the revolving keepers should be short. The most important application of a magnetic shunt occurred, he said, in d'Arlincourt's Relay, described in vol. iv. of the *Journal of the Society of Telegraph Engineers and Electricians*, and shown diagrammatically in Fig. 1. In this relay the polarised tongue, T, plays between two projections, *a* and *b*, near the yoke, Y, and it is claimed to have a quicker action than ordinary kinds. The reason of this the author explained as follows:—

When a current flows through the coils, the greater part of the magnetic lines pass through the yoke, but a few leak across from *a* to *b*, and move the tongue against the contact, P. On stopping the current, the magnetism in extremities A and B dies away much more rapidly than in the yoke; consequently the direction of the field between *a* and *b* is reversed, and the tongue, T, thrown back against the stop, Q.



Prof. PERRY asked if any experiments had been made to test whether the throwing back actually occurred. He also enquired whether such action would be augmented or otherwise by having a thick copper tube round the yoke, or by laminating the iron.

Mr. BLAKESLEY asked if placing a yoke across A B would not improve the action.

The PRESIDENT said he would be glad to know whether the relay was any more sensitive than an ordinary one as regards the ampère-turns or the watts required to actuate the instrument. In India he remembered that they use inductive coils shunting the ordinary relays, in order to expedite the action and to avoid confused signals arising from the electrostatic capacity of long lines.

In reply, Prof. THOMPSON said he had tried an experiment on a horse-shoe electromagnet, and found evidence of throwing back when working near the bend or yoke. Putting a yoke across A B would, he thought, tend to neutralise the effect desired.

"*An Alternating Current Influence Machine.*" By JAMES WIMSHURST.

This machine consists of a varnished glass disc, with or without metallic sectors, mounted on an axis, and rotating within a square wooden frame fixed in the plane of the disc. The frame carries four square glass plates, each of which has one corner cut away so as to clear the boss of the disc. These plates are placed one at each corner of the frame, alternately on the two sides, and the disc revolves between them. There are thus two plates on one side of the disc situated at opposite ends of a diagonal of the frame, and two on the other side of the disc at opposite ends of the other diagonal. Tin-foil sectors fixed to the outer sides of the plates act as inductors, and wire brushes connected with them touch the disc about 90° behind the centre of the inductors.

The peculiarity of the machine is that although sparks can be readily obtained from it, a Leyden jar cannot be charged by bringing it to one of the terminals. From this the author concluded that the electricity produced was alternately of positive and negative sign, and this he showed to be the case by means of an electroscope. The alternations, he said, occurred about every $\frac{1}{4}$ of a revolution, the suspended paper disc which he used as electroscope remaining apart for that period and collapsing during the next quarter of a turn.

Using discs with various numbers and sizes of sectors, the author finds that the smaller the sector and the fewer the number, the greater the quantity of electricity produced. Plain varnished glass is the best in this respect. Such a disc, however, does not excite itself quite so freely as one having numerous metallic sectors.

By removing two of the inductors and placing an insulating rod carrying collecting brushes at its ends across a diameter of the disc, the machine was used to produce direct currents. Numerous discs and various shaped inductors accompanied the machine, by means of which a Holtz, Voss, or ordinary influence machine could be imitated.

Prof. S. P. THOMPSON congratulated the author on the most interesting and puzzling machine he had brought before the Society. He enquired if the machine would work if the direction of the rotation was reversed, or if two of the inductors were removed, and also whether all the four inductors are electrically of the same sign at the same instant.

In reply, Mr. WIMSHURST said the machine would not excite if the direction of rotation be changed without also changing the direction of the brush arms, but it would work as a direct current machine when two inductors were removed.

"*On Erecting Prisms for the Optical Lantern, and on a New Form of Erecting Prism made by Mr. Ahrens.*" By Prof. S. P. THOMPSON, D.Sc.

The ordinary form of erecting prism, viz., a right-angled isosceles one, was, the author pointed out, open to the objection that the top halves of the faces enclosing the right angle were nearly useless, for only the light which after the first refraction is totally reflected by the hypothenuse face can be utilised. The fraction of the side which is useful varies with the refractive index, being 0·46 when $\mu = 1·5$, and 0·525 when $\mu = 1·65$. To increase these proportions, prisms with angles of 105° and 126° have been used by Wright and others, and in some cases the prisms have been truncated. With such large angles, much light is lost by reflection. Bertin employed two truncated right-angled prisms placed base to base with an air film between them. Nachet has also made erecting prisms for microscopes, in which internal reflections occur from faces inclined at an angle of 81° to each other. This form of prism suggested to Mr. Ahrens the new form now shown, and which may be described as a long right-angled prism whose ends are cut off so as to be parallel to each other and inclined at 45° to the hypothenuse face. The longitudinal acute angles, not being required, are truncated.

Light falling parallel to the axis on one end of the prism is refracted, and after internal reflections emerges parallel but perverted.

It is claimed that this form of prism gives, weight for weight, a larger angular field than any previously made.

The performance of the new form of prism and also of the ordinary form was tested before the Society.

At the close of the meeting, Dr. Atkinson, who had previously taken the chair, announced that the next meeting would be held at Cambridge on May 9th, instead of May 8th as previously intended.

NOTICES OF BOOKS.

A System of Inorganic Chemistry. By WILLIAM RAMSAY, Ph.D., F.R.S., Professor of Chemistry in University College, London. London: J. and A. Churchill (8vo., pp. 700).

WITH the exception of bulky works of reference, such as those of Watts and of Roscoe and Schorlemmer, it is rare to meet with a systematic treatise on chemistry which can be examined without weariness. We have generally to exclaim: "all this is no doubt quite accurate, but it has already been written, with unimportant verbal modifications, over and over again. Wherefore *cui bono?*" The present work forms a happy exception. In size it is a useful medium between the encyclopædic treatises above referred to, and the bald manuals and manualettes admittedly written to meet the requirements of this or that syllabus. Professor Ramsay writes to teach chemical sciences, not to aid in that unhappy "sacrifice of education to examination," which is still going on as grimly and as ruinously as ever.

He bases his work on the periodic classification of the elements, which, long as it has been in our hands, has been neglected by the routine teachers of chemistry. He ignores the absolute boundary line between the metals and the non-metals, or "metalloids," as France still persists in calling them. He protests against the undue importance still allotted to the supposed antithesis between the acid and the basic hydroxides, and regrets that our text-books, whilst professing to teach *pure* chemistry, have still been too much swayed by commercial considerations. Why, indeed, should the notions of rarity or abundance, of utility or uselessness, be regarded at all in a scientific work. Such considerations we must hand over to works on technical and industrial chemistry, where they are all important. It is scarcely necessary to add that none of the elements are omitted. The rare earths are most ably discussed in a separate chapter in conjunction with spectrum analysis, which has played so important a part in their discovery and study. We are exceedingly glad to find this important method of research receiving here an attention which contrasts happily with the perfunctory notice which it meets with in books not a few.

The arrangement adopted in the work is first to take the elements in their periodic order, next their halogen compounds, single and double, the oxides, sulphides, selenides, and tellurides following next. The borides, carbides, and silicides, the nitrides, phosphides, arsenides, and antimonides succeed, along with the organo-metallic compounds, the double ammonia compounds, and the cyanides.

Manufacturing processes are transferred to the end of the work, those substances which are usually made in the same class of establishments being treated together. The chemical principles involved are brought into prominence rather than the details of the plant.

After a careful examination we must declare ourselves well satisfied with this work. We consider it especially adapted for that numerous class of readers who need something superior to the current cram-books, but who yet have not time to devote to such works as that of Roscoe and Schorlemmer.

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. Sixteenth Edition. London: Perken, Son, and Rayment.

This work must have met a public want, as we see at once from the fact of its having reached its sixteenth edition. Some of the matter which is added scarcely falls within the original scope of the work, though it may attract public attention at present. The author describes, with the necessary illustrations, a number of experiments calculated to explain the construction, properties, and uses of the battery, and of the Ruhmkorff coil. This important instrument of research is figured three times, on pp. 5, 28, and 38. We are not quite sure whether here or in other departments of physical science the amateur will derive much advantage from making or attempting to make his own apparatus.

Supposing him completely successful it will still have been at the cost of a great outlay of time which might have been better employed. The experiments are, generally speaking, described with correctness, and the work will doubtless be of advantage to persons who wish to acquire a practical knowledge of the rudiments of electric science.

As regards the final chapter, "seeing by electricity," we must not forget that the question can scarcely be considered within the bounds of possibility. That its importance, if really effected, would be almost infinitely greater than that of all the devices for transmitting sound is undeniable.

A Treatise on Chemistry. By Sir H. E. Roscoe, F.R.S. and C. Schorlemmer, F.R.S. Volume III. *The Chemistry of the Hydrocarbons and their Derivatives or Organic Chemistry.* Part III. New and thoroughly revised Edition. London and New York: Macmillan and Co.

The volume before us discusses that most important series of bodies known as the aromatic compounds, which indeed have increased so rapidly in numbers that the authors are justified in speaking of "Aromatic Chemistry." It has been found necessary to re-cast the present edition of the work to a very great extent. The rapid flow of discovery involves not merely additions to what is already known, but very often important modifications. Hence the task of keeping fully abreast of the present position of the science is most arduous, and the credit due to the authors for the manner in which they are executing their undertaking is correspondingly high.

After an introduction the authors describe benzene, hydroxybenzene, and its allies, its amido-derivatives, its diazo-hydrazine and azo-derivatives, including the azo-dyes, the thio-amido compounds, and the phosphorus, arsenic, antimony, bismuth, boron, silicon, tin, lead, and mercury derivatives of benzene.

As a systematic treatise on chemistry, the work taken in its entirety has no equal in the English language.

Examen Quimico y Bacteriologico de las Aquas Portables. Par A. E. Salazar y C. Newman. Con un Capitulo del Dr. Rafael Blanchard solne los Animales Parásitos introducidos par el Aqua en el Organism. ("Chemical and Bacteriological Examination of Potable Waters," by A. E. Salazer and C. Newman; with a Chapter by Dr. R. Blanchard on Parasitic Animals, introduced into the Organism by Water). London: Burns and Oates.

The present work is a step in a direction very much needed. Spain and her former magnificent colonies in America have not been precipitate in sanitary reforms, and it is therefore very pleasing to welcome a volume on this subject, which, if published in London, has been written in Chili, and is based upon researches conducted in the laboratory of the Naval School of Valparaiso.

The authors have taken up their subject in a comprehensive manner, treating successively of the search for mineral impurities, for organic pollutions, and for microbia.

They consider that a good potable water should contain 0·30 grm. of useful saline elements per litre. They suggest that bright, hard waters are likely to contain less organic impurity than such as are soft. They admit, however, that waters containing much magnesia, especially in the state of nitrates, have a debilitating action. The presence of copper they regard as less formidable than that of lead.

As noxious salts they class those of iron, lead, and copper. Now iron salts are certainly very objectionable in technical operations, but they may be pronounced harmless to the human system in any proportion in which they are likely to occur in potable waters. Instructions are given for the detection of arsenic, barium, and zinc, but chrome is overlooked—an impurity which sometimes finds its way into the waters of industrial districts.

For the determination of the organic impurities the authors give in full the processes of Wanklyn, Chapman, and Smith, and three modifications of the permanganate process, that with alkaline permanganate and ferrous sulphate, that with alkaline permanganate and oxalic acid, and that with acid permanganate and oxalic acid.

The remainder of the work is devoted to an account of the methods for detecting bacteria, taking the term in its widest sense. The authors lay great weight upon such researches, but they insist upon the necessity for experimental infection as the means of verifying the results obtained. This method is at present open to sanitary experts in Chile; but as that country has succeeded in naturalising cholera it may sometime be visited by an epidemic of "zoophily."

The work is illustrated with 127 engravings, sixteen micro-photographs, and five photographs of cultivations. It will be found a most valuable contribution to sanitary science wherever the Spanish language is spoken.

Die Elektischen Verbrauch's Messer. ("Measuring Instruments for the Consumption of Electricity.") By Etienne de Foder. Vienna, Port, Leipzig: Hartleben (small 8vo., pp. 219).

This work forms the 43rd volume of the "Electrotechnical Library" (*Elektrotechnische Bibliothek*), issued by the well-known publisher whose name it bears. It appears that almost all the operations of the electric current have been pressed into the important service of measuring its quantity. Thus we have electro-chemical, electro-motive, galvanometric (so-called), electro-thermic, and electro-capillary measuring instruments. More than eighty such appliances are described in the work before us, though many others are admittedly left out of consideration. As units of consumption there are described the Edison lamp-hour, the Ampère-hour, and the Watt-hour.

The properties which an electrical measuring instrument must possess are enumerated, as accuracy, capacity—*i.e.*, adaptability to currents of great and small strength—minimum waste of energy, simplicity—a point in which most instruments are sadly deficient—durability, care, registration of results, an object which is far from having been attained. The author in discussing this point goes out of his way to defend the accuracy of gas-meters, an utterly untenable position in the face of demonstrated facts.

Another property required from a good instrument is that it should admit of ready verification. A very important condition is that the instrument should not admit of fraudulent interference.

The author divides the instruments into the following classes: electro-chemical meters without self-registering mechanism depending on the laws of electrolysis; similar instruments with a registering mechanism; electro-chemical meters with a movable or reversible electrode; gas-expansion meters depending on the volt-metre; electro-mechanical meters; electro-motive meters in which the current effects the rotation of a motor; alternating current meters on the electro-motive principle; ampère or coulomb meters, in which the vibrations of the needle of an ammeter are registered by clockwork; mercurial rotation meters, electro-thermic meters; photographic meters; meters depending on Foucault's disc; meters worked by accumulators; meters with electrodynamometers; and lamp-hour or consumption meters. The author then proceeds to an account of the most successful of these instruments, descriptions being made more intelligible by means of seventy-seven well executed illustrations.

This work must be pronounced exceedingly useful, though it is, perhaps, written too much in the interests of the supplier, who it is to be hoped will act more uprightly than gas companies have generally done.

An appendix gives an account of the conditions under which electric current is supplied in various cities whether for lighting or as a source of motive power.

Examination of Horse-Hair.—M. Goeldner (*Pharm. Zeit.*).—The presence of oil is detected by pressure between silk-paper. Vegetable fibre is recognised by its different behaviour on burning, and by its resisting prolonged treatment (12 hours) with dilute soda-lye (1 : 5).

CORRESPONDENCE.

A GERMAN ACCOUNT OF JOSEPH PRIESTLEY.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lxii., p. 84), I pointed out some singular mis-statements by French authors concerning the biography of the discoverer of oxygen.[*] Though I lay no claim to be a champion of Priestley in particular, I do like to have justice done, and I love truth; allow me, therefore, to use your columns to direct attention to a brief biography of Priestley, recently published in Germany, that contains an amazing number of gross mis-statements and makes important omissions.

Dr. Carl Schaedler in his "Biographisch-litterarisches Handwörterbuch der wissenschaftlich bedeutenden Chemiker" (Berlin 1891), writes of Dr. Priestley thus:—"Im Jahre 1761 war er Sprachlehrer an der Academie zu Warrington nachdem er die verschiedensten Länder Holland, Frankreich, Italien, Deutschland bereist bratte. In diesen Ländern machte er, nicht vorbereitet durch ein eigentliches naturwissenschaftliches Studium, seine glänzenden Untersuchungen," [&c.].

The facts are as follows:—Priestley did not make his journey on the Continent with Lord Shelburne until the summer of 1774, and he visited, as he himself wrote, "Flanders, Holland, and Germany as far as Strasburgh," and spent one month in Paris. Priestley never visited Italy, but it is not this trifling inaccuracy nor the error of thirteen years for the date of his travels of which I would complain; I earnestly protest against Schaedler's ingenious attempt to transfer the scene of Priestley's memorable chemical discoveries to the Continent; "*In diesen Landern*," forsooth, "*machte er*" his investigations on different kinds of airs.

After quoting Priestley's own account of his discovery of oxygen Dr. Schaedler writes:—"Priestley ist mit van Helmont Begründer der pneumatischen Chemie," an association tending to belittle the Englishman's renown.

Again we read:—"Die Unduldsamkeit in religiösen Dingen entzweite Priestley mit seinem Gönner Lord Shelborne (*sic*), er verarmte und wanderte 1794 nach America aus, liess sich an den Quellen des Susquehannah als Farmer nieder und wurde 1804 vergiftet."

To anyone familiar with the life of Priestley, this sentence combines an amazing number of mis-statements; Priestley himself wrote he never knew the exact cause of the coolness that arose between himself and Lord Shelburne. In place of a reference to the unhappy Birmingham Riots of 1791, we are told that "er verarmte"; and finally a statement so baselessly persisted in by the French writers, that Priestley died by poison, completes this parody of a biography.

Such blunders are inexcusable because accurate information as to Priestley's life is accessible to every one; he left autobiographical "Memoirs" that furnish data for the innumerable biographies published in dictionaries and encyclopedias of every nation during nearly one hundred years.

Dr. Schaedler's volume shows other signs of careless compilation; the discovery of bromine is ascribed to "Ballard," this is perhaps a mere typographical slip. The author states that Kunckel prepared phosphorus from bones in 1678, whereas every tyro knows that nearly one hundred years elapsed between the preparation of the element from urine and its discovery in bones by Gahn, or Scheele (1769).

Dr. Schaedler's little work does not claim completeness, but it is difficult to understand on what principle he selects the "wissenschaftlich bedeutenden Chemiker," whom he honours. He does not even include all the honorary members of the German Chemical Society, omitting the names of Dr. Warren de la Rue, F.R.S., Dr.

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[*] "French Accounts of Joseph Priestley," Chemical News, lxi., 84.

W. H. Perkin, F.R.S., and Dr. Wolcott Gibbs (the latter of the U.S.A.).

Of Frenchmen eminent in Chemistry we miss the names of Lecoq de Boisbaudran, Friedel, Grimaux, Moissan, and others. Americans fare badly, but four being named. Can it be that the author is not acquained with the researches of such men as Robert Hare, Professor Frederick A. Genth, Professor T. Sterry Hunt, Dr. J. Lawrence Smith, Professor J. W. Mallet, F.R.S., Prof. Josiah P. Cooke, and a host of others whose scientific labours entitle them to high places in the annals of chemistry. Their biographies and writings are found in the late Professor Silliman's "American Contributions to Chemistry," presented in 1874 at the Northumberland celebration of the centennial of the discovery of oxygen.

Dr. Schaedler's work is very unequal in its bibliography—a title more in accordance with it contents would be:—"Handwörterbuch *einige in Deutschland* wissenschaftlich-bedeutenden Chemiker."—I am, &c.,

H. C. B.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Justus Liebig's Annalen der Chemie.

Vol. cclv., Parts 1 and 2.

Researches from the Chemical Institute of the University of Strasburg.—These communications consist of memoirs by R. Fittig on lactonic acids, lactones, and non-saturated acids, commencing with the synthesis of lactonic acids by the condensation of aldehyds with bibasic acids and their behaviour on dry distillation; by Ignaz Fraenkel on acetaldehyd and succinic acid; by H. East Miller on chloral and succinic acid; by Alf. Delisle on propionic aldehyd and succinic acid; by Alb. Schmidt on butyric aldehyd and succinic acid; by Adolf Zauner on isobutyraldehyd and succinic acid; by August Schneegans on valeraldehyd and succinic acid; by Franz Feist on valeraldehyd and pyrotartaric acid; by an anonymous chemist on œnanthol and succinic acid; by R. Reichelmann on œnanthol and pyrotartaric acid, and by R. Fittig on benzaldehyd and succinic acid.

Communications from the Chemical Laboratory of the University of Erlangen.—These consist of memoirs by O. Fischer and E. Hepp on para-nitrosodiphenyl-meta-phenylendiamine; by A. Harden on β-nitroso α-naphthylamine; by A. Reichold on phenyl-paratolylamine; by L. Pflug on paraxylidine; by Th. T. Best on monomethyl-ortho-anisidine; and by C. Heucke on para-amido-diphenylamine.

Researches from the Agricultural Chemical Laboratory of the University of Göttingen; consisting of papers by Dr. K. Beythien and B. Tollens on the compounds of raffinose with bases; by the same authors on the behaviour of inverted raffinose with phenylhydrazine; by the same authors on the melting-points of the osazones, and on researches with phenylhydrazine; and by Dr. K. Beythien, Dr. E. Parcus, and B. Tollens, on the formation of lactic acid from raffinose, and from cane-sugar with bases, the conclusion being that raffinose cannot be formed from cane-sugar by the action of lime or strontia, and by the same authors on lactic acid from treacle. The quantity of lactic acid present in (beetroot) treacle may reach ½ per cent. For its formation a double weight, or upwards, of sugar must have been decomposed.

Compounds of Alloxan with the Pyrazol bases.—By Guido Pellizzari.—Alloxan, although it has acid functions, behaves with bases quite differently from the other acetones and aldehyds. In consequence of the instability of the alloxan chain this reaction may serve for the preparation of bodies which are not easily obtained in any other manner. Skatol and phenylpyrazol do not combine with alloxan. Methylketol forms a saline compound which is again resolved into its two constituents by alkalies and acids. Anilalloxan, if heated with acids, gives off carbonic acid, ammonia, and formic acid, and yields the salt of an aminic acid.

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.

India-Rubber.—A correspondent asks if any one can tell him of a chemical which will keep raw india-rubber pulp in a plastic state of the consistency of china-clay or dough. Raw india-rubber pulp is of a stringy, plastic nature, and the object is to reduce the stringiness and make it of shorter consistency, like dough or china-clay. The substance added must not injure the rubber and must be capable of being expelled by boiling or at a similar heat after it has done its service.

MEETINGS FOR THE WEEK.

Monday, 4th.—Medical, 8.30. (Annual Oration).
—— Society of Arts, 8. "The Decorative Treatment of Natural Foliage," by Hugh Stannus, F.R.I.B.A.
—— Society of Chemical Industry, 8. "An Improved Process for Softening and Clarifying Water," by Mr. L. Archbutt and Mr. R. M. Deeley. "The Chemistry of Whisky and Allied Products," by Mr. A. H. Allen.
—— Royal Institution, 5. General Monthly Meeting.
Tuesday, 5th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30
—— Royal Institution, 3. "Bacteria: their Nature and Functions," by Edward E. Klein.
—— Society of Arts, 5. "Armenia and the Armenians," by Capt. Buchan Telfer, R.N.
Wednesday, 6th.—Society of Arts, 8. "The Sources and Applications of Borax," by Mr. E. L. Fleming.
—— Geological, 8.
Thursday, 7th.—Royal Institution, 3. "Recent Spectroscopic Investigations," by Prof. Dewar, M.A., F.R.S.
—— Institute of Electrical Engineers, 8.
—— Chemical, 8. Ballot for the Election of Fellows. "The Action of Alkalies on the Nitro-compounds of the Paraffin Series," by Prof. Dunstan and T. S. Dymond. "The Addition of the Elements of Alcohol to the Ethereal Salts of Unsaturated Acids," by Prof. Purdie and W. Marshall. "On some New Addition Compounds of Thiocarbamide affording Evidence of its Constitution," by Prof. Emerson Reynolds. "On the Action of Acetic Anhydride on Substituted Thiocarbamides, and an Improved Method of Preparing Aromatic Mustard Oils."
Friday, 8ht.—Royal Institution, 9. "Liquids and Gases," by Prof. W. Ramsay, F.R.S.
—— Physical, 5.
Saturday, 9th.—Royal Institution, 3. "The Artificial Production of Cold," by H. Graham Harris, M.Inst.C.E.

THE CHEMICAL NEWS.

Vol. LXIII., No. 1641.

A SYSTEM OF INTERNATIONAL MEASURE AND WEIGHT.

By C. J. HANSSEN, Civil Engineer.

To the great nations who, entirely or partly, use the British standards of measure and weight, and for reasons of practical utility and convenience hesitate to adopt the metric system, the author most respectfully offers a system of decimal measure and weight, based upon the present Anglo-American system, which, by only a minute increase in the length of the foot, is converted into a decimal system of measure and weight, combining the convenience of the present Anglo-American standards, with all the scientific and theoretical advantages of the metric system, viz., a simple relation between the unit of length (which determines volume), the unit of mass, and the unit of specific gravity.

In case England adopts this system, no doubt the United States and Russia would follow, and it would finally become the *world's standard.*

The author's new system is simply this :—

The foot is increased by about $\frac{1}{2500}$ of its present length, or the thickness of ordinary note-paper,—(exactly from 1·0000 to 1·000403), while the pound avoirdupois, the ounce, and the imperial gallon remain unaltered. By this very slight alteration of the length of the foot, which hardly will be noticed in trade, manufacture, and commerce, the present system of standards is at once converted into a decimal system. While the present cubic foot only contains 436971·78 grains of distilled water, the new standard cubic foot would contain exactly 1000 ounces (437,500 grains) of distilled water of 4° C. temperature*) ; 16 cubic feet consequently will be equal to 100 gallons (called 1 hectogallon), and 1 hectogallon of distilled water of 4° C. weighs 1000 lbs. The new standard foot will be divided into deci-, centi-, and millifoot, and by multiplying the foot we get :—

Surveyors and Nautical Measure.

Length.

1 rod = 5 ft. = 10 links.
1 chain = 10 rods = 100 ,,
1 mile = 100 chains = 10,000 ,,

Square.

1 sq. rod = 100 sq. links.
1 sq. chain = 10,000 ,, ,,
1 sq. mile = 10,000 sq. chains.

Cube.

1 cube rod = 1000 cube links.
1 ,, chain = 1000 ,, rods.
1 ,, mile = 1000·000 ,, chains.

1 knot or nautical mile ($\frac{1}{60}$° latitude) = 6080·22 ft. (The Admiralty knot is now 6080 ft.).

Fluid and Dry Measure.

(The imperial gallon remains unaltered).

			Lbs. of distilled water at 4° C.	
1 hectogallon	= 100	gallons =	1000	= 16 cubic feet.
1 gallon	= 0·01	hgal. =	10	= ,, ,,
1 dion (decigal.)	= 0·1	gallon =	1	= ,, ,,
1 centigallon	= 0·01	,, =	0·1	= ,, ,,
1 milligallon	= 0·001	,, =	0·01	= ,, ,,

Weights.

The pound avoirdupois, and the ounce remain unaltered.

		Distilled water.		
1000 lbs.	= 1 hgal.	= 1 kilopound	= $\frac{1}{2}$ new ton.
1000 ozs.	= 1 cubic ft.	= 1 kilounce	= $\frac{1}{16}$ kilopound.

The pound is divided into deci-, centi-, and millipounds.

The ounce is divided into deci-, centi-, and milliounces.

Trade and Commercial Standards.

The new standard foot divided into 12 inches, &c., may be used where convenient. The ton reduced to 2000 lbs. and the cwt. of 100 lbs. to be legalised.

Terms and Units Based upon the New Decimal Standards.

Specific Gravity.—The weight of one cubic deci-foot of a substance in ounces, or the weight of a dion (decigallon) of a substance in pounds, expresses the specific gravity of the substance. Quotations of specific gravity could be made perfectly international if they were referred to the 42° latitude and sea level. Mean atmospheric pressure at that latitude is 759·72353 m.m. of mercury (760 m.m. is commonly reckoned as mean atmospheric pressure), and under this pressure the specific gravity of oxygen gas is $\frac{1}{700}$ of the weight of distilled water, or :—

1 hectogallon oxygen gas of 0° C. weighs exactly $\frac{10}{7}$ lbs., and 1 lb. of oxygen contains exactly $\frac{7}{10}$ hectogallon ; the specific gravity of any other aeriform substance is found with absolute accuracy by multiplication with the substances atomic number, and *these figures also hold good for metric standards.*

1 *hectogallon weighs*	.. *lbs.*	1 *lb. contains*	*hectogallons.*
1 *cubic foot* ,,	.. *ozs.*	1 *ounce* ,,	*cubic feet.*
1 *cubic metre* ,,	.. *klgr.*	1 *kilogr.* ,,	*cub. metres.*
Hydrogen	.. $\frac{5}{56}$.	Hydrogen	$\frac{56}{5}$
Oxygen.. .. ($16\times\frac{5}{56}$)	$\frac{10}{7}$.	Oxygen	$\frac{7}{10}$
Carbon vapour ($12\times\frac{5}{56}$)	$\frac{15}{14}$.	Carbon vapour ..	$\frac{14}{15}$
Carbonic oxide ($14\times\frac{5}{56}$)	$\frac{5}{4}$.	Carbonic oxide ..	$\frac{4}{5}$, &c.

The specific heats of gases are found and expressed in equally plain manner, and all calculation relating to aeriform substances are thereby immensely simplified.

Unit of Heat.—1 lb. of water heated 1° C. called one calor.

The *centigrade thermometer* must be adopted, and its boiling-point lowered 1-4000th in accordance with the international barometric standard.

Atmospheric pressure is usually measured by inches or m.m. of mercury, but if atmospheric pressure at 42° latitude were adopted as the universal mean atmospheric pressure, and this unit divided into 1000 or 10,000 parts, we should have a far more convenient measure and expression of the pressure of the atmosphere for steam, gases, or fluids, than the present inches of mercury or pounds per sq. in.

The readings of the barometer would be 0·947—1·000—1·012, &c. (atmosphere).

72 lbs. per sq. in., steam pressure in a boiler would be expressed : 4·91 atmosphere.

Pressure in a gas-pipe, say 0 6 inch head of water = 15 (ten thousands), &c.

Numerous problems, especially in steam and gas engineering, dynamic, thermo-dynamical, and thermo-chemical science (which now are a task for eminent engineers and professors*), become, by the introduction of the new decimal standards and the international standard of gravity, so extremely simple that practical men of ordinary capacity and even clever schoolboys are able to understand and to solve them.

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* At 4° C. water has its point of greatest density, and this temperature also is adopted in the metric system.

* See the discussion in the Institution of Mechanical Engineers, July, 1889, on Mr. Macfarlane Gray's paper, "The Rationalisation of Regnault's Experiments on Steam."

The system fully worked out and its applications are nearly ready for the press.

The author respectfully solicits thorough discussion of this system.

Copenhagen, 3, Valdemarsgade, V.,
April, 1891.

EIGHTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee reports the publication of the following works:—

1. "Index to the Literature of the Butines and their Halogen Addition Products" (1863—1887). By Mr. Arthur A. Noyes, in the *Technological Quarterly*, Boston, for December, 1888.

This should have been noticed earlier, but owing to the absence of the author, now in Europe, it was overlooked. It comprises an author- and a subject-index; the abbreviations used are those of the Standard List prepared by this committee.

2. "Index to the Literature of Thermodynamics." By Dr. Alfred Tuckerman. Miscellaneous Collections of the Smithsonian Institution, No. 741. Washington, D.C., 1890, pp. vi.—239.

This contains an author-index and a subject-index.

3. "Index to the Literature of Amalgams." By Prof. Wm. L. Dudley. In his Vice-Presidential Address to the Amer. Assoc. Adv. Science at Toronto.—*Proc. Amer. Assoc. Adv. Science* for 1889, pp. 161—171, 1890, 8vo.

4. "A Bibliography of Analytical Chemistry for 1883."—*Journ. Anal. Chem.*, iii., 1889.

5. The same for 1889.—*Journ. Anal. Chem.*, iv., 1890; and,

6. "A Bibliography of Chemistry for the Year 1886." Smithsonian Report for 1886—87. Washington, 1889.

These brief bibliographies are by Dr. H. C. Bolton.

7. Professor A. A. Breneman, in a "Historical Summary to his Memoir on the Fixation of Atmospheric Nitrogen" (*Journ. Amer. Chem. Soc.*, xi.), gives many bibliographical data.

The "Index Pharmaceuticus," published in the *Pharmaceutical Era* (monthly), and noticed in our sixth annual report, grows in scope and value. It is an alphabetical subject-list of original papers and important reprints and abstracts, appearing in thirty-two periodicals, English, American, French, and German. Although pharmacy is dominant, chemical topics are often included. The subject-index is followed by an author-index referring to the former.

The committee further report that several volunteer indexers are making progress. Dr. Alfred Tuckerman is engaged on an Index to the Chemical Influence of Light, and is planning more work of great value. Dr. James Lewis Howe is indexing the metals of the platinum group. Dr. H. C. Bolton reports progress on a Select Bibliography of Chemistry, which is an extension of the Bibliography of Historical Chemistry previously noticed; in the enlarged plan he is being assisted by Dr. Alfred Tuckerman.

As often stated in these annual reports, the Committee limits its duties to the encouragement of volunteer-indexers and to chronicling work performed. The fact that undertakings announced several years ago have not been recently noticed does not always indicate their abandonment; many will undoubtedly be brought to completion by their authors. Many chemists who are willing to contribute their quota to the general scheme are, however, deterred from making definite offers by the inadequacy of the libraries to which they have convenient access. This difficulty is a real one, and suggests that much might be accomplished by co-operation of several persons in a single subject, each indexing the sets of periodicals available, and submitting the partial work to one of the number for editing. In such an enterprise, conference between the several chemists uniting on a given topic would be necessary to avoid duplication and to secure a uniform plan.

Prof. W. O. Atwater, Director of the Office of Experiment Stations, Department of Agriculture, Washington, D.C., in conference with the committee, calls attention to the desirability of securing bibliographies and indexes to certain topics in the chemistry of plants and animals, such as (1) chemistry of albumenoid compounds; (2) chemistry of the so-called amid-compounds and kindred bodies; (3) chemistry of the fatty bodies; (4) chemistry of the lecithins, waxes, chlorophylls, chloresterin, &c.; (5) chemistry of the carbohydrates. These to meet a need which is being more and more keenly felt by physiological and agricultural chemists.

Subsequent to the presentation of this report, the Chemical Section authorised the insertion of the following minute:—

After a discussion in the Section on the continuance of a committee to confer with others with a view to founding a National Chemical Society, Dr. Albert B. Prescott suggested as a proper function of such a society the publication of an index to periodical chemical literature. He deprecated the multiplication of periodicals, and maintained the utility and importance of an index to the contents of those already in existence.

Respectfully submitted,

H. Carrington Bolton, *Chairman.*
F. W. Clarke.
Albert R. Leeds.
Alexis A. Julien.
John W. Langley (in Europe).
Albert B. Prescott.

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* From advance proofs of the "Proceedings of the American Association for the Advancement of Science," vol, xxxix. Communicated by H. Carrington Bolton.

CONCERNING THE PENTAGLUCOSES.*

By W. E. STONE.

(Concluded from p. 207).

B.—*Quantitative Reduction of Fehling's Solution by the Pentaglucoses.*

Both arabinose and xylose reduce Fehling's solution strongly, but their quantitative relation to it has not previously been studied, with the exception of a brief mention by Bauer of some limited determinations for arabinose, from which he concluded that it possessed in a slight degree greater reducing power than dextrose (*Landwirthschaftliche Versuch-Stationen*, xxxvi., 304).

In view of the common occurrence of the pentaglucoses, as already pointed out, it is evident that in the quantitative examination of any material for carbohydrates by hydrolytic methods, *i.e.*, by inversion with acids and titration of the glucose thus formed with Fehling's solution, we may be dealing not only with the true glucoses derived from starch, cane sugar, &c., but also with more or less of one or both of the pentaglucoses, since we know that the gums from which the latter are derived easily undergo hydrolytic change by the action of acids. Such analytical results may, therefore, be erroneous from two causes: first, from the assumption that the reduction of Fehling's solution is due solely to the presence of the true glucoses; or, second, from the assumption that the pentaglucoses, when present, reduce Fehling's solution in the same degree as the true glucoses.

Take, for example, such a material as brewers' grains,

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* Contributions from the Chemical Laboratory of Purdue University. From the *American Chemical Journal*, Vol. xiii., No. 2.

in which it might be desired to ascertain the thoroughness of malting and fermentation by determining the residual carbohydrate. Such material might contain no trace of starch or sugar, and yet might give abundant indications of the presence of these substances after inversion, because it contains so large an amount of the pentaglucose bodies that it is possible to isolate from it 2 per cent, or more, of the crystallised pentaglucoses (*Liebig's Ann. Chem.*, ccxlix., 241).

It seemed important, therefore, to know the relations existing between these bodies and the true glucoses, and I therefore determined the comparative values of arabinose and dextrose in dilute solutions toward Fehling's solution.

1. *Arabinose.*—The material used was prepared by me from cherry gum, and was pure, as was shown by its specific rotation ($[\alpha]_{D} = 104{\cdot}1^{\circ}$). From this material, solutions of 1, ¾, ½, and ¼ per cent strength were made. The Fehling's solution was prepared according to the standard formula, viz., 34·639 grms. of hydrous copper sulphate dissolved to a volume of 500 c.c., and 60 grms. sodium hydrate with 173 grms. sodium potassium tartrate dissolved to a volume of 500 c.c., the two solutions being preserved separately, and mixed in equal volumes just before using. The determinations were made gravimetrically as follows:—

70 c.c. of the Fehling's solution were brought to boiling, and exactly 25 c.c. of the arabinose solution quickly run in from a full pipette, after which the whole was kept over the flame exactly four minutes, of which the first fifty to sixty seconds were consumed in bringing the liquid to boiling again. The time of boiling and filtering was observed carefully. The precipitated cuprous oxide was collected on a Soxhlet asbestos filter with the aid of a pump, washed with boiling water, alcohol, and ether, reduced to metallic copper in a current of dry hydrogen over a low flame, and, after cooling in hydrogen, weighed. The following are the results obtained:—

1 *per cent Solution.*—25 c.c., containing 0·250 grm. arabinose, precipitated respectively:—

1. 0·4850 grm. copper.
2. 0·4874 ,,
3. 0·4860 ,,

An average of 0·48623 grm. copper, or for 0·001 grm. arabinose 0·001945 grm. copper.

¾ *per cent Solution.*—25 c.c., containing 0·1875 grm. arabinose, precipitated respectively:—

1. 0·3621 grm. copper.
2. 0·3631 ,,
3. 0·3640 ,,

An average of 0·36187 grm. copper, or for 0·001 grm. arabinose 0·001929 grm. copper.

½ *per cent Solution.*—25 c.c., containing 0·125 grm. arabinose, precipitated respectively:—

1. 0·2446 grm. copper.
2. 0·2430 ,,
3. 0·2479 ,,

An average of 0·2448 grm. copper, or for 0·001 grm. arabinose 0·001958 grm. copper.

¼ *per cent Solution.*—25 c.c., containing 0·0625 grm. of arabinose, precipitated respectively:—

1. 0·1264 grm. copper.
2. 0·1248 ,,
3. 0·1250 ,,

An average of 0·1254 grm. copper, or for 0·001 grm. arabinose 0·002 grm. copper.

From this it appears that in solutions of 1 per cent, or less, strength, 1 m.grm. of arabinose precipitates 1·9—2 m.grms. of copper.

2. *Xylose.*—The material used was prepared from wheat straw, and was of the desired purity, as shown by its specific rotation ($[\alpha]_{D} = 18{\cdot}41^{\circ}$).[*] The determinations were made under conditions as nearly as possible identical with those for arabinose, with the following results:—

1 *per cent Solution.*—25 c.c., containing 0·250 grm. xylose, precipitated respectively:—

1. 0·4686 grm. copper.
2. 0·4640 ,,
3. 0·4667 ,,

An average of 0·4664 grm. copper, or for 0·001 grm. xylose 0·001864 grm. copper.

¾ *per cent Solution.*—25 c.c., containing 0·1875 grm xylose, precipitated respectively:—

1. 0·3444 grm. copper.
2. 0·3446 ,,
3. 0·3462 ,,

An average of 0·3451 grm. copper, or for 0·001 grm. xylose 0·001841 grm. copper.

½-*per cent solution.*—25 c.c., containing 0·125 grm. xylose, precipitated respectively:—

1. 0·2378 grm. copper.
2. 0·2366 ,, ,,
3. 0·2381 ,, ,,

An average of 0·2375 grm. copper, or for 0·001 grm. xylose 0·0019 grm. copper.

¼-*per cent solution.*—25 c.c., containing 0·0625 grm. xylose, precipitated respectively:—

1. 0·1235 grm. copper.
2. 0·1222 ,, ,,
3. 0·1217 ,, ,,

An average of 0·1224 grm. copper, or for 0·001 grm. xylose 0·001959 grm. copper.

Under the stated conditions, therefore, 1 m.grm. of xylose precipitates 1·86—1·959 m.grms. of copper.

Dextrose, the most strongly reducing glucose heretofore studied, precipitates, under similar conditions, 1·8—1·9 m.grms. copper, or slightly less than the pentaglucoses. Stated in another way, the amounts of the different sugars in 1 per cent solution required to precipitate the entire copper from 1 c.c. of Fehling's solution are:—

Arabinose	0·004523 grm.[†]
Xylose	0·004617 ,,
Dextrose	0·004753 ,,
Levulose	0·005144 ,,
Invert sugar	0·004941 ,,
Galactose	0·005110 ,,
Milk sugar	0·006757 ,,
Maltose	0·007780 ,,

From this it appears that the two pentaglucoses are the most strongly reducing sugars yet studied, and this is particularly true of arabinose. Both differ from the value for invert sugar sufficiently seriously to effect the accuracy of analyses in which they are concerned but not recognised.[‡]

C.—*Fermentability of the Pentaglucoses.*

In connection with the history of arabinose, mention is made by various investigators of its behaviour toward fermenting agents, in which it is regarded as not subject to alcoholic fermentation. In some earlier studies of this body by Prof. Tollens and myself this view was substantiated, and it was further shown that this was a specific property of arabinose, in contradistinction from the true glucoses, galactose, levulose, and dextrose, which are all fermentable, some conflicting views regarding galactose being at that time cleared up.[§]

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[*] This unusually fine preparation was kindly furnished me by Dr E. W. Allen, of Washington, D.C. who prepared it himself, and to whom my thanks are due.

[†] Tollens, *Handbuch der Kohlenhydrate*, p. 284.

[‡] H. Ost (*Ber. d. Chem. Ges.*, 23, 3006), notes the reducing effect of arabinose on a solution of potassium-copper carbonate, and finds its value lower than that of dextrose, but higher than that of galactose, toward this reagent.

[§] *nn. Chem.* (*Liebig*), 249, 257; and *Ber, d, Chem. Ges.*, 21, 1572.

In his original paper, in which the discovery of xylose was announced, Koch described the same as non-fermentable, which was somewhat remarkable if it were a true glucose, as was at that time supposed. Its identity as a pentaglucose being afterwards established, it was of importance to show that it is, like arabinose, strictly non-fermentable, thus fixing this as a character of the $C_5H_{10}O_5$ group. In order to determine the non-fermentability of a given substance it is very essential that such a fermentation test shall be made under conditions favourable to the requirements and activity of the yeast plant used. No better example of this is known than that of galactose, which has been reported non-fermentable by some experimenters, who seemed to have worked with poorly nourished yeast or that deficient in vitality. Where there has been due regard for these conditions, galactose will produce nearly theoretical results of fermentation, although it is plain that it is less rapidly and easily subject to the influence of yeast than its isomers, levulose and dextrose. The method used for xylose was the same as that formerly applied to arabinose. Its special feature consists in supplying the yeast used with a nutrient extract, made by boiling 100 c.c. of the semi-fluid brewery yeast with 100 c.c. of water, and filtering off the dark brown extract resulting. Such a solution contains the natural constituents of the yeast, and, as a nutrient, seems to give better results than artificially prepared solutions of salts.

In the study of xylose two sets of experiments were performed. In one the carbon dioxide produced was collected, and in the other the alcohol. The former were conducted in eudiometer tubes which were first filled to within 15 c.c. of their capacity with mercury; then were added 5 c.c. of distilled water, 5 c.c. of the above-described nutrient solution, 5 c.c. of a mixture of 5 grms. of Fleischmann's compressed yeast with 50 c.c. of water, and lastly the weighed xylose. The tube was then inverted in a mercury trough, and the gaseous products of fermentation were allowed to collect in the upper end. A second tube filled in exactly the same way, but containing cane sugar instead of xylose, was arranged for comparison, and as an index of the activity of the yeast.

For the first experiment were taken 0·139 grm. xylose and 0·1566 grm. cane sugar. Within a quarter of an hour lively fermentation had begun in the cane-sugar solution, and after ten hours seemed practically complete. In the xylose solution no action was observed. After six days, no further action being noticeable, the necessary readings were taken for calculating the amount of gas collected (including that absorbed by the liquid) from the cane sugar. Less than 0·5 c.c. of gas had collected on the xylose solution, too little to indicate any appreciable fermentative action. The gas produced from the cane sugar was wholly absorbed by potassium hydrate solution, and was therefore carbon dioxide. Reducing the temperature and pressure to 0° and 760 m.m., the volume of the undissolved gas from cane sugar was 31·07 c.c., and of that absorbed in the solution, 13·16 c.c., or a total of 44·23 c.c., equal to 78·7736 m.grms., or 50·49 per cent of the sugar used.

In the second experiment were taken 0·1526 grm. of cane sugar and 0·1572 grm. xylose under the same conditions as before. In this case also the cane sugar underwent active fermentation, but no action was observed in the xylose solution. After seven days, measurements of the gas from the cane sugar, which was found to be carbon dioxide, gave a total of 78·506 m.grms., or 51·5 per cent.

The yield of alcohol was next determined in a third experiment. 1 grm. each of xylose and cane sugar was placed in flasks of about 200 c.c. capacity, with 35 c.c. of water, 5 c.c. of the nutrient fluid, and 10 c.c. of the yeast mixture. The flasks were closed with a water-valve. As in the other cases, the cane sugar showed active fermentation, but no action was detected in the xylose. After five days both solutions were neutralised with sodium carbonate, and after slight dilution, 50 c.c. distilled off and the alcohol determined in the distillates by taking their specific gravities with a Sprengel's specific-gravity flask.

50 c.c. of distillate from the cane sugar solution had the specific gravity 0·9982, equal to 0·472 grm. alcohol, or 47·2 per cent.

50 c.c. of distillate from the xylose solution had the specific gravity 0·9999, showing no appreciable amount of alcohol present.

Summing up the results of these experiments, we have:—

		Carbon-dioxide. Per cent.	Alcohol. Per cent.
1.	Xylose	—	—
	Cane sugar	50·49	—
2.	Xylose	—	—
	Cane sugar	51·50	—
3.	Xylose	—	—
	Cane sugar	—	47·20
Calculated for $C_{12}H_{22}O_{11}$		51·46	48·54

From this it appears that under those conditions which produced almost theoretical fermentation of cane sugar, xylose did not ferment in the least. It is therefore, like its isomer arabinose, non-fermentable, and this becomes a specific characteristic of the pentaglucoses.

It seems, therefore, that the pentaglucoses are of abundant occurrence in nature in the form of gum-like constituents of vegetable tissues; that these bodies are easily converted into the pentaglucoses themselves, and in such form are liable to be confused with the true glucoses, from which, however, they have quite different analytical, and as far as we know economic, values. In addition to the furfurol reaction, non-fermentability seems to be a further distinguishing property of the pentaglucoses.

In view of the importance of this group, a method by which they may be determined quantitatively in the presence of the true glucoses seems desirable. Such a method has lately been proposed by Günther and Tollens (*Ber. d. Chem. Ges.*, 23, 1751). Simultaneously with them I have been engaged upon the same subject with somewhat similar results, a more extended report of which is for the present reserved.

THE VOLUMETRIC COMPOSITION OF WATER.

By EDWARD W. MORLEY.

UNTIL recently our knowledge of the volumetric composition of water depended on the results of Humboldt and Gay-Lussac. They presented their memoir to the Academy of Sciences at Paris. The memoir was printed in full in the *Journal de Physique*, vol. lx., p. 129, and translated in Gilbert's *Annalen der Physik*, vol. xx., p. 38, 1805. Chaptal and Berthollet made a report on the memoir to the Academy, which is contained in the *Annales de Chimie de et Physique*.* Humboldt and Gay-Lussac made twelve experiments with an excess of hydrogen, and twelve with an excess of oxygen. They determined the amount of nitrogen in their oxygen by absorption with an alkaline sulphide, and with this oxygen determined the amount of nitrogen in the hydrogen. The mean error of the measurement of the residue after explosion with an excess of hydrogen was one part in five hundred, and in the experiments with excess of oxygen, one part in two hundred and fifty. From the experiments with excess of hydrogen they deduce 1·9989 as the measure of the ratio sought; from the experiments with excess of oxygen, they infer that both series together justify the conclusion that one hundred volumes of oxygen

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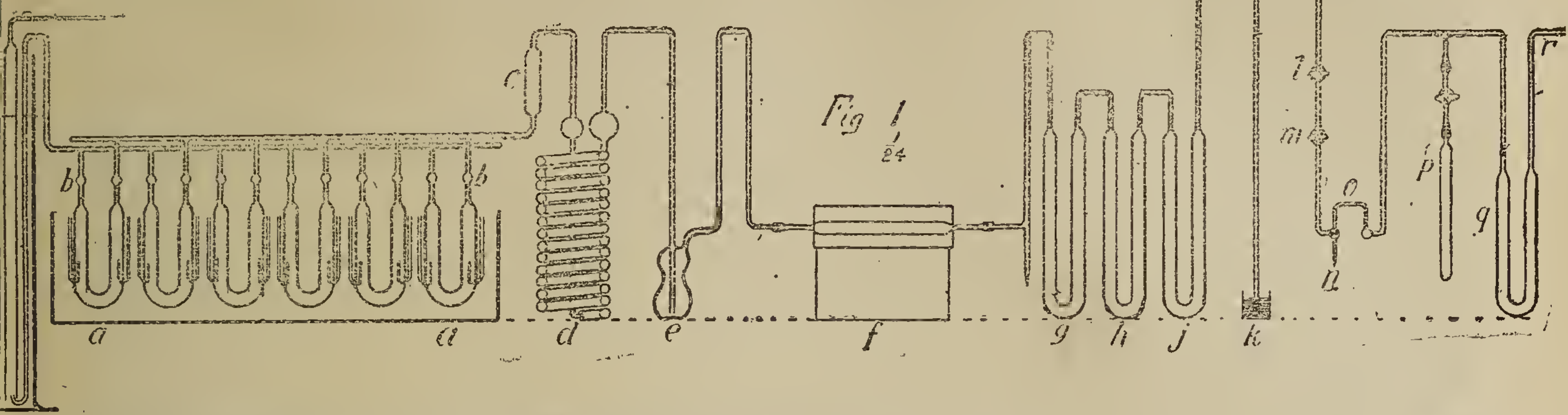
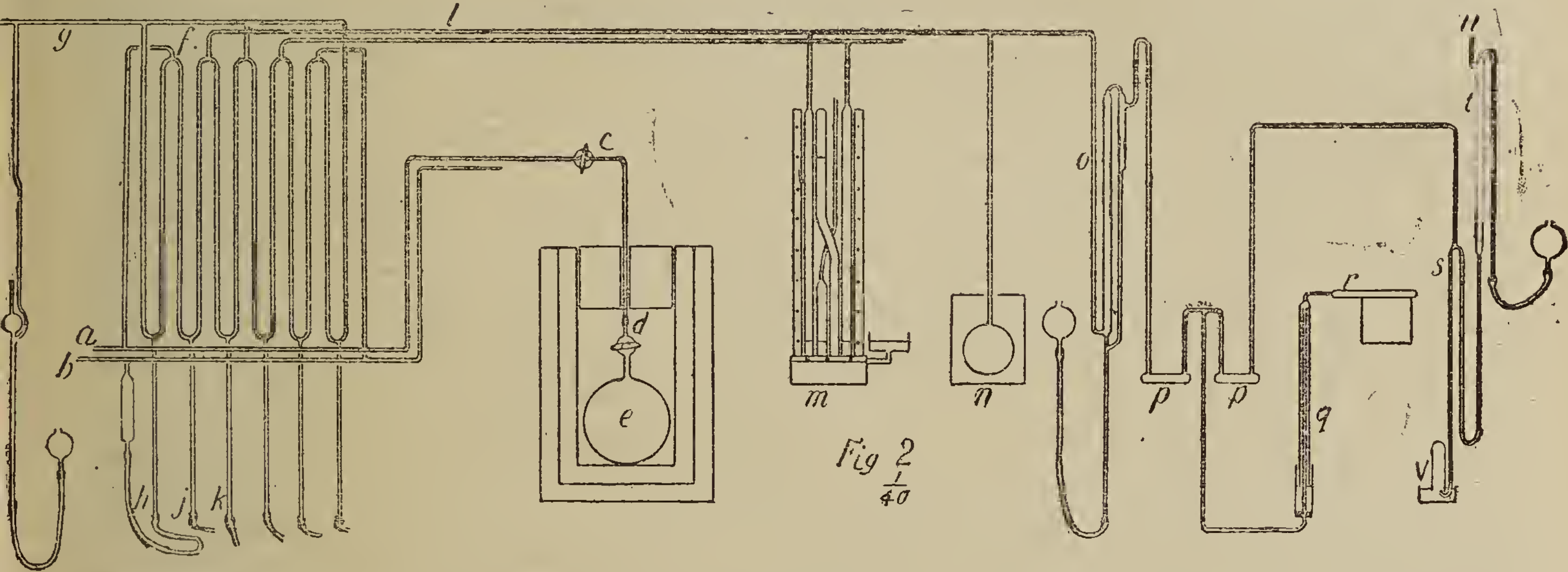
* Vol. liii., p. 239, 1805.





combine with very nearly two hundred volumes of hydrogen. They do not compute the ratio from the experiments with excess of oxygen: it would be 1·982. Since I began experiments on the matter, Scott has published several statements of his results. In his first paper,[*] he gives the results of twenty-one experiments. He gives two sets of values of the ratio sought; one computed on the assumption that the impurities found in the residue after explosion were originally distributed proportionally between the two gases, and the other on the assumption that all the impurity was contained in the oxygen. From the whole twenty-one experiments he gets the two values 1·9857 and 1·9941 respectively; excluding two experiments in which the impurity was very great, he gets 1·9897 and 1·9959; from the best four experiments he gets the values 1·9938 and 1·9964; from the six best, he gets the values 1·9938 and 1·9967. The mean error of a determination was one part in two hundred and fifty on the first assumption, and one part in five hundred on the second. Rejecting the two worst experiments, the mean errors become one part in five hundred and one part in seven hundred and fifty parts. He gives the value 1·994 as the most probable value of the ratio sought; but from a consideration of the same experiments, Young[†] judges that the value of the ratio is between 1·996 and 1·998, and may perhaps be taken as 1·997.

In the autumn of 1887, Scott[‡] stated that he had then made over thirty experiments, and gave the most probable value of the ratio as 1·996 to 1·997. In the spring of 1888, Scott[§] published four other experiments with a new and larger apparatus; their mean is 1·997; the gases used sometimes contained as little impurity as one part in fifteen thousand. In the autumn of 1888, Scott[||] stated that the volume of hydrogen required seemed to decrease when it was evolved continuously from the same apparatus; and that the variation showed some impurity at present undetected. He published the results of four experiments giving values varying from 2·001 down to 1·995.

My own experiments on this matter are a part of one of my processes for determining the ratio of the atomic weights of oxygen and hydrogen. In this determination the ratio of the densities of the two gases under ordinary conditions is one factor, and the ratio of their combining volumes under the same conditions is a second factor. Since it is difficult to free hydrogen from nitrogen, I hoped to obtain it free from every other impurity, and to determine the amount of nitrogen contained in it, so that I could compute a numerical correction to the observed density. I have now finished the determination of the combining volumes of the gases unless some as yet undetected error should necessitate further investigation. I have been able to reduce the mean error of a determination to less than one half of that which I ventured to predict early in the volumetric studies preliminary to the actual determination.[*] As the degree of accuracy which I hope it will be found that I have attained is very considerably greater than in determinations of the same kind by others, I have thought it needful to give a somewhat minute account of the details of the work, in order that those interested in the matter may better judge what degree of confidence mao fairly be reposed in the result, or may be in a position to suggest improvements or corrections needed in my processes. Though some parts of the work go back for many years, yet, thoroughly agreeing with the expression of Ostwald that he undertakes a heavy responsibility who publishes values of constants, I have made public no figures obtained till I have done the best that I know how to do.

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[*] *Proceedings R. S.*, vol. xlii, p. 398.
[†] *Nature*, vol. xxxvii., p. 390. 1888.
[‡] *Br. Assoc. Trans.*, 1887, p. 668.
[§] *Nature*, vol. xxxvii., p. 439, 1888.
[||] *Br. Assoc. Trans.* 1888, p. 631

[*] *Am. Chem. Journal*, vol. x, p. 23, 1888,

Preparation of Pure Hydrogen.—The preparation of pure hydrogen has been difficult. I tried long to obtain it by the action of dilute acids on zinc. It is in this way not difficult to obtain a gas free from arsenic and sulphur (or chlorine), and easy to obtain it free from oxygen by passing the hydrogen over heated copper; but two difficulties remain, one of which is serious. The amount of hydrogen which can be obtained from a given weight of materials is not always enough to sweep out all the nitrogen present in the apparatus or contained in the liquids used and still leave much of the gas to be utilised. Perhaps, by constructing the apparatus so that it can be repeatedly exhausted, this difficulty could be overcome. But a difficulty which I have not yet surmounted proceeds from impurities found in every sample of zinc which I have heretofore obtained. The metal contains gases which were absorbed by it during metallurgic processes; of such gases, carbon dioxide is but one; this could be easily removed, but there are present other gases which contain carbon; until they shall have been sufficiently investigated it is not certain whether they can be removed by absorption.

It is to be noted that this last difficulty is by no means removed by amalgamating the zinc, and using it as one pole of a voltaic element or of a decomposing cell. The best zinc I have found gave when so used hydrogen which after combustion in no very long time caused a precipitate in lime water. The gas also contained nitrogen which came from the zinc employed;[*] I therefore abandoned for the present the use of zinc. Dr. W. H. Burton kindly distilled in a vacuum for me some kilogrms. of so-called perfectly pure zinc; with which product I shall some time resume the preparation of pure hydrogen.

Having abandoned, perhaps too hastily, the attempt to get pure hydrogen from zinc, I resorted to electrolysis. The decomposition of an alkaline hydroxide seemed promising; by it one would expect to get nothing but hydrogen, oxygen, hydrogen dioxide, and ozone. From the decomposition of absolutely pure potassium or sodium hydroxides, no doubt this pleasing ideal might be realised. But two decomposing cells which I constructed for the purpose and filled with so-called pure potassium hydroxide yielded hydrogen containing carbon. This might possibly come from organic matter adhering to the interior of the cells, although I was at that time especially on my guard against carbon; but it was more probable that it came from the simultaneous electrolysis of an alkaline carbonate. I therefore made a new decomposing cell most carefully of clean glass and platinum, cleaned it from organic matters derived from glass blowing manipulations by long immersion in chromic acid, but filled it with potassium hydroxide to which I purposely added potassium carbonate. The electrolysis of this solution yielded hydrogen which instantly clouded lime water on combustion. It was therefore plain that the alkaline solution submitted to electrolysis must not contain any carbonate. This might no doubt be attained by using barium hydroxide, either alone, or added to potassium hydroxide to remove carbon dioxide. But since the so-called pure potassium hydroxide is purified by solution in alcohol, it is by no means certain that it may not contain carbon other than that existing in an alkaline carbonate. The matter, therefore, began to assume such an aspect that I resorted to the use of sulphuric acid.

Decomposing Cell for 25 Litres an Hour.—I have at command, through the courtesy of the East Cleveland Railroad Company, by day and night an electromotive force of five hundred volts. It was obviously proper to use the current from this source by passing it in succession through many small decomposing cells, rather than through one large cell. It was convenient to have at command a current of hydrogen up to twenty-five litres an hour. To obtain this from a single cell would require a current of some fifty amperes, consuming thirty-three horse-power. But if a current of one-thirtieth this amount is passed through thirty cells in succession, the same amount of hydrogen is obtained from one horse-power. I therefore sealed thirty decomposing cells to two delivery tubes, so that when the electric current is passed through them, the hydrogen produced is all given off at one tube, and the oxygen at the other. These cells were made by an eminent firm in Germany; twenty-six of them, on treating them precisely as those of my own construction had been treated, cracked at the bottom of the U-tube, having been obviously bent at too low a temperature. After this dismal accident, I had myself to make the set of decomposing cells shown in Fig. 1 at *aa*. Each of the six cells shown is the front one of a column of five which are fused into the transverse delivery tubes shown in section at *bb*. Six such columns are fused to the longitudinal delivery tubes. It is convenient to immerse the cells in water to keep them cool; it is therefore necessary to insulate each electrode in a glass tube as seen in the figure. The oxygen produced was led off to the tall cylinder seen to the left, containing a column of water such as to make the pressure on the escaping oxygen nearly equal to that on the hydrogen when it was permitted to escape at the end of the purifying train. This oxygen was sometimes utilised, as for oxidising copper. The set of decomposing cells was supported in a copper trough for water for cooling. It was filled with distilled water containing one-sixth its volume of pure sulphuric acid, which I distilled just before using it. The decomposing cells had a capacity of six litres; a little more than five litres dilute acid was put into them.

Purifying Train.—At *cc* is an enlargement to prevent the passage of acid over into *d*[*] when the current is rather rapid. *d* contains a 50 per cent solution of potassium hydroxide. *e* contains sulphuric acid for the preliminary drying of the gas. In the furnace at *f* is a tube filled with copper; this tube of hard glass is joined to the soft glass tubes of the rest of the apparatus by ground joints made tight with syrupy phosphoric acid. As this part of the apparatus was not exhausted, no difficulty was experienced in keeping the joints tight. At *g* is a tube containing glass beads and sulphuric acid; this (as well as the two following tubes) lay horizontally, so that the acid should remain well distributed throughout the beads. At *h* is a tube filled with powdered potassium hydroxide, and at *j* is a tube filled with glass wool and phosphorus pentoxide. At *k* is a vent through mercury; at *m* are two glass stop-cocks in succession, which have been lubricated with syrupy phosphoric acid. Their office is at present simply to regulate the flow of gas when the valve at *o* is opened.

At *o* is a valve consisting of glass tubes containing plugs of fusible metal. Two tubes which are perpendicular to the plane of the paper are seen in section; between them are placed several inverted U-tubes. Each one contains a plug of metal; when it is desired to admit hydrogen to the part of the apparatus to the right of the valve, one of the plugs is fused; when it is desired to close the valve, the glass tube is fused together. It may be noted that with a proper composition of the metal, these valves make a joint as tight as could be desired, and that there was no failure by the splitting of the glass tube. By having several of these tubes it was possible to make and again to cut off the connection between the two parts of the apparatus as often as desired. Of course new tubes were put in before each experiment: in this way air was admitted to the tube between the valves *o* and the stop-cock *m*, but air never was admitted into the part of the apparatus to the left of *m* except by fracture of the apparatus. To remove the air from the tube *mo*, a tube was provided as shown at *n*; from which hydrogen was permitted to escape for a long time before each experiment. When *n* was closed by

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[*] *Amer. Chem. Journal*, vol. xii., p. 461, 1890.

[*] The individual parts of the apparatus are drawn accurately to scale, as noted; but the connections between parts are represented more compactly than in the actual apparatus.

fusion, one of the valves at *o* was opened and the connecting tube between *m* and *o* was exhausted by the pump which had exhausted the apparatus to the right of *o*. During this exhaustion the two stop-cocks *m* had to withstand a difference of pressure equal to that of the atmosphere. This they could not do without permitting some leakage of hydrogen into the vacuum which was then producing to the right of *m*. This, however, gave no difficulty, the exhaustion of the large volumes *e* and *n* had already been accomplished under the security of the perfectly tight metal valve, and then these were shut off, so that the leakage during the subsequent exhaustion of *m o p q r*, Fig. 1, and *a c d*, Fig. 2, was so slight that a vacuum of 1-50000 could be obtained in the small volume in question.

It was desirable that the hydrogen to be analysed should not pass over any organic lubricant unless the lubricant were proved not to give up any carbon compound to the gas. Rather than investigate lubricants, I used syrupy phosphoric acid on the glass stop-cocks, and at first used no fusible metal valves, but prevented leakage while the exhaustion of the large valumes *c* and *n*, Fig. 2, was in progress by maintaining a vacuum between the two stop-cocks by means of a second mercurial pump; but the manipulation was troublesome, and if the exhaustion was interrupted, the whole labour had to be recommenced.

In some of my experiments, I used hydrogen purified by the process suggested by Chirikoff,* namely, by utilising the power of palladium to absorb hydrogen, and to give it off again at a higher temperature. In such experiments, a tube containing palladium was connected as shown at *p*, but a tube containing phosphorus pentoxide should have been shown between *o* and *p*, intended to arrest any aqueous vapour which might possibly be given off by the syrupy phosphoric acid at *m*. A second drying tube was placed at *q*, to answer the same purpose for the gas which should pass directly to *r* and the following parts of the apparatus.

The apparatus so far described serves to prepare pure hydrogen. In the case of all impurities to be feared, except oxygen and nitrogen, their absence is capable of proof by direct experiment, as sensitive reagents are applicable. It was not expected that hydrogen free from nitrogen could be prepared, and apparatus designed to measure the residual nitrogen was constructed, and will shortly be described. The only question remaining is as to the possible presence of oxygen after the hydrogen had passed the tube containing heated copper at *f*. To determine how much of a given substance fails to be absorbed by the best absorbent of the substance can be determined commonly only by indirect means which are of limited application. But in regard to the absorption of oxygen by hot copper, I think we can answer the question, and can perhaps also judge whether the presence of a great quantity of hydrogen will lessen the completeness of the absorption. If we pass a current of air containing a little aqueous vapour through a tube filled with phosphorus pentoxide, and also pass a current of air over heated copper in another tube, we can in some sort compare the activity of the two absorptions by observing how far each absorbent is visibly affected. I think we may judge that the copper is not enormously less active than the phosphorus pentoxide. Suppose the phosphorus pentoxide is a hundred or a thousand times more active. Now, partly to obtain a solution of the present problem, I have determined† the amount of aqueous vapour which fails to be absorbed by a phosphorus pentoxide tube containing 25 c.c., when the rate of the current of gas is two litres an hour; the volume of the aqueous vapour left unabsorbed is not more than a thirty-millionth of that of the air. If then we make the surfaces exposed and the time of exposure comparable for the two absorbents, we may expect that the copper will permit not over a hundred or a thousand times this quantity to escape; by increasing the exposed surface, and the time of exposure, the absorption may be made as complete as we please, for at the temperature used, we have reason to believe that the reaction between copper and oxygen is not reversible. Considering also the action of hydrogen which accompanies the oxygen and is heated with it, it seems to me impossible to suppose that the gas of my experiments contained any such quantity of oxygen as 1-200000 its volume.

Purity of the Hydrogen Obtained.—Each time when a globe was filled with hydrogen for the determination of density, the amount of nitrogen in the hydrogen was determined. The first trial was made when a current of two or three litres an hour had been evolved for three days; the gas then contained 0·00035 volumes of nitrogen. The amount became gradually less as the amount of hydrogen obtained from the apparatus increased. When the apparatus was not in use, it was always left closed by fusion against the entrance of nitrogen except by diffusion through the water in which the oxygen delivery tube ended. When about six hundred litres had been obtained, it became difficult to detect nitrogen; that is, its amount was less than one part in one hundred thousand. Sometimes concordant determinations of the amount of nitrogen showed only one part in two hundred thousand.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

April 16th, 1891.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

MESSRS. J. C. Ayland, J. E. Marsh, G. A. Pingstone, and G. H. Robertson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Duncan, 10, Plough and Harrow Road, Edgbaston, Birmingham; Alfred John Gregory, The Bays, Knights Hill, West Norwood, S.E.; John Knowles, Northwich, Cheshire; Frank H. Leeds, 29, Bouverie Road, Stoke Newington, N.; Robert Andrew Scott Macfie, Rowton Hall, Chester; Frank O. Solomon, North-Eastern County School; Dr. Otto Carl Weber, Rectory Road, Crumpsall, Manchester; Seward W. Williams, East Orange, New Jersey, U.S.A.

The following papers were read:—

5. "*Studies on the Formation of Substitution Derivatives.*" By H. GORDON, M.A.

The following notes relate to a part of a series of investigations undertaken by the author, in the laboratory of the Central Institution, with the object of throwing further light on the laws which govern substitution in the case of benzenoid compounds. It was stated by Armstrong in 1875 (*Chem. Soc. Journ.* 520), that when *parabromo*diorthonitrophenol was warmed with bromine, it underwent isomeric change into *orthobrom*orthoparadinitrophenol. Several other cases, in which, perhaps a similar change takes place, were briefly discussed in the same paper. The author, at Dr. Armstrong's suggestion, has revised these observations, and, while confirming the main result, is able to correct and explain others.

The Action of Bromine on Diorthonitrophenol.—The action of bromine on an acetic acid solution of diorthonitrophenol was found to give, at *ordinary temperatures*, the normal product, namely, *parabrom*diorthonitrophenol. On the other hand, when the mixture was heated for a short time at 100°, the product consisted of a mixture of the two isomers, *parabrom*diorthonitrophenol and *orthobrom*orthoparadinitrophenol. This mixed product by continued heating at 100° with small quantities of bromine was gradually converted into *orthobrom*orthopara-

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* *Journal Russ. Phys. Chem. Soc.*, 1882, Chemical Part, p. 47.
† *American Journal of Science*, vol. xxxiv., p. 199, 1887.

dinitrophenol. *Parabrom*diorthonitrophenol is therefore completely converted by the action of heat and bromine into the isomeric orthobromorthoparadinitrophenol.

In connection with the above facts, it is of interest to note that, whereas Körner (*Gaz. Chim. Ital.*, 1874, 327—397), found that on nitrating crude bromphenol, *parabrom*dinitrophenol was obtained, Hübner and Brenken (*Ber.*, 6, 170), obtained *orthobrom*dinitrophenol. At the time, Armstrong suggested that these facts might be explained by assuming that Hübner and Brenken had carried out the nitration in such a way as to condition isomeric change. Some experiments were made with the view to ascertain whether nitric acid would bring about this change, and it was found that by heating an acetic acid solution of *parabrom*diorthonitrophenol with a few drops of nitric acid at 100° for a short time, the whole was converted into the isomeric *orthobrom*diorthonitrophenol.

At this point it was thought important to ascertain whether similar changes could be brought about in the corresponding chloro-compounds. Some difficulty was encountered in preparing the parachlorodinitrophenol from diorthonitrophenol, and it was found that chlorine had no action on the phenol dissolved in acetic acid at 100°, even in the presence of iodine. The chlorination was effected by passing chlorine into a solution of diorthonitrophenol in antimony pentachloride heated to about 105°. Only the normal product, parachlorodinitrophenol, was obtained.

Action of Bromine on Parachlordiorthonitrophenol.—Various experiments were carried out under different conditions to ascertain whether any isomeric change could be effected by the action of bromine on parachlordinitrophenol, but in every case with negative results, the normal product, parachlororthobromorthonitrophenol, being formed in every case and no isomer. The result appeared to be in opposition to results published by Ling (*Chem. Soc. Journ.*, 1887, 789), which stated that the action of bromine at 100° on parachlororthonitrophenol is to form parabromorthochlororthonitrophenol. Ling, however, on repeating his experiments (*Chem. Soc. Journ.*, 1889, 588), found that his former statement was incorrect, and that no isomeric change had taken place. The author considers that the probable explanation of the isomeric change observed in the case of bromdinitrophenol is that the bromine first *combines* with the nitro-compound, and that, at the moment of breaking up, the bromine and NO_2 change places; in the case of the chlorine compound, a similar change does not take place, probably because the chlorine is more firmly held than bromine.

Action of Sulphuric Acid on Orthoparadichlorphenol-orthosulphonic Acid.—In the paper to which reference has already been made, Armstrong indicates that possibly, by the combined action of heat and sulphuric acid, orthoparadichlorphenolsulphonic acid could be converted into the isomeric diorthochlorparaphenolsulphonic acid. As this would be a very remarkable change, the experiments were repeated under a great variety of conditions of temperature, &c., but in no case was such a change found to take place. Armstrong was no doubt misled by the presence of some diorthochlorphenol in his orthoparadichlorphenol, prepared by the action of chlorine on phenol, which gives rise to both dichlorphenols. It appeared possible that, although no isomeric change took place in the case of dichlorphenol, yet it might occur in the case of the corresponding dibromphenol. The results tended to show that this was not the case; but as several secondary reactions set in, such as the formation of tribromphenol, &c., this reaction was not further investigated.

The Chlorination and Bromination of Phenol.—Phenol, when chlorinated in the ordinary manner, yields a mixture of para- and ortho- chlorphenol (Peterson and Bähr-Predani). As shown by Dubois in 1867, phenol may also be chlorinated by means of SO_2Cl_2, but it was not known whether the product in this case was a mixture of the two isomers; the author has therefore examined it, and finds it to be a mixture similar to that obtained by means of chlorine alone.

Further, he has investigated the action of bromine on phenol under the conditions described by Hübner and Brenken (*Ber.*, 6, 170), and finds that the product is practically pure parabromophenol. If it be assumed that the initial action of chlorine and bromine on phenol is to form an additive compound, which then becomes resolved into hydrogen chloride or bromide and the mono-substituted phenol, it would appear that, at the moment of change, the resulting ortho-compound, in the case of bromine, at once undergoes conversion into the para-derivative; but in the case of chlorine this only partially takes place, owing to the chlorine being more firmly held.

The Sulphonation of the Nitrophenols.—Orthonitrophenol and paranitrophenol, according to experiments published by Armstrong (*Chem. Soc. Journ.*, 1871, 175), are both readily acted upon by SO_3HCl; the former yields the well-known sulpho-acid; the product from the latter, however, is decomposed by water and is not identical with the sulpho-acid subsequently obtained by Post. It was to be supposed that the product obtained by Armstrong was the sulphate, and this the author finds to be the case. It is scarcely probable that the initial action is different in the two cases; it is more likely that the sulphate formed from the orthonitrophenol at once undergoes isomeric change, and that, owing to its greater stability, does not occur in the case of the paranitrophenol. The author did not succeed in obtaining any sulpho-acid by heating at 100° the sulphate from the paranitrophenol. On adding SO_3HCl (2 mols.) to paranitrophenol (1 mol.) and heating at 100°, however, a not inconsiderable amount of sulpho-acid was formed, although much of the material was carbonised.

There can be little doubt, therefore, that the paranitrophenol-sulphonic acid is formed by the sulphonation of the previously formed sulphate.

Metanitrophenol closely resembles the para-compound in being readily converted into the sulphate, but not into the sulpho-acid even by the action of heat. The author is engaged in further investigating the action of sulphonating agents on metanitrophenol.

Discussion

Mr. A. R. Ling said that unfortunately he had made a mis-statement in his work on isomeric change (*Trans.*, 1887, 789), and he wished to thank Mr. Gordon for pointing it out; he had, however, corrected it in a subsequent communication (*Trans.*, 1889, 588). In the latter paper he had recorded a case of isomeric change (when orthochloroparabromophenol is nitrated), similar to that observed by Hübner and Brenken, cited by the author. Referring to the action of SO_2Cl_2 on phenol and its derivatives, Mr. Ling said that he agreed with the author that this agent yielded the same mixture of monochloroderivatives as chlorine alone; he remembered, moreover, having once made an experiment to prepare dichlorophenol from SO_2Cl_2 and phenol, and finding that the reaction apparently stopped at the formation of the mono-derivative; this was the more remarkable as parabromophenol may readily be chlorinated by SO_2Cl_2 (*cf. Trans.*, 1889, 587). His experience of the difficulty of obtaining chloro-derivatives of the nitrophenols by acting on the latter with chlorine was the same as Mr. Gordon's, and on this account he preferred to prepare the chloronitrophenols by nitrating the chloro-derivatives. On other points, including the tendency of the bromonitro-derivatives to undergo isomeric change, and the apparent absence of this property in the case of the chloronitro derivatives, their results were in complete accord.

6. "*Compounds of Dextrose with the Oxides of Nickel, Chromium, and Iron.*" By Alfred C. Chapman.

The author describes compounds of dextrose with the oxides of nickel, chromium, and iron respectively. The nickel compound was prepared by adding a solution of nickel hydrate in strong aqueous ammonia to a concentrated solution of dextrose in 90 per cent alcohol. It is a green, amorphous substance, insoluble in water and alcohol, of the formula $C_6H_{12}O_6\cdot 2NiO+3H_2O$.

To prepare the chromium compound, an excess of dextrose is dissolved in an aqueous solution of chromic chloride, and this solution is poured into an excess of cold strong ammonia. The precipitated hydrate partly re-dissolves on standing, and the purple solution so obtained gives, on pouring it into 90 per cent alcohol, a lilac-coloured precipitate of the chromium dextrosate. The dry compound is a slate-coloured, amorphous substance, insoluble in water and alcohol. Its composition appears to be represented by the formula

$$C_6H_{12}O_6\cdot Cr_2O_3+4H_2O.$$

The compound of dextrose with ferric oxide is prepared by adding a slight excess of ammonia to a solution of ferric chloride in which an excess of dextrose has been dissolved. The red precipitate which at first forms soon re-dissolves on standing, giving a deep red solution. If this liquid be poured into 90 per cent alcohol, a red, flocculent precipitate of the dextrosate of iron at once forms. The moist compound dissolves easily in water, giving a red solution which is decomposed on boiling, but is not decomposed by ammonia, potassic ferrocyanide, or potassic thiocyanate. The dry compound is an orange-red, amorphous substance, insoluble in water and alcohol. It has the formula $2C_6H_{12}O_6\cdot 3Fe_2O_3+3H_2O$.

Discussion.

Remarks were made by several speakers with reference to the possible influence on the composition of such substances as described by the author of variations in the proportions of the interacting compounds, their stability in aqueous solution, and their behaviour towards polarised light. Dr. **Teed**, referring to the circumstance that the ordinary iron reactions were not manifest in the case of the compound of iron oxide with glucose until after the addition of chlorhydric acid, pointed out that the thiocyanate colouration ordinarily regarded as characteristic of ferric salts was also only developed in presence of certain acids, especially chlorhydric acid. The **President**, referring to the tendency of chromium to form basic salts, pointed out that the formula of the chromium compound would be analogous to those of the zinc and nickel compounds if it were written $C_6H_{12}O_6\cdot 2(CrO\cdot HO)\cdot 3H_2O$; the iron compound, however, did not appear to have an analogous composition.

The author, in reply, after describing the behaviour of the compounds when boiled with water, said that he had not yet completed their examination.

7. "*A Rapid Method of Estimating Nitrates in Potable Waters.*" By G. Harrow, Ph.D.

The method depends on the reduction of nitric to nitrous acid by means of zinc dust and chlorhydric acid, in a very dilute solution, in presence of α-naphthylamine and sulphuric acid, the estimation being made by comparing the depth of the pink azo-colouration developed in the solution with that arising on similar treatment of standard nitrate solutions. A beaker, containing 50 c.c. of the water, is placed on a sheet of white paper side by side with other beakers holding 50 c.c. of standard solutions containing 1·0, 0·1, and 0·01 of nitrogen as nitrate per 100,000, and to each is added 10 c.c. of a test solution, prepared by dissolving 1 grm. of α-naphthylamine, 1 grm. of sulphanilic acid, and 25 c.c. of chlorhydric acid in about 200 c.c. water, boiling with a small quantity of animal charcoal, filtering, and making up to 500 c.c. A very small quantity of zinc-dust—7 to 8 milligrms.—is added to each beaker. If nitrate be present in the water, a more or less intense pink colour is developed, which may be compared, at the end of 15 minutes, with that arising in the standard solutions. By diluting the water until the tint produced is judged to be of the same intensity as that of one of the standards—preferably the most dilute—a first approximation is arrived at; and the water, having been diluted to the extent indicated by the results, a fresh experiment is made with this diluted water. When nitrites are present, the amount is estimated in a similar manner prior to the addition of zinc-dust, and due allowance is subsequently made. The author quotes a considerable number of comparisons with the Crum method, which show that very satisfactory results are obtainable.

Discussion.

Mr. **Warington** said that he looked doubtfully on the method proposed, as nitrous acid was not the only product of the action of zinc. The result would be accurate only if the conditions were precisely the same in the solutions compared. The author was right in making a final experiment in which the solutions to be compared were of the same strength. Quantitative analysis by means of colour-depths is perfectly safe only when, as in the old Nesslerising method, the final comparison is between solutions of equal strength. In not a few cases the depth of tint produced is not uniformly proportional to the quantity of substances present, very dilute solutions generally giving a weaker tint in proportion to their strength than strong solutions; this is, for instance, the case in the well-known interaction of metaphenylenediamine and nitrous acid. The speaker also questioned whether the method was more rapid than the indigo method.

Professor P. F. **Frankland** suggested that probably in presence of the naphthylamine, which would tend to destroy the nitrous acid as it was formed, the reduction of the nitrate would be confined to the production of nitrous acid.

8. "*The 'Gravivolumeter': an Instrument by means of which the Observed Volume of a Single Gas gives directly the Weight of the Gas—a Preliminary Note.*" By Francis R. Japp, F.R.S.

An apparatus for effecting this object has been described by Lunge (*Ber.*, 23, 448; see also *Ber.*, 24, 735); but his method labours under the disadvantage of requiring for each gas a separate apparatus with a special graduation. Thus Lunge's apparatus for measuring nitrogen is a "gas volumeter," with divisions of 0·798 c.c. (further subdivided into tenths), each of which divisions will contain a milligrm. of nitrogen under standard conditions. The reduction to standard state is effected mechanically by means of the "regulator" attached to his gas-volumeter.

The author desires to point out how a gas apparatus may be constructed, by means of which, with an ordinary graduation in cubic centimetres, any required single gas may, without observation of temperature or pressure, and without calculation, be measured under such conditions that each cubic centimetre represents a milligrm. of the gas. The form of the apparatus is, with slight modifications, that of Lunge's gas volumeter (*Ber.*, 23, 440); the method of employing the regulator is, however, different.

The apparatus consists of two gas burettes of, say 50 c.c. capacity each. One of these is the gas measuring tube; the other performs the function of the "regulator" in Lunge's gas volumeter, and may be termed the "regulator tube." Both are connected, as in Lunge's gas volumeter, by means of stout flexible tubing and a T-piece, with the *same* movable reservoir of mercury. Both are moistened internally with a drop of water, in order that the gases they contain may be saturated with aqueous vapour.

The 25 c.c. division of the regulator tube is taken as the starting point in calculating what the author terms the "gravivolumetric values" of the different gases to be measured. Thus in the case of nitrogen he calculates to what volume 25 c.c. of "standard-dry" nitrogen must be brought in order that 1 c.c. would correspond with 1 m.grm. of the gas: that is to say, 25 c.c. of standard-dry nitrogen $0·001256\times 25=0·0314$ grm.; and, therefore, these 31·4 m-grms. of nitrogen must be brought to the volume of 31·4 c.c. The division 31·4 on the *regulator* tube is marked N_2. Corresponding points are in like manner determined for the various other gases which it is desired to measure, and these points are similarly marked O_2, CO_2, &c., as the case may be, on the regulator tube. Finally, the thermometer and barometer are read (a process which is only necessary once for all in setting the regulator); the volume which 25 c.c. of standard-dry air would occupy if measured moist at the observed temperature and pressure is calculated; and this calculated volume of air is admitted into the regulator tube and the tap closed. The instrument is now ready for use.

Suppose it is desired to ascertain the weight of a quantity of nitrogen contained in the measuring tube. The mercury reservoir is lowered until the mercury in the regulator tube stands at the nitrogen mark, 31·4, at the same time adjusting the regulator tube itself, by raising or lowering it bodily, so that the mercury level in the measuring tube and the regulator tube may be the same. *Under these circumstances each c.c. of gas in the measuring tube represents a m.grm. of nitrogen.* For since in the regulator tube 25 c.c. of standard-dry air have been made to occupy the volume of 31·4 c.c., and as the gases in the two tubes are under the same conditions as regards temperature, pressure, and saturation with aqueous vapour, therefore, in the measuring tube, every 25 c.c. of standard-dry nitrogen has also been made to occupy the volume of 31·4 c·c. But 25 c.c. of standard-dry nitrogen weigh, as we have seen, 31·4 m.grms.; so that the problem is solved, and the c.c. and tenths of c.c. give directly the weight of the gas in m.grms. and tenths of m.grms.

The various other single (*i.e.*, unmixed) gases may be weighed in like manner by bringing the mercury in the regulator tube to the "gravivolumetric mark" of the gas in question, and adjusting the levels as before. An exception would be made in the case of hydrogen, which would be brought to such a volume that the c.c. would contain a tenth of a m.grm.

Lastly, if the mercury in the regulator tube be brought to the mark 25, a gas or mixture of gases in the measuring tube will have the volume which it would occupy in the standard-dry state. In this form the instrument is merely a gas-volumeter, as described by Lunge, and may be employed for ordinary gas analyses.

The "gravivolumeter" is thus designed to fulfil a variety of purposes for which Lunge employs a number of different gas-volumeters. Whether it will fulfil these purposes equally well remains to be seen. The theoretical principle is unimpeachable; but there are doubtless practical difficulties to be overcome before the "gravivolumeter" can rank as a working laboratory appliance. Very likely the foregoing (merely provisional) dimensions of the regulator would have to be increased in order to give sufficient accuracy of adjustment. The author proposes to have the instrument constructed in various forms, so as to ascertain the most suitable. He anticipates that it will, at all events, give results sufficiently accurate for technical purposes. Meanwhile he desires, by this preliminary note, to place on record this principle of gas analysis, which he believes to be new—the principle of measuring the various single gases at such a volume that each c c. contains a m.grm. of the gas.

Mr. de Mosenthal exhibited one of Lipmann's "coloured" photographic negatives.

9. "*The Action of Acetic Acid on Phenylthiocarbimide.*" By J. C. Cain and J. B. Cohen, Ph.D., Owens College, Manchester.

The authors have repeated the experimens of Hofmann, and show that the product of the action of pure glacial acetic acid on phenylthiocarbimide is not diacetanilide as stated by Hofmann; but that two compounds are formed, viz., diphenylurea and acetanilide. The proportion of these products depends upon the temperature at which the mixture is heated. At a lower temperature, diphenylurea is mainly formed, and at a higher temperature, acetanilide.

The action, which appears to take place in two stages, may be expressed by the following equations:—

1. $2C_6H_5NCS+6C_2H_4O_2=(C_6H_5NH)_2CO+$
$+3(C_2H_3O)_2O+2H_2S+CO_2$.

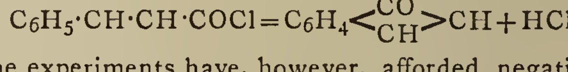
2. $(C_6H_5NH)_2CO+2C_2H_4O_2=2C_6H_5NH_2+$
$+(C_2H_3O)_2O+CO_2$.

These interactions are independent of the presence of water.

10. "*The Action of Aluminium Chloride on Benzenoid Acid Chlorides.*" By R. E. Hughes, Jesus College, Oxford.

At Mr. Marsh's suggestion, the author has examined the action of aluminium chloride on cinnamic and hydrocinnamic chlorides in the expectation that pentamethylene derivatives might result from the occurrence of an internal condensation analogous to the external condensation which attends the formation of acetophenone from acetyl chloride and benzene, thus:—

$$CH_3{\cdot}COCl+C_6H_6=CH_3{\cdot}CO{\cdot}C_6H_5+HCl.$$



$$C_6H_5{\cdot}CH{\cdot}CH{\cdot}COCl=C_6H_4{<}{\substack{CO\\CH}}{>}CH+HCl.$$

The experiments have, however, afforded negative results. The chloride was either dissolved in or mixed with (in the case of hydrocinnamic chloride) light petroleum, and aluminium chloride was then added; action set in at 80—90° in the case of cinnamic, and at about 50° and more briskly in the case of hydrocinnamic, chloride. The chief product in either case was an ill-characterised substance, the nature of which remains to be determined. Both chlorides afforded a small amount of the aluminium salt of the corresponding acid in the form of a microcrystalline powder, insoluble in alcohol, benzene, ether, and petroleum, slightly soluble in a warm solution of sodium carbonate.

The author incidentally describes the following hydrocinnamic derivatives.

Hydrocinnamic chloride, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COCl$, boils at 117—119°, under 13 m.m. pressure; the author specially points out that the properties of this chloride are strikingly similar to those of benzoic chloride and characteristically different from those of cinnamic chloride, which, unlike most acid chlorides, is a remarkably inert substance, being only very slowly decomposed by water or caustic alkalis.

Hydrocinnamide crystallises from hot alcohol, in which it is readily soluble, in stellate groups of needles melting at 82°; it is readily soluble in hot water.

Hydrocinnamanilide crystallises from hot alcohol in faintly yellow plates melting at 92°.

It is noted that benzoic and cinnamic acids may be readily separated by treating the mixture with phosphorus pentachloride and distilling the product under reduced pressure, the portion passing over below 95° under 10 m.m. pressure contains the benzoyl chloride.

OBITUARY.

THE LATE JAMES BUCKTON MACKINTOSH, C.M.

It is our painful duty to put on record the death of an eminent American chemist, James Buckton Mackintosh, C.M. The deceased, one of the many victims of the prevailing epidemic of influenza or dengue-fever, died at New York on April 15th last. Mr. Mackintosh had made a speciality of the rare earths and was collecting materials for a monograph on the methods for their separation. He was born either at Montrose or Birkenhead, and obtained his chemical education in the Liverpool Schools. In 1873 he emigrated to the United States, and, until his death, resided at Hoboken. We regret that our informant, though an old friend and family connection of the deceased, has not been able to give us the titles and dates of his researches, having been at the time away from home. For some years he was chief chemist to the New York Consolidated Gas Company and principal assistant to Prof. Eggleston, of the School of Mines.

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. cxii., No. 15, April 13, 1891.

Transformation of Cupreine into Quinine.—E. Grimaux and A. Arnaud.—On comparing the formula of cupreine, $C_{19}H_{22}N_2O_2$, with that of quinine, $C_{20}H_{24}N_2O_2$, these two bodies seem to have the same relation as phenol, C_6H_6O, and its methyl-ether, C_7H_8O. Cupreine being a body of mixed functions, partly a base and partly a phenol, quinine would be its methyl-ether—a view which is completely confirmed by experiments. The natural products extracted from plants often contain the methyl group, but never the ethyl group. The reason for this fact is probably that plants, in absorbing carbonic acid, convert it by a reductive process into methylic aldehyd, and then into methylic alcohol.

The Action of Hydrobromic Acid upon Silicon Chloride.—A. Besson.—Theory enables us to foresee the existence of three silicon chlorobromides, all of which the author has obtained by the action of HBr upon S_2Cl_4.

Thermo-Chemical Study of Platinum Chloride and its Combinations.—L. Pigeon.—This paper does not admit of useful abstraction.

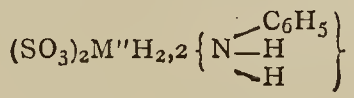
Electrolytic Determination of Rhodium.—A. Joly and E. Leidié.—Rhodium may be electrolytically determined with great accuracy in compounds which contain no other metals save those of the alkaline class. It should be present preferably as chloride or sulphate. An excess of acid delays but does not prevent the deposition of the metal, and the decomposition yields no products save the metal at the negative pole and the products of decomposition of the acid at the positive pole. The present study is the first portion of an extended research which the authors have undertaken on the separation of the metals of the platinum group from each other and from the common metals, such as copper, lead, iron, bismuth, and zinc, which accompany them in their ores.

On an Amidoisoxazol.—M. Hanriot.—This memoir is not adapted for useful condensation.

The Use of Phenylhydrazine in the Determination of Sugars.—M. Maquenne.—The action of phenylhydrazine upon the reductive sugars is the only means of precipitating these bodies in a definite form from solutions in which they are mixed with other substances. The weight of the osazones thus obtained on heating a given weight of the different sugars for the same time with the same quantity of the hydrazinic reagent varies from one sugar to another within very wide limits if we operate under strictly identical conditions.

On a Violet Colouring Matter derived from Morphine.—P. Cazeneuve.—The action of paranitrosodimethylaniline ether upon the phenols or the aromatic amines leads to the formation of indophenols and safranines. With morphia the same reaction leads to the formation of an azine or more probably an indamine. It is a fine violet colour of a definite composition. The author boils for 100 hours in an apparatus furnished with an ascending condenser 7 grms. morphine, 5 grms. paranitrosodimethylaniline, in 500 grms. methylic or ethylic alcohol. The compound obtained is amorphous, sparingly soluble in water, very soluble in the methylic, ethylic, and amylic alcohols, in which it shows a well-marked dichroism. It is red by reflected, but violet by transmitted light. It dyes wool, silk, and gun-cotton, directly in a bright violet tone which is not permanent in light. This violet is conjectured to be the first colour derived from a natural alkaloid.

New Compounds obtained with Certain Sulphites of Metals and Aniline.—G. Denigès.—The author studies the compounds by aniline and the cuprous, cadmium, zinc, manganese, ferrous, cobalt, nickel, and mercuric sulphites. These compounds may be represented by the general formula—



$$(SO_3)_2M''H_{2},2\left\{N\begin{matrix}\diagup C_6H_5\\ -H\\ \diagdown H\end{matrix}\right\}$$

They are most easily obtained by treating with an aqueous solution of aniline water, a mixture of sodium bisulphite, and a soluble salt of the metal which it is intended to combine with the aromatic base.

On Aspergilline—a Vegetable Hematine.—Georges Linossier.—The author shows that Dr. Phipson's palmelline has no analogy either with aspergilline or with hematine.

Influence of Neutral Mineral Potassium Salts upon the Solubility of Potassium Bitartrate.—Ch. Blarez.—For potassium chloride, bromide, iodide, chlorate, and nitrate, one and the same influence upon the solubility of potassium bitartrate, other things being equal, is produced by quantities of salts proportionate to their molecular weights.

On the Characteristic of Fig-Wine.—Wine is abundantly made in Algeria from figs. These wines are used to mix with grape wines, and their presence may be detected by the mannite which they contain in the proportion of 6—8 grms. per litre.

A Method for Recognising Margarine mixed with Butter.—R. Lézé.—The author pours 1·5 c.c. of strong syrup into a glass tube, stoppered, and having a mark at 10 c.c. This tube is set in a water-bath at a gentle heat; the butter in question is added in small portions until it reaches the mark 10. The tube is then stoppered and gently agitated, tied to a string and turned round like a sling. In pure butter the fatty matter remains transparent and limpid; the whitish emulsion is bulky and collects well together. In butters containing margarine the fatty matter remains soluble and milky.

Purification of a Phlegm of Molasses Alcohol during Rectification.—D. Mohler.—The rectification of the phlegms gives alcohols of a good taste almost entirely pure, the toxicity of which may be considered nul.

Revue Generale des Sciences pure et Appliquées. Vol ii., No. 7.

On Electric Discharges in Rarefied Gases and the Constitution of Matter.—W. Crookes, F.R.S.—Concluded from the previous number.

Obituary Notice.—Auguste Cahours.—This illustrious *savant*, born in 1813, will be honourably remembered as one of the creators of modern organic chemistry. A mere catalogue of his researches would exceed the space at our disposal. He was a member of numerous scientific bodies, including the Academies of Berlin and of St. Petersburg, and in 1868 he reached the great object of his ambition—the membership of the Academy of Sciences of Paris. His private life, from 1867 to 1874, was a tissue of misfortunes, as he lost in succession his brother, his wife, and his two sons.

Justus Liebig's Annalen der Chemie.
Vol. cclv., Parts 1 and 2.

On Crystalline Mercuric Oxichloride and the Determination of Mercury.—J. Volhard.—The oxichloride, $Hg_3O_2Cl_2$, is easily obtained by allowing a cold saturated solution of mercuric chloride, mixed with sodium acetate, to stand for some days, when the crystals form on the surface in groups and sink to the bottom. Mercury sulphide dissolves in caustic alkalies in presence of alkaline sulphides. The solution, which must contain the mercury in the mercuric state, is nearly neutralised with pure sodium carbonate, and is then completely precipitated with ammonium sulphide. It is preferable to use sulphide which has been quite recently prepared from the strongest liquid ammonia. Soda-lye is then added whilst shaking, until the dark liquid begins to clear. It is heated to a boil, and more soda-lye is added until the liquid becomes quite clear. The lye must of course be free from silica, alumina, and all metals precipitable by ammonium sulphide. Soda from metallic sodium is best, ascertaining first that it contains no silver. From the alkaline solution the sulphide is re-precipitated at a boil with a solution of ammonium nitrate. The ebullition is kept up until the ammonia is nearly expelled. If it has to be collected on a weighed filter, the precipitate has to be first washed with boiling water by decantation, and not placed on the filter until the washings no longer react with a solution of silver nitrate.

Revue Générale des Sciences Pures et Appliquées.
Vol. ii., No. 6.

Electric Discharges in Rarefied Gases and the Constitution of Matter.—W. Crookes, F.R.S.—The first part of the Presidential Address delivered before the Institution of Electrical Engineers.

MEETINGS FOR THE WEEK.

SATURDAY, 9th.—Physical. (At Cambridge).
TUESDAY, 12th.—Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, .30.
— Photographic, 8.
— Royal Institution, 3. "Bacteria: their Nature and Functions," by Edward E. Klein.
— Society of Arts, 8. "Glass Painting," by Arthur Kennedy.
WEDNESDAY, 13th.—Society of Arts, 8. "Fast and Fugitive Dyes." by Prof J. J. Hummel.
THURSDAY, 14th.—Royal, 4.30.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Recent Spectroscopic Investigations," by Prof. Dewar, M.A., F.R.S.
— Society of Arts, 4.30. "Description of the Growing Uses of Tussur Silk in the European Textile Manufactures," by Thomas Wardle.
FRIDAY, 15th.—Quekett, 8.
— Royal Institution, 9. "Crystallisation," by Prof. G D Liveing, M.A., F.R.S.
SATURDAY, 16th.—Royal Institution, 3. "The Artificial Production of Cold," by H. Graham Harris, M.Inst.C.E.

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THE CHEMICAL NEWS.

Vol. LXIII., No. 1642.

THE CAUSE OF IMPERFECTIONS IN THE COLOUR OF SHEET BRASS.*

By THOMAS TURNER, Assoc.R.S.M., F.C.S., F.I.C.,
Lecturer on Metallurgy at Mason College.

During the last few years, and particularly in connection with the evening Metallurgical Classes held at Mason College, my attention has frequently been directed to a particular kind of copper-coloured or brown stain, or marking, which not uncommonly occurs on the surface of finished sheet brass. Many sheets are quite free from this imperfection, but in others the stains cover a considerable proportion of the surface, being sometimes in the form of distinct spots or rings, but usually in bands or belts such as one might suppose could be produced by the rolling out of a small globule of copper or rich copper alloy, embedded in a matrix of yellow brass. These imperfections, of which examples are shown, are met with in brasses of varying composition, and are common in button metal, cartridge metal, and other forms of good sheet brass, and their presence frequently involves considerable loss and trouble. Thus, in the case of button metal, the blanks have to be sorted to separate those which are discoloured, and which are therefore unsuited either for use as bright brass or for bronzing or tinning. These discoloured blanks are of inferior value, and are usually japanned and sold as black buttons. In many other branches of the Birmingham sheet metal trades, these discolourations are equally troublesome.

A number of explanations have been suggested in order to account for the production of these copper-coloured stains, among the chief being the following:—

1. That they were caused by inattention on the part of the workman in allowing the sheets to become overheated during annealing, by which it is alleged that zinc is volatilised from the surface of the sheet, and a coating of copper produced. To this it may be objected that if such an action took place there is no reason why the copper should be produced in spots or bands instead of a uniform film, as might be expected if the whole sheet were overheated. But in addition it is easy to experimentally prove that overheating does not produce this effect; for if a sheet of brass be heated in a muffle until a portion actually melts, it will still be found, on removing the scale from the remaining portion by pickling, that a fairly uniform colour is obtained.

2. The workmen themselves assert that these stains are due to sulphur in the coal. Of course, "sulphur" as used by the workman includes combustible gases and the products of combustion, and does not necessarily mean the element sulphur at all. But, as in the previous case, it is not easy to see why, if the whole of the sheet is exposed to the same gases, these gases should produce a deep colour in one portion of the surface, and no colour at all on the parts immediately adjacent.

In order to test this matter I heated ordinary sheet brass in a gas muffle to a full red heat, and from time to time introduced fragments of sulphur so as to keep the atmosphere charged with sulphur dioxide. The result is shown in sample 1, the surface of which, after having been cleaned in dilute sulphuric acid, is rather rough and dull, but practically free from the stains referred to. To further test this point, samples 2 and 3 were prepared. On sample 2 flowers of sulphur were sprinkled in the form of a letter S, and the metal was then heated as before. After pickling, the position of the sulphur is only indistinctly seen on the surface by dark coloured stains. On sample 3 a heap of sulphur was placed, but after heating and subsequently pickling the result obtained was a dark coloured stain with light coloured spots. Obviously, therefore, sulphur or sulphurous gases cannot be responsible for the production of the red stains previously mentioned. But it appeared possible that coal dust or coal ashes, or soot, or a reducing atmosphere, might assist in the reduction of zinc oxide, which is non-volatile, and so assist in liberating zinc from parts of the brass and produce the objectionable red colouration. I therefore tested a number of samples by covering a portion of each of them with coal-dust, coal ashes, charcoal powder damped with a solution of gum, chalk, &c. In each case the result was very similar and is illustrated by sample 4, on which coal ashes were dusted in the form of a letter A, and, after pickling, the pattern is observed to remain as a faint and not very definite dark stain. It appears to me, therefore, that the imperfections we are considering cannot be due to variations in any of the furnace conditions above enumerated.

3. Perhaps the most natural suggestion from the general appearance of the imperfect sheets is that which has met with considerable favour in some quarters, namely, that the brass is not uniform in composition, but that owing either to imperfect mixture or to separation during cooling, the constituent metals have more or less separated in places, and that the red colouration is due to the greater concentration of copper in certain parts. It must be remembered, however, on the other hand, that all trustworthy experiments on this subject have shown the very remarkable uniformity of composition which exists in copper zinc alloys. Dr. Tilden allows me to mention that in connection with his experiments on the "Corrosion and Pitting of Copper and Brass by Saline Waters" (*Journ. Soc. Chem. Indust.*, Feb. 1886), he paid special attention to the question of the uniformity in composition of the sheet metal employed, and as the result of a large number of tests he was unable to find any evidence to support the view that separation of richer copper alloys occurred. The researches of Laurie (*Journ. Chem. Soc.*, 1888, p. 88), also give strong support to Dr. Tilden's conclusions. In one sample of doubtful origin I believe I have obtained distinct evidence by etching with nitric acid that such a separation had taken place, though probably the specimen was from the "spilley" end of the strip, as the little grains of red alloy were distributed in a manner such as might be expected under the circumstances. But by etching a large number of other samples of sheet brass with varying proportions of copper, I have never met with another instance of the same thing, and any such separation must be very unusual.

In order to test this third explanation I have selected a number of strips of sheet brass which were very plainly marked with bright copper-red spots and bands, the markings being on both sides of the sheet, and giving the appearance of nodules of a separated alloy passing through the thickness of the sheet. These strips were etched by immersing in diluted nitric acid for about 12 hours, but the resulting strip was in each case quite uniformly crystalline in texture after the outer surface had been removed, and no indication of variation in composition was obtained. Samples 5 and 6 illustrate these experiments, the part which was etched and now shows a perfectly uniform crystalline character being originally very plainly marked with copper-red discolourations. Further proof that only the surface is affected by these discolourations is afforded by the fact that the copper can be scraped off with a knife, when ordinary yellow brass is found underneath, while, on the other hand, so far as I am aware, these red markings are not laid bare when, in the process of working, the surface is removed from a piece of ordinary bright brass. It appears evident, therefore, that the imperfection of surface cannot be due to

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* Read before the Birmingham Philosophical Society, May 6, 1891.

irregular distribution of the constituent metals of the alloy, and I have previously shown that it is not caused either by overheating or by furnace gases, &c., during annealing.

Attention was thus directed to the method whereby the sheets are cleansed from scale between each annealing. This is usually accomplished by dipping the sheets in diluted sulphuric acid and subsequently washing with water. The washing is often doubtless far from perfect, and the wash water is generally impure, so that it is not unreasonable to suppose that sheets are frequently subjected to a second annealing when their surfaces are by no means chemically clean.

In order to test these points the following experiments were made. A small sheet of brass was prepared and the corners slightly turned up so as to make a very shallow evaporating pan; about 5 c.c. of distilled water was evaporated to dryness on this pan, and it was then heated to redness in a muffle, and afterwards cleaned with dilute sulphuric acid. The surface was found to be marbled all over with faint reddish brown stains (sample 7), doubtless due to the action of the minute quantity of solid residue left by ordinary distilled water.

Birmingham tap water, which is moderately hard, when tested in the same manner (samples 8 and 9), gave very distinct red discolourations, though these were not so plain as those commonly observed in commercial samples of sheet brass. Dilute sulphuric acid, containing 1 per cent of commercially pure acid, gave a very marked dull copper brown stain (sample 10), darker than that obtained in practice, and this stain was quite visible with water, containing so little sulphuric acid as 1 part in 500 (sample 11). A solution of sodium chloride containing 1 per cent of $NaCl$ gave a very marked bright copper-red stain (sample 12), which is still very visible with 1 part of salt in 1000 of water (sample 13).

Solutions of calcium, magnesium, and potassium chlorides produce a similar effect. Galvanisers' waste pickle (a solution of ferrous chloride not unknown in local canal water), gives a similar bright copper stain even when diluted with 500 parts of water (sample 14). Ordinary ink, as might be expected, produces a bright red discolouration (sample 15). Copper sulphate produces a faint light-coloured stain (sample 16), copper nitrate a copper-red (sample 17), while zinc chloride gives scarcely any copper colour at all (sample 18). This apparently indicates that the chlorides, or other salts of metals other than zinc, are decomposed at a high temperature, and the liberated acid attacks the zinc in preference to the copper which is thus left and causes the red stain on the surface of the sheet.

In the foregoing experiments, though the cause of the colouration was discovered, no really quantitative values were obtained as to the amount of the substances necessary to produce a distinct effect, since the liquid became concentrated during evaporation, and the colour observed was due to the concentrated liquid thus obtained. To obviate this difficulty a few more samples were prepared in which the liquids to be tested were used as writing fluids, and applied with an ordinary pen for the purpose of recording the substance and strength of solution. By this means a thin film of liquid of a definite shape was obtained, and the effect produced could be easily observed. Thus, sample 19 is marked with a faint dull brown stain, "H_2SO_4 1 per 100," while in sample 20 the "H_2SO_4 1 per 500" is incomplete, and is very faint when it can be seen. Hence the limit of ill-effect of sulphuric acid is reached with 1 of acid to 500 of water. On sample 21 can be plainly seen in bright copper "Salt 1 per 100," while on sample 22 "Salt 1 per 1000" is still distinctly visible, showing that salt not merely produces a brighter stain, but that an exceedingly small quantity is required to produce a discolouration. In fact, this reaction is so delicate that it might be used as a qualitative test for the presence of chlorides in water. On sample 23 can be read in bright letters "Waste pickle 1 in 50," while sample 24 shows that "Waste pickle 1 in 100" produces a very marked discolouration, and this probably corresponds to about 1 part of chlorine per 1000 of water. When so thin a film of liquid produces so distinct a stain with only 1 part of chlorine in 1000 of water, it is evident that by using a few drops of the water to be tested 1 grain of chlorine per gallon might be readily detected.

From these facts I concluded that the use of impure water for washing the sheets after pickling was the most probable cause of much of the discolouration noticed in sheet brass. On inquiry as to the practice at certain works in the neighbourhood this view was amply confirmed, for I am informed that at one of the rolling mills from which I have received a number of samples of discoloured metal, they are in the habit of washing the sheets in canal water,, and not unfrequently the metal is allowed to dry spontaneously by the action of the atmosphere, thus depositing a thin saline crust on the sheets. When it is added that a galvanising works is situated on the same canal in the vicinity of the rolling mills no further explanation is needed as to the cause of the red spots or bands on their finished brass.

In such a case the remedy is simple. Care should be taken to wash away all the sulphuric acid pickle used in cleansing the sheets, and the last washing water should be as pure as possible, while the presence of chlorides in any form should be especially avoided. Probably also when water of only moderate purity can be obtained some method of drying the sheets instead of spontaneous evaporation would be a considerable improvement.

ON A SOURCE OF ERROR IN THE DETERMINATION OF NITRATES IN WATER BY THE PHENOL-SULPHONIC ACID METHOD.*

By GEORGE H. BARTRAM.

Owing to certain discrepancies in duplicate estimations of nitrates, by the phenol-sulphonic acid process, I was requested by Dr. Samuel C. Hooker, to make a series of experiments to ascertain under what conditions this process, which had hitherto been considered reliable, gave these varying results. The work was performed in Dr. Hooker's laboratory and under his direction.

As the principal result of these experiments, it was found that phenol-sulphonic acid undergoes a change shortly after preparation, as shown by the fact that chlorides, which have no effect on the determinations when made with freshly prepared phenol-sulphonic acid, bring about low figures when the acid has been kept for some time before use.

The disturbing action of the chlorine is already well marked, when the quantity present in a given volume of water is about four times as great as the nitrogen of the nitrates. Correct figures were, however, obtained even when the phenol-sulphonic acid had been kept eighteen months, with water in which the chlorine did not much exceed the nitrogen of the nitrates. Water containing twenty parts chlorine to 0·5 part nitrogen gave the following decreasing quantities of N as the age of the solution increased:—

N present.	N found.	Age of phenol-sulphonic acid.
0·5	0·5	Freshly prepared.
0·5	0·5	1 day old.
0·5	0·45	2 days ,,
0·5	0·42	13 ,,
0·5	0·40	17 ,,
0·5	0·40	27 ,,

Water containing 10 parts chlorine to 0·5 part nitrogen gave a similar series of figures:—

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* Read at the Chemical Section of the Franklin Institute March 17, 1891.

N present.	N found.	Age of phenol-sulphonic acid.
0·5	0·5	Freshly prepared.
0·5	0·5	2 days.
0·5	0·42	13 „
0·5	0·40	17 „

With water containing 2 parts chlorine to 0·5 part nitrogen the results similarly fell off.

N present.	N found.	Age of phenol-sulphonic acid.
0·5	0·50	Freshly prepared.
0·5	0·50	13 days.
0·5	0·40	27 „

The above determinations were made in duplicate, and the standards were always freshly prepared.

A solution of phenol-sulphonic acid two and a half months old gave, as the mean of four determinations, 0·30 instead of 0·5 N in the water containing 10 parts chlorine to 0·5 N.

A solution eighteen months old also gave 0·30 N for the same water.

By the removal of the chlorine correct results were obtained.

The above experiments show that in the presence of relatively large quantities of chlorine 20 per cent of the nitrates, or in extreme cases even as much as 40 per cent, may fail to be recorded by the use of this process, unless the precaution be taken to use freshly prepared phenol sulphonic acid, or to remove the chlorine.

THE VOLUMETRIC COMPOSITION OF WATER.

By EDWARD W. MORLEY.

(Continued from p. 221).

Apparatus for Storing Hydrogen for Several Experiments on the Same Sample.—Figure 2 shows the part of the apparatus serving for certain processes in the determination of the composition of water. In my methods it was necessary to secure two considerable volumes of hydrogen which should be absolutely identical in composition, one to be weighed, and one to be analysed. It was also necessary to preserve the second for several days, with no possibility of contamination by leakage or diffusion. Moreover, the sample for analysis must not come in contact with fatty lubricants, nor that for weighing in contact with mercury, from which it would take up mercury vapour affecting its weight. It would no doubt have been possible to have found a fatty lubricant which it would have been safe to use; but so many difficulties had to be surmounted that the pleasure of evading some was not to be disregarded, and I used no organic matter about the apparatus.

The tube *r* yielding pure hydrogen is continued in the tube *a* in Fig. 2. And *a* leads directly to the stop-cock *c*, just outside the calorimeter case containing *e* and to the stop-cock of the globe *e*. The manipulation of *c*, *d*, *e* will be described in a paper on the density of hydrogen and of oxygen; the gas in passing to *e* does not go near mercury. At *g* is seen a tube connected to a McLeod guage, and leading to a Geissler air-pump having a capacity of 2·3 litres. This was kept in such condition that it was not difficult to exhaust the pressure gauge and the connecting tubes with a total volume of 700 c.c. to one part in five million. It is therefore obvious that the amount of leakage through its ground joints which could take place during the exhaustion was negligible, and when the pump was not in use for exhaustion, it was shut off by a mercurial valve which was perfectly tight.

The vertical tubes seen immediately above the horizontal part of *a* form a six-way mercurial valve, of which three ways were used in the manipulation of hydrogen, and three in the manipulation of oxygen. When mercury is lowered in the tube *h*, a free passage exists between the Geissler pump with its McLeod gauge and the tube *a* leading to the valve at *o*, Fig. 1, as well as to the weighing globe *e*, Fig. 2. When the mercury is lowered in the tube *k*, there is a free passage from the pump to the mano-barometer and the store globe, *n*. And when the mercury is lowered in the tube *j*, there is a free passage between the tube *a* and the mano-barometer and the store globe. Of course, this valve will saturate the hydrogen with mercurial vapour, but this part of the hydrogen is to be analysed over mercury. Any hydrogen stored in the globe *n* is perfectly safe from contamination. The tubes were all most scrupulously cleaned, all joints were made by fusion, when possible, and the others are mercurial seals of sufficient depth; at the mercury six-way stop-cock, the hydrogen is shut off by at least thirty centimetres of mercury, at the mano-barometer by thirty, and at the valve *o* by eighty centimetres. It was accordingly found that that hydrogen stored in *n* contained no more nitrogen after keeping it for a month than on the day of its preparation.

Introducing Hydrogen into the Storage Apparatus.—In filling *n* with hydrogen, *n* was exhausted to a twenty-five thousandth or a fifty thousandth part, and was then shut off from the pump. Then the tube between *d*, Fig. 2, and *o*, Fig. 1, was exhausted to a hundred thousandth. During these exhaustions, hydrogen had been escaping at *n*, Fig. 1. The tube at *n* was then fused together, the stop-cocks at *m* closed, and the valve *o* opened. A good exhaustion was now produced back to the glass stop-cocks. The valve shutting off *n*, Fig 2, was now opened, as well as the stop-cock of the globe *e* (but of this elsewhere), and hydrogen admitted to a tension of ten or twenty centimetres. Then the valve *o*, Fig. 1, was closed, and a good exhaustion again produced in the whole apparatus, *m*, *n*, and *e*, Fig. 2. The degree of exhaustion thought proper depended on circumstances. The pump was then shut off, the fusible metal valve opened, and hydrogen admitted till its pressure was a little greater than that of the atmosphere. The valve *j* being then closed, the hydrogen in *n* was ready for use.

The apparatus for preparing oxygen is not shown. Potassium chlorate was placed in a hard glass tube; this was fused to a similar tube containing finely divided silver and heated in a furnace. These two tubes were connected to the soft glass tubes of the remaining apparatus by a ground joint. First was a tube like *g* and *h*, Fig. 1, with a 50 per cent solution of potassium hydrate, and then a similar tube with glass beads and sulphuric acid. Then followed a stop-cock used to keep the pressure in the apparatus so far nearly equal to that of the atmosphere. This stop-cock was lubricated with syrupy phosphoric acid, and was followed by a tube filled with phosphorus pentoxide, and ending at the tube *b*, Fig. 2. This tube could be connected to the globe *e*, Fig. 2, by making a fused joint at the proper place. It was also connected to the three mercurial valves, and also to a system for storage of oxygen identical with that for hydrogen. The manipulation in filling this system with oxygen was much like that for filling with hydrogen.

Apparatus for Extracting Hydrogen and Oxygen from the Stores, and for Preparing to Determine Residual Nitrogen in Hydrogen.—At *o*, Fig. 2, is a mercurial valve which can be opened under difference of pressure. Those at the left of this figure can be opened only when the two pressures are equal. It also permits some regulation of the rate of flow. The descending tube which is connected directly to *n* contains a part so narrow that only a certain amount of gas can pass in a minute; the amount is calculated according to the size of the wider tube next following. Suppose this tube and those following to the right to be vacuous; when the mercury in the valve *o* is lowered so as to uncover the end of the descending tube where it enters the wider tube, gas will bubble up through the mercury which stands in the wide tube, and the rate can be adjusted by altering the level of the mercury. When the flow is rather rapid, the bubbles burst with such force as to throw some mercury over into the short wide tube at the right, whence it flows back by the tube provided for the purpose. By the use of this valve, it is possible to exhaust everything to the right of o, and then to introduce any required volume of gas from the store in n. At p are two drying tubes intended simply to prevent aqueous vapour produced at r from entering o or s, and interfering with their action. At s is a Sprengel pump. The mercury which operates it first falls through the tube t, kept exhausted by a Toepler pump fused to u. This trap is made long as shown, so that even when the gas in p, q, r is at atmospheric pressure, mercury falling into t has still to pass through many centimetres of vacuum. At v is the jar in which the gas is transferred to the measuring apparatus. It is plain that, disregarding for the moment the apparatus r, we can, on opening the valve o, transfer gas from the store in n to the jar at v. But the apparatus at r has sometimes to perform an office which has made it possible to obtain from impure gases results as accurate as from pure gases. It will be recalled that Humboldt and Gay-Lussac obtained, although they worked with very impure gases, results whose mean errors are comparable with those of Scott, whose gases were far purer. This was owing to the fact that they devised means for measuring the impurities of one gas by some process other than the eudiometric explosions which determine the total nitrogen in both gases, and also the volume of the gas which has disappeared in the explosion. If Scott had succeeded in refining on the methods of Humboldt and Gay-Lussac in this respect as much as in his methods of preparing and measuring the gases, he might well have attained a degree of accuracy satisfactory to himself and answering the present demands of science. The apparatus r was designed to make possible the determination of the nitrogen contained in the hydrogen used. It consists of a hard glass tube filled with copper oxide, and united to the rest of the apparatus by means of a mercurial seal. The apparatus to the right of n was duplicated for oxygen, except that the tube r contained copper instead of the oxide, and no drying tubes pp were needed.

To get copper oxide which could be heated in a vacuum without giving off gas cost much trouble. Electrotype copper was oxidised in a current of oxygen; but when it was heated in a vacuum, it gave off a gas for a long time. In some cases, heating for several days answered the purpose; but some samples had to be rejected and the heating re-commenced with a new sample. The gas given off was mostly absorbed by potassium hydrate, but as yet has not been further studied.

The mano barometer m served partly in preparing for weighing the gas in the globe e, and partly in preparing for determining the amount of nitrogen in the hydrogen by means of the apparatus r. For the last purpose, an accuracy permitting readings to a thousandth of an atmosphere was sufficient; the apparatus will therefore not be described at present.

Apparatus for Accurate Measurement of Volumes of Gases.—My measuring apparatus has finally become rather elaborate. It is shown in Fig. 3. It is mounted on a stone pier, independent of the floor of the room in which it stands. The eudiometer and measuring tube ends above in a stop-cock and recurved tube whose end is seen to emerge inside the left hand gas jar in the cistern. The stop-cock is manipulated by means of a metal shaft and long handle seen at the top of the column which carries the reading microscope. At the bottom of the eudiometer is a glass stop-cock of large bore intended to facilitate the washing out of the eudiometer after an analysis. For this purpose the glass plug of the stop-cock is withdrawn and a duplicate plug inserted in which there are such connections that the part below the stop-cock is shut off, and an opening is left between the eudiometer and the outside of the apparatus. By connecting the top of the eudiometer to an air pump, aqua regia or potassium hydroxide can be drawn into the eudiometer; then by connecting the bottom of the eudiometer to the pump, distilled water can be drawn in at the top. In this way the tube was kept so clean that carbon dioxide was formed only twice, when this washing was omitted; accurate reading of volumes were also facilitated. Below the glass stop-cock, the eudiometer is connected by a rubber connector to a steel tube screwed into an iron stop-cock. The key of this stop-cock is prolonged upwards some four decimetres, and ends in the handle seen just above the reading microscope. A small wheel imperfectly seen under the reading microscope carries a series of stops of which any one can be brought into position so as to arrest the opening of the stop-cock at a determinate point. This stop-cock governs the admission of mercury from the movable reservoir carried vertically by an apparatus placed on a table to the left,

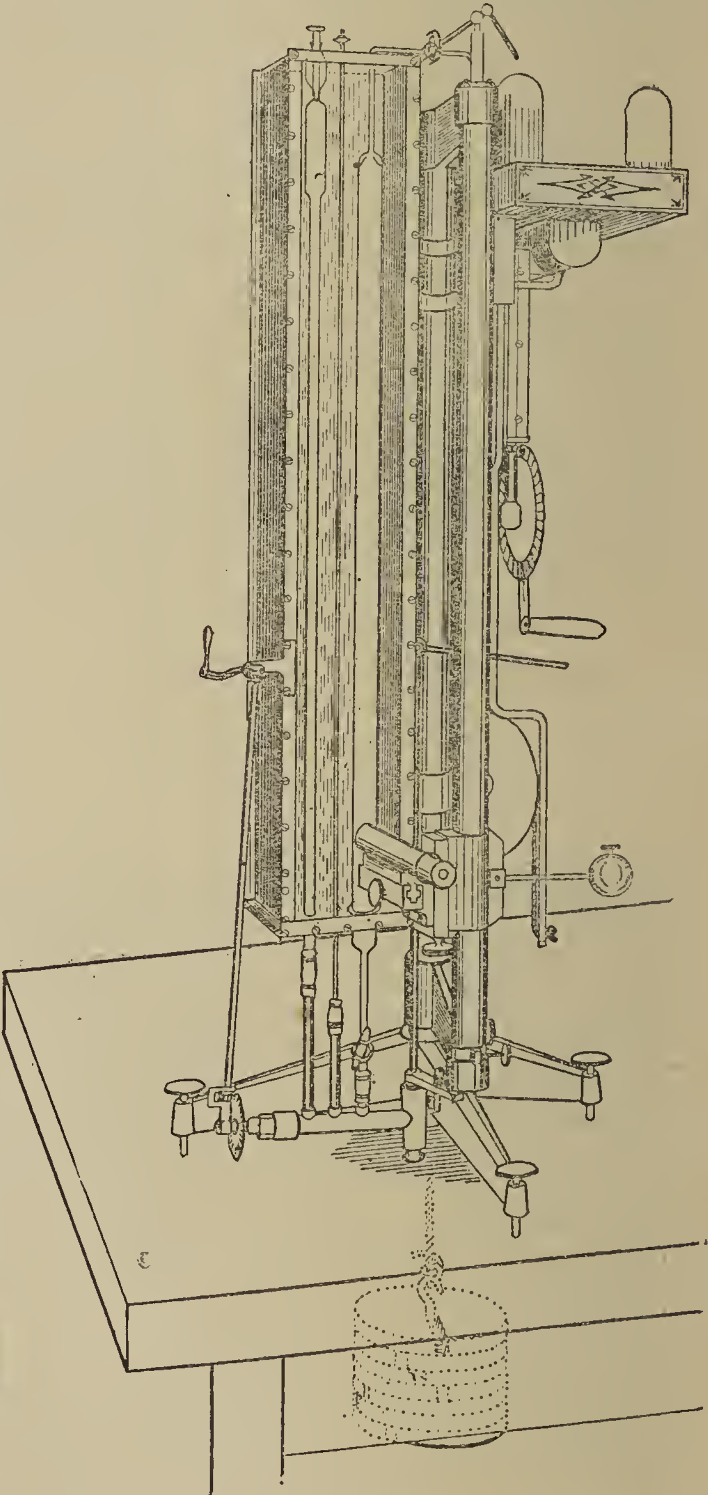

Fig. 3.

The iron stop-cock has three steel tubes which are connected, one to the eudiometer as said before, the others to the two pressure tubes; the smaller of these is an auxiliary, used for all rough measurement, so as to reserve the other for the final accurate measurement. This tube is shut off from connection with the other tubes by a piston valve whose motion is produced by the geared wheels seen at the left of the iron stop-cock. Its vacuum was easily kept unimpaired for months, as was proved by repeated determinations. But further, this piston valve also served as a micrometric adjustment of the level of the mercury in the eudiometer and pressure tubes. The use made of this will be mentioned below, and it contributed greatly to the accuracy obtained. These three tubes were enclosed in a box with glass front and back, and filled with clear water kept stirred by a current of air. The eudiometer is secured into a brass plate which is ground water-tight to the bottom of the box; on removing a clamp, the eudiometer can be lifted out of place if necessary, and can be replaced without a variation of its level amounting to the hundredth of a millimetre. It was convenient to compute the measured volumes of gases by means of an interpolation formula whose constants depended on the relative levels of fiducial marks on the eudiometer and pressure tubes, and constancy of this relation even after removing the eudiometer was highly desirable. The pressure tube was provided with a fine screw motion by which it could be adjusted vertically while in position and filled ready for use.

The recurved tube at the upper end of the eudiometer serves for the introduction of gas into the apparatus. The cistern containing the jars of gas is capable of the motion required to bring the open end of this recurved tube inside of the jar *a b* and to its top. When the cistern is in its highest position, the recurved tube is wholly contained within the well seen under the cistern, and the cistern can be moved vertically by a distance equal to the height of the tallest jars used. It is fitted with sliding ways, counterpoised, and moved by a screw; by means of a multiplying gear, its motion can be made as rapid as is convenient; by means of the adjustable counterpoise, the cistern with its 35 kilogrms. of mercury can be moved up and down and placed accurately at the required level with ease and safety. In the centre of the cistern is a well for filling the jars used; the rest of the bottom is inlaid with a smooth surface of slate. Care was taken to have no crevices in which air could be entangled, from which perhaps it should rise into a jar of gas. The mercury was always kept as much as three centimetres deep, to lessen the probability that gas in the jars should be contaminated by diffusion between the walls of the jar and the mercury in contact with them. But the danger of this contamination is very slight. I left two jars of hydrogen standing in the cistern for eleven weeks, after which time I was unable to detect any contamination. The reason of this, so different from the result obtained by Faraday,* is probably the great care taken in filling the jars with mercury. The jar was always put entirely under the surface of the mercury while it was closed with a glass plate, so that no dust from the free surface of the mercury could get to the inside of the jar.

The vacuum in the pressure tube was obtained by exhausting the tube from above while the bottom was closed, then admitting mercury till it rose above the glass stopper at the top of the tube; during the exhaustion, the stopper was loosely in place, and was in the vacuum. When the stopper was covered by mercury, it was forced into place; a drop of water had previously been put in the upper part of the pressure tube. In the pressure tube were two Jolly points, of which sometimes one was used, sometimes the other, an interpolation formula having been computed for each of the two systems of pressures measured by the mercury when brought to one of the points. The vacuum in the pressure tube was often measured, or rather, the real zero of pressures was determined by producing a good vacuum in the eudiometer, bringing the mercury in the pressure to one of the Jolly points, and observing the level of the mercury in the eudiometer; this level was the zero from which pressures were counted, and could be verified as often as desired, and did not change during the series of experiments.

The measurement of the reduced volume of a gas is effected by adjusting the apparent volume till the mercury in the pressure tube stands at one of the Jolly points, and measuring the level of the mercury in the eudiometer. This reading determines the apparent volume, and the difference between this reading and the reading of the zero point gives the pressure under which the gas is measured. A convenient interpolation formula reduces the computation to the addition of a constant to the reading, taking the doubled logarithm of the sum, and adding a logarithmic constant.

The measurement of the level of the mercury in the eudiometer is made by means of a reading microscope. This is carried on a cylinder supported on the framework of the instrument, and provided with a tangent motion. On this cylinder slides a piece which can be tightly clamped, and which carries ways on which the microscope can be moved vertically by a micrometer screw. When the microscope is made to give distinct vision of a scale engraved on the eudiometer, the terminal lines of an eyepiece micrometer are made to agree with two successive millimetre divisions of the scale. As these are but the three-hundredth of a millimetre wide, the coincidence can be made accurately. When coincidence is secured, the microscope is made to give distinct vision of the meniscus and the illumination arranged. When the mercury is now made to coincide accurately with one of the Jolly points in the pressure tube, the reading of the fraction of a millimetre by which the mercury in the eudiometer stands above a millimetre division of the scale is accomplished in a few seconds. Great care was taken in the calibration of the eudiometer. For this I fused to the end of the recurved tube, mentioned before, a further tube opening downwards. Through this air-free water was introduced into the eudiometer. The mercury reservoir being raised, mercury was admitted by opening the iron stop cock against the proper stop. Water then began to drop from the added tube. The rate of admission of mercury must be so slow that the amount of water left adhering to the inside of the eudiometer is small, and is nearly constant from one experiment to the next. Three hours for the admission of eighty centimetres of mercury gave concordant results. When the mercury reached the lowest point to be calibrated, the iron stop cock was closed, and the level of the mercury and the temperature of the water determined. The tube from which the water had been dropping was wiped in a constant manner, and a tube put in place to collect the water which now issued on opening the iron stop-cock. When the mercury rose to the next standard point, level and temperature were measured, and another tube placed to collect water, while the water already issued was weighed. True volumes at zero were computed from the weights and temperatures observed. The calibration was made four times; I give the values found for the points at which oxygen and hydrogen were measured in the experiments, and the differences between the mean and the several determinations. It will be seen that the mean error of a single determination of volume is five cubic millimetres. A tube was previously calibrated with a mean error only three-fifths as much; but it broke during the first experiment. The sky was so cloudy while this the present tube was calibrated, that illumination was defective and work very trying. But in the determination of the volumetric composition of water, any slight errors, either in the calibration of the standard points, or in the interpolation at intermediate points, was nearly eliminated by

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* *Annals of Philosophy* (II.), vol. xii., p. 389, 1826; *Poggendorff' Annalen der Physik*, vol. viii., p. 124, 1826.

a proper distribution of the points used in the measurements.

Scale division.	Volume found.	Errors (cubic millimetres).			
		1.	2.	3.	4.
600	184·323	0	12	−7	−4
625	191·849	−3	−4	4	4
650	199·442	1	−2	10	−10
675	207·082	7	−15	2	7
700	214·766	−1	3	5	−7
725	222·460	1	4	−10	5
750	230·132	−1	−3	−1	5

Since, in my way of manipulating, the gas, scale, mercury, and eudiometer are all at the same temperature, the effects of the expansions of all were taken into account in one factor, which, moreover, was determined for the actual degrees of the thermometer used.

In measuring the volume of a quantity of gas in the eudiometer, the mercury in the recurved capillary tube was brought to a certain mark. The level of the mercury in the eudiometer was so adjusted that when the pressure tube was opened, the mercury in it would stand near one of the Jolly points. Then the level of the reading microscope was adjusted, and the meniscus was brought into focus. During this time, the water surrounding the eudiometer was stirred by a current of air. When everything was ready the current of air was shut off, and the piston valve slowly moved till the mercury exactly coincided with the Jolly point. Then, within five or ten seconds, the thermometer was read and the fraction of a millimetre shown in the reading microscope was determined. The water was then again stirred, the adjustment at the Jolly point, and the reading of the thermometer and of the reading microscope was repeated. By means of the fine adjustment of the level of the mercury which has been mentioned, the adjustment at the Jolly point could be made within the 500th of a millimetre, and it could be repeated as many times as was desired. It was also possible to make the final adjustments, and the two readings, within a time too short for any change of temperature in the gas to be measured. Readings of temperature were to the two hundredth of a degree, and of level to the two-hundredth of a millimetre. To show what degree of accuracy can be obtained by an apparatus such as is here described, including both errors of readings and errors of transfer due to bubbles of gas entangled in the capillary tube, I put a quantity of gas in a jar in the cistern, transferred it to the eudiometer and measured it, transferred it back to the jar and measured it again, and so ten times. I give the reduced volumes so found. From this it seems that the probable error of measurement, not including errors of calibration, are something like a 70,000th part of volumes like those used in the determinations of the volumetric composition of water. I also found the mean error of a single measurement by computation from the mean error of a determination of the ratio sought. In this way it seems that the mean error of a single measurement of such a volume as 150 or 200 c.c. is its 50,000th part. This value *includes* the errors of calibration as far as they affect a determination of the ratio. The direct determination of mean error of measurement was made under selected conditions as to illumination and health which could not be secured in the determinations of the ratio.

Repeated Measurements of the same Volume of Gas transferred to Jar after each Measurement.

210·81 c.c.	210·805 c.c.
210·815 ,,	210·815 ,,
210·815 ,,	210·81 ,,
210·815 ,,	210.81 ,,
210·815 ,,	210·81 ,,

(To be continued).

AN APPARATUS FOR HEATING SUBSTANCES IN GLASS TUBES UNDER PRESSURE.*

By H. PEMBERTON, Jun.

CHEMISTS who do not happen to have in their laboratories oil or air baths for heating closed tubes can make an air bath at short notice from materials furnished by all dealers in steam fittings.

Order :—

(1) One four-inch wrought-iron pipe, eighteen inches out to out, with usual thread on each end. At about nine inches from either end this pipe is drilled and tapped for a one-inch nipple in such a manner that a pipe introduced would pass, not on a line with the radius, but about halfway between the axis of the four-inch pipe and its walls; in other words, it would be on a line with a chord of the circle.

(2) One one-inch wrought-iron nipple, two inches long, one-inch thread on one end.

(3) Two four-inch malleable iron caps, drilled and tapped for a one-inch pipe.

(4) One one-inch wrought-iron pipe, twenty-four inches out to out, with a three-inch straight thread on each end.

(5) Two one-inch iron caps. A hole, one-eighth of an inch in diameter, is drilled in the end of one of these caps.

The above order can be given *literatim*, and will be understood by the dealer, who will furnish, at a trifling cost, the materials, cut and tapped as ordered.

Fig. 1 shows how the whole is put together. The numbers on the figure correspond also to the numbers of the paragraphs of the order as given above.

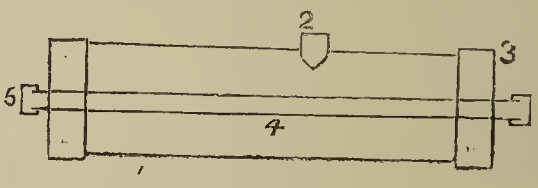

FIG. 1.

FIG. 2.

Fig. 2 is an end section. A cork is inserted in 2, and through it a thermometer, the bulb of which is on a level with the interior pipe. The whole is supported on a few bricks at either end, and is kept steady and in place by a couple of weights or half bricks. It is heated by one or two Bunsen burners, according to the temperature desired.

Determination of Actual Glycerin in Crude Glycerins. — F. Filsinger (*Chem. Zeit.*), continuing his controversy with Lewkowitsch, has again examined a number of samples of glycerin both by the permanganate method and by the acetin process. The results of the latter are too high and mutually discordant.

Quantitative Determination of Paraffin especially in Mineral Oils.—R. Zaloziecki (*Dingler's Polyt. Jour.*). —The author dissolves the paraffin in amylic alcohol and precipitates it with ethylic alcohol. 10—20 c.c. or grms. of the sample are mixed with 5 parts of amylic alcohol, and then with the same quantity of ethylic alcohol at 75° Tr. The mixture is let stand for some hours in a cold place (if possible not above 4°), filtered through a dry, cold filter, and the residue is washed on the filter with a cooled mixture of 2 parts amylic and 1 part ethylic alcohol at 70°. The deposit dried in the air is exhausted on the filter with either or benzine in a suitable apparatus, the solvent evaporated, the residue dried at 125° for two hours, and weighed. The method cannot be used for examining wax, as it contains constituents precipitable by alcohol.

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* Read at the Chemical Section of the Franklin Institute, March 17, 1891.

ON THE ACTION OF PHOSPHORUS OXYCHLORIDE ON THE ETHERS AND CHLORHYDRINES OF SILICIC ACID.*

By H. N. STOKES.

That silica can combine with other acids, forming mixed anhydrides, has long been known, and several such bodies have been described. Friedel and Ladenburg (*Ann. Chem.* (*Liebig*), cxlvi., 174) obtained the tetra-acetyl derivative $Si(O{\cdot}CO{\cdot}CH_3)_4$ by treating silicon tetrachloride with acetic acid or anhydride. Friedel and Crafts (*Ann. Chim. Phys.* [4], ix., 47) obtained $Si(OC_2H_5)_3O{\cdot}CO{\cdot}CH_3$ from ethyl orthosilicate and acetic anhydride. Hautefeuille and Margottet (*Compt. Rend.*, xcvi., 1052) described a crystalline compound, $SiO_2{\cdot}P_2O_5$, formed by fusing amorphous silica with metaphosphoric acid.

By the action of phosphorus oxychloride on silicic ethers and their chlorine derivatives, I have obtained bodies which consist of phosphoryl chlorides in which the chlorine is partly replaced by a residue of silicic acid, and which are therefore chlorides of silicophosphoric acids.

Phosphorus oxychloride was caused to react upon *orthosilicic ethyltrichlorhydrine*, $SiCl_3{\cdot}OC_2H_5$, hoping thereby to obtain the silicon oxychloride described by Friedel and Ladenburg (*Liebig's Ann. Chem.*, cxlvii., 355) and by Troost and Hautefeuille (*Ann. Chim. Phys.* [5], vii., 465):—

$$3SiCl_3{\cdot}OC_2H_5 + POCl_3 = (SiCl_3O)_3PO + 3C_2H_5Cl, \text{ and}$$
$$2(SiCl_3O)_3PO = 3Si_2OCl_6 + P_2O_5.$$

The experiment proved that this reaction does not take place.

If the trichlorhydrine he heated in a sealed tube with an excess of phosphorus oxychloride, no reaction is apparent below 175°, the contents remaining perfectly clear. If the temperature be kept at 180°—200°, a white amorphous substance is soon formed which is sufficiently porous to absorb all the liquid products. After two to three hours' heating the tube is opened, when ethyl chloride escapes in large quantities. On placing the tube in an air-bath heated at about 150°, and connecting it with a condenser, a large amount of liquid may be collected. The solid remaining in the tube may then be freed from excess of phosphorus oxychloride by passing a current of dry air over it by means of a capillary.

The liquid, on fractionating, is readily separated into phosphorus oxychloride (boiling at 110°) and silicon tetrachloride (boiling at 57°—61°), though much of the latter is lost, being carried off by the ethyl chloride which is abundantly held in solution. The product obtained after six distillations was analysed.

	Calculated for $SiCl_4$.	Found.
Si	16·52	16·24

The view with regard to its nature was confirmed by converting it into ethyl orthosilicate (boiling at 165·5°). As the liquid passed over entirely below 112°, no silicon oxychloride was formed, and no substances other than those mentioned could be detected.

Analyses of the solid substance gave:—

	Calculated for $SiP_2O_6Cl_2$.	Found. I.	Found. II.
Si	10·92	10·17	10·06
P	24·15	25·16	25·11
Cl..	27·59	27·33	—

The agreement is only approximate, as the substance could not be purified in any way; and on heating too long or at too high a temperature when drying, phosphorus oxychloride is slowly given off. It is possibly a mixture of substances, in the formation of which the one supposed represents one stage. If heated above 200° phosphorus oxychloride is given off, and, at a red heat, phosphorus pentoxide; and the residue left at a white heat consists of amorphous silica imbedded in a vitreous substance, probably the compound $SiO_2{\cdot}P_2O_5$ of Hautefeuille and Margottet. The loss on heating corresponds to the equation $6SiP_2O_6Cl_2 = 3SiO_2 + 3(SiO_2{\cdot}P_2O_5) + 4POCl_3 + P_2O_5$.

	Calculated.	Found.
Loss	49·01	51·86

The formation of the substance, which, for reasons given below, may be designated as *silicopyrophosphoryl chloride*, is most simply expressed by the equation—

$$4SiCl_3(OC_2H_5) + 2POCl_3 = 3SiCl_4 + SiP_2O_6Cl_2 + 4C_2H_5Cl.$$

Silicopyrophosphoryl chloride is a very bulky substance, resembling the lightest form of amorphous silica. It may be obtained perfectly colourless, but is usually more or less coloured by organic matter, formed by secondary reactions, when heated too high. It is extremely hygroscopic, and gives off hydrochloric acid instantly when exposed to moist air. It is readily soluble in absolute alcohol—a proof that it contains no free silica. The alcoholic solution, which probably contains an ether of silicophosphoric acid, may be evaporated nearly to dryness, or heated any length of time at 150° without decomposition. On heating at 225° it soon deposits transparent gelatinous silica. The solution in alcohol is attended with considerable rise of temperature. The substance is insoluble in ether. If cold water be poured on the fine powder it readily dissolves, with the exception of a few flakes of silica; but if first moistened, or if in lumps, most of the silica remains undissolved: the best way to get a clear aqueous solution is to dissolve in a little alcohol and then to dilute with water. The reaction with water alone is somewhat violent. The aqueous solution may be kept a long time—indeed, may be strongly concentrated on the water-bath—but on evaporation *to dryness* a vitreous mass is left, from which water extracts phosphoric acid only.

All attempts to prepare salts of silicophosphoric acid have failed. Ammonium carbonate precipitates gelatinous silica. If the cold aqueous solution, prepared as described above, be acidified with nitric acid, excess of silver nitrate added, and filtered from silver chloride, a clear solution it obtained. If to this be added, drop by drop, dilute ammonia, a white precipitate is formed, which at a certain point changes to yellow. The analysis of the white substance (dried at 100°) gave—

	Calculated for $Ag_4P_2O_7$.	Found.
Ag	71·17	71·25

The yellow precipitate proved to be merely silver orthophosphate.* The filtrate from the silver salts gives an abundant precipitate of silicic acid when warmed with ammonia. The magnesia precipitate also shows the characteristic reaction of magnesium pyrophosphate, dissolving in acetic acid when precipitated in the cold, and being re-precipitated from this solution on boiling.

The substance is therefore a derivative of pyrophosphoric acid, and the formation of some orthophosphoric acid may be explained by the decomposition of the former —pyrophosphoryl chloride dissolving in water with forma-

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* *American Chemical Journal*, Vol. xiii., No. 4.

* The reaction described above affords a convenient method for separating, at least approximately, ortho- from pyrophosphoric acid. A solution of the acids—or their soluble salts—is acidified in the cold with nitric acid, and silver nitrate added in excess. On adding dilute ammonia, drop by drop, all the pyrophosphoric acid is precipitated before any of the orthophosphoric acid comes down. At this point a single drop of ammonia gives a yellow tinge to the precipitate, which a drop of dilute nitric acid causes to disappear. If the liquid be now filtered, all the pyrophosphoric acid will be in the precipitate and all the orthophosphoric acid in the filtrate. The reaction is so sharp that it might possibly be used to separate the acids quantitatively.

tion of orthophosphoric acid (Michaelis, *Ber. d. Chem. Ges.*, iv., 767).

Heated with phosphorus pentachloride at 100°, silico-pyrophosphoryl chloride is readily and quantitatively converted into silicon tetrachloride and phosphorus oxychloride, $SiP_2O_6Cl_2+4PCl_5=SiCl_4+6POCl_3$

The tetrachloride was isolated, and expectations with regard to its nature were confirmed on converting it into the ether (b. p., 165·5°). No silicon oxychloride could be obtained. If heated with an insufficient amount of phosphorus pentachloride, the excess remains apparently unchanged.

The conversion of a derivative of silicic acid into silicon tetrachloride at so low a temperature has not been hitherto observed. R. Weber (*Ann. der Phys. Pogg.*, cxii., 619) obtained the tetrachloride and phosphorus oxychloride by passing the vapour of phosphorus pentachloride over silica at a red heat. As the pentachloride is completely dissociated at 300° into trichloride and chlorine, the reaction is due to the action of chlorine, combined with the reducing action of the trichloride—

$$SiO_2+2PCl_3+2Cl_2=SiCl_4+2POCl_3—$$

which is analogous to the old method of preparing the tetrachloride, $SiO_2+2C+2Cl_2=SiCl_4+2CO$.

As I have convinced myself, phosphorus pentachloride does not act on amorphous silica (dried at 100°), even at 250°, further than to dehydrate it.

The action of a smaller quantity of phosphorus oxychloride on the trichlorhydrine is similar. 3 mols. trichlorhydrine and 1 mol. oxychloride, heated at 180°, gave ethyl chloride, silicon tetrachloride, and a solid product completely soluble in alcohol and water, the composition of which differed, however, from that of the substance above described. (Found: Si, 15·25; P, 22·30; Cl, 14·13).

The action of an excess of phosphorus oxychloride on the chlorhydrines $SiCl_2(OC_2H_5)_2$ and $(SiCl(OC_2H_5)_3$ is essentially similar. At 180—200° a solid substance is formed, with much ethyl chloride and silicon tetrachloride. The amount of the tetrachloride is directly, and that of the solid inversely proportional to the amount of chlorine in the chlorhydrine. In each case the tetrachloride was isolated in a state of approximate purity, and converted into the ortho ether, boiling at 165·5°. No other volatile substances could be detected. The solid body was completely soluble in alcohol, and, in brief, showed all the properties above described as belonging to silico-pyro phosphoryl chloride.

The analysis of the product from $SiCl_2(OC_2H_5)_2$ gave—

	Calculated for $SiP_2O_6Cl_2$.	Found. I.	Found. II.
Si . ..	10·92	11·68	11·80
P.. ..	24·15	24·53	24·91

The product from $SiCl(OC_2H_5)_3$ gave—

	Calculated for $SiP_2O_6Cl_2$.	Found.
Si	10·92	10·15
P	24·15	24·54
Cl	27·59	24·73

The results, as before, are only approximate; but, it must be remembered, the body loses phosphorus oxychloride slowly on heating, and only the crude product could be analysed.

The reactions in these cases are—

$$4SiCl_2(OC_2H_5)_2+4POCl_3=2SiCl_4+2SiP_2O_6Cl_2+\\+8C_2H_5Cl,$$

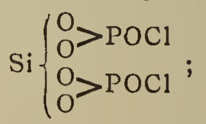
$$4SiCl(OC_2H_5)_3+6POCl_3=SiCl_4+3SiP_2O_6Cl_2+\\+12C_2H_5Cl.$$

Orthosilicic ether, $Si(OC_2H_5)_4$, was heated with excess of phosphorus oxychloride for two hours at 180—200° The tubes contained a solid substance and ethyl chloride. On distilling off the excess of oxychloride and decomposing it with water, only a trace of silica was left after evaporation, showing that practically no volatile silicon compound was formed. The solid, the properties of which were in every respect identical with those of the body above described, gave on analysis—

	Calculated for $SiP_2O_6Cl_2$.	Found. I.	Found. II.	Found. III.
Si	10·92	9·92	10·05	10·21
P	24·15	25·52	25·63	25·84
Cl	27·59	29·66	29·90	—

The reaction is, therefore, represented by the equation, $Si(OC_2H_5)_4+2POCl_3=SiP_2O_6Cl_2+4C_2H_5Cl$.

The constitution of the silico-phosphoryl chloride is possibly very complex. The simplest constitutional formula, deduced from the last equation, would be—



$$Si\begin{cases}\begin{matrix}O\\O\end{matrix}>POCl\\ \begin{matrix}O\\O\end{matrix}>POCl\end{cases};$$

but as this would give no pyro-phosphoric acid on decomposition with water, we must assume that it is—

$$SiO<\begin{matrix}O\cdot PO\cdot Cl\\O\cdot PO\cdot Cl\end{matrix}>O;$$

or a polymer containing the group —O·PO·O·PO·O—, which makes it a derivative of metasilicic acid. The cause of the formation of silicon tetrachloride from the chlorhydrines is not clear. It is obviously not due to a direct replacement of ethoxyl by chlorine, for then it should be obtained in the same amount from each chlorhydrine or from the ether; whereas the latter does not give it, and the amount obtained from the former is proportional to the amount of chlorine they already contain. Besides, no phosphoric ethers are formed. Nor does the supposition explain the formation of silico-pyrophosphoryl chloride in quantities inversely as the amount of chlorine. A possible explanation is the following:—The chlorhydrines* are formed by heating mixtures of orthosilicic ether with silicon tetrachloride, or of either of these with other chlorhydrines, that one being formed in largest amount which corresponds in composition to the mean composition of the mixture; for example—

$$3Si(OC_2H_5)_4+SiCl_4=4SiCl(OC_2H_5)_3.$$

$$2SiCl_3(OC_2H_5)+Si(OC_2H_5)_4=3SiCl_2(OC_2H_5)_2.$$

These reactions take place below 200°, partial dissociation occurring, the products re-uniting to form that body which tends to give the liquid a homogeneous composition. Doubless the reverse process takes place at the same time; for example—

$$4SiCl(OC_2H_5)_3=3Si(OC_2H_5)_4+SiCl_4;$$

and if phosphorus oxychloride be present—which, as just shown, destroys the ether—this can go on until all the chlorhydrine has been converted into ether and tetrachloride. This explanation is simple enough, but, as shown by the action of phosphorus oxychloride on *disilicic* chlorhydrines, the actual process is possibly more complicated.

By heating a mixture of trichlorhydrine, phosphorus, and iodine, a solid of similar properties was obtained, and silicon tetrachloride was formed. The reaction was not followed further.

Action of Phosphorus Oxychloride on Derivatives of Disilicic Acid.

Hexethyl disilicate,† $O<\begin{matrix}Si(OC_2H_5)_3\\Si(OC_2H_5)_3\end{matrix}$, was heated with an excess of phosphorus oxychloride in sealed tubes at 180—200° for two or three hours. The tubes contained a white solid, outwardly resembling silico-pyrophosphoryl chloride and much ethyl chloride. No volatile silicon

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* Friedel and Crafts, *Ann. Chim. Phys.*, [4] ix., 11, 14, 15.

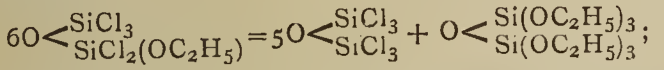
† *Ibid*, [4] ix., 24.

compound was formed. The solid resembled in its general properties the one described. It was completely soluble in alcohol, and therefore contained no free silica. The solution gave the reactions of pyro-phosphoric acid. It differed markedly in composition from the ortho-silicic derivative, the analysis giving—

	Calculated for $SiP_2O_6Cl_2$.	Found.
Si	10·92	17·03
P	24·15	23·91
Cl	27·59	21·04

This corresponds to no probable formula, but contains 4 atoms Si to 5 atoms P, instead of 1 atom Si to 2 atoms P. Phosphorus pentachloride converts it readily (at 100) into silicon tetrachloride and phosphorus oxychloride. No silicon oxychloride is formed, the product passing over entirely below 112°. The tetrachloride was isolated and converted into the tetrethyl ether (boiling at 165·5°).

The ease with which the ortho-chlorhydrines give, with phosphorus oxychloride, silicon tetrachloride, led to an analogous experiment with the *disilicic chlorhydrines*, in the hope that in this way silicon oxychloride might be obtained. On the above hypothesis, we should have, in the presence of phosphorus oxychloride, the following reaction:—



$$6O{<}\substack{SiCl_3\\SiCl_2(OC_2H_5)}=5O{<}\substack{SiCl_3\\SiCl_3}+O{<}\substack{Si(OC_2H_5)_3\\Si(OC_2H_5)_3},$$

and analogous reactions with the other chlorhydrines.

The disilicic chlorhydrines, which have not hitherto been prepared, are formed by heating disilicic ether with an excess of silicon tetrachloride for several hours at 200°. A gradual exchange of ethoxyl and chlorine occurs, disilicic chlorhydrines and orthosilicic trichlorhydrine being formed. After distilling off the latter, the residue is again heated with silicon tetrachloride, whereby the conversion is carried further. In this way a mixture of disilicic chlorhydrines was obtained, which, after freeing from all orthosilicic compounds by repeated distillation, boiled at 170—220°. A chlorine determination showed that it contained the equivalent of 65 per cent Si_2OCl_6. No attempt was made to isolate any of these chlorhydrines, as no less than eight are theoretically possible, and it was presumed that they would all act in the same way toward phosphorus oxychloride. The mixture was heated with excess of phosphorus oxychloride (based on the amount of chlorine shown by analysis), for 2½ hours at 180—200°; after which no further action was observed. The appearance of the product was the same as in previous experiments. The liquid product was distilled off and fractioned. It was found to consist of an excess of phosphorus oxychloride, of *silicon tetrachloride*, which was recognised through conversion into the ether, and ethylchloride. The liquid boiled entirely below 112°, and therefore none of the expected silicon oxychloride was formed. The solid product was markedly different from those before obtained. It was only partly soluble in alcohol, and on boiling out with the solvent, a large residue of *silica* was left. Besides a soluble silico-phosphoryl chloride and ethyl chloride, the only products were silicon tetrachloride and silica. If the oxychloride be formed at all, it is at once decomposed in the presence of phosphorus oxychloride—

$$2Si_2OCl_6=3SiCl_4+SiO_2.$$

Whether this actually occurs is questionable, as the oxychloride and all the other substances concerned are, by themselves, stable at a very much higher temperature than that employed. I am unable to give any satisfactory explanation of the reaction.

Amorphous silica, prepared from water-glass and dried at 100°, gives with phosphorus oxychloride a small amount of silicophosphoryl chloride, soluble in alcohol: 3·5 per cent of the silica was converted into this compound.

The silicon tetrachloride used as the starting material of these experiments was made by the admirable method of Gattermann (*Ber. d. Chem. Ges.*, xxii., 186-8). For preparing the silicon mixture I used, instead of test-tubes, sheet-iron crucibles of about 200 c.c. capacity. These are nearly filled with an intimate mixture of three parts quartz powder and one part magnesium powder, tightly pressed down. On heating over a blast lamp, the reaction starts in a few seconds, and is indicated by the whole crucible suddenly becoming red-hot. During the reaction the lid must be held down firmly. I prefer to extract the magnesia from this product before using it, as less care has to be used in regard to temperature when passing chlorine over it. By using ice alone, to condense the chloride, nearly the theoretical yield is obtained: the crude product loses about 15 per cent in the process of purification.

The *orthochlorhydrines* were prepared essentially according to the method of Friedel and Crafts (*loc cit.*). Any mixture may be used which coincides in composition with that of the chlorhydrine desired. The yield is never theoretical, no matter how long the heating may be continued. The yields of pure substance, obtained after six distillations, were as follows:—Monochlorhydrine, 65 per cent; dichlorhydrine, 40 per cent; trichlorhydrine, 47 per cent. More can, of course, be obtained by uniting and heating the residues.

Friedel and Crafts (*Ann. Chim. Phys.*, [4], ix., 26) obtained the disilicic ether by adding to silicon tetrachloride, drop by drop, alcohol containing the calculated amount of water. They claim that the yield is nearly theoretical. I am not able to confirm this statement. By following their directions exactly, I obtained a mixture of ortho and disilicic ethers, with ethers of much higher boiling-points. After repeated fractioning, only 33 per cent of the theoretical yield of disilicic ether was obtained, and the amount of ortho-ether was much greater. This is due to the fact that the added water acts on the disilicic ether already formed, giving more complex bodies, so that there is an excess of tetrachloride, which is converted into ortho-ether.

The essential results of these experiments may be summed up as follows:—

Phosphorus oxychloride acts on orthosilicic ether and its chlorine derivatives according to the following equations:—

$$\text{I. } 4Si(OC_2H_5)_4+8POCl_3=4SiP_2O_6Cl_2+16C_2H_5Cl.$$

$$\text{II. } 4SiCl(OC_2H_5)_3+6POCl_3=SiCl_4+3SiP_2O_6Cl_2+ +12C_2H_5Cl.$$

$$\text{III. } 4SiCl_2(OC_2H_5)_2+4POCl_3=2SiCl_4+2SiP_2O_6Cl_2+ +8C_2H_5Cl.$$

$$\text{IV. } 4SiCl_3(OC_2H_5)+2POCl_3=3SiCl_4+SiP_2O_6Cl_2+ +4C_2H_5Cl.$$

The body $SiP_2O_6Cl_2$ is the chloride of a silico-pyrophosphoric acid, is decomposed by water into silica and pyrophosphoric acid, and is easily converted by phosphorus pentachloride into silicon tetrachloride and phosphorus oxychloride.

The ether of disilicic acid acts similarly, giving a silico-phosphoryl chloride of different composition but analogous properties.

The chlorhydrines of disilicic acid do not give with phosphorus oxychloride, as might be inferred, a silico-phosphoryl chloride and silicon oxychloride, but a mixture of the first with free silica and silicon tetrachloride.

Phosphorus trichloride also acts on orthosilicic ether at 200°, giving a white solid, and liquid products, which will be further studied.

In conclusion, I wish to express my indebtedness to Prof. F. W. Clarke for liberally placing at my disposal the means of carrying out these experiments.

The Atomic Weight of Bismuth.—Alex. Classen (*Ber. Deutsch. Chem. Gesell.*).—If we take O = 16 the author finds Bi = 208·918; if we assume O = 15·96 Bi = 208·396.

NOTICES OF BOOKS.

A Dictionary of Applied Chemistry. By T. E. Thorpe, B.Sc. (Vict.), Ph.D., F.R.S., Treasurer C.S., Professor of Chemistry in the Royal College of Science, London. In Three Volumes. Vol II. London and New York: Longmans, Green, and Co.

Among the more elaborate articles in this volume must be mentioned those on "Evaporation" and on "Explosives." The latter subject is becoming increasingly complicated from the number of patented and secret compounds and the perplexed synonymy.

"Extraction Apparatus" forms the subject of a thorough-going and well-illustrated article.

The chapter on Fermentation naturally includes a careful study of bacteria or schizomycetes.

In the article on "Filtration" we find a remark which does not agree with our experience. The writer says:—"There are precipitates which instead of forming a bed through which the liquid can percolate form a gelatinous layer over the filtering surface practically impervious to water. As an example, precipitated sewage sludge, to which insufficient lime has been added, may be taken." We have proved, on the contrary, that sewage sludge is capable of filtration in the total absence of lime.

Under water-gas we do not find any caution as to its poisonous character, though analyses quoted show the presence of carbon monoxide in proportions up to 43 per cent. The conclusion is expressed that water-gas, whose actual heating-power is to that of coal-gas only as 2 to 5, cannot compete with the latter, even if it could be produced at the works for nothing.

The article on Lakes is fairly exhaustive, and is ably written.

General Chemical Mineralogy. (Allgemeine Chemische Mineralogie). By Dr. C. Doelter. Leipzig: Engelmann (8vo., pp. 227).

This useful little work, after an introduction expounding general chemical principles, discusses crystallo-chemistry, including dimorphism, physical and chemical isomerism, enanti-tropismism, inootropism, isomorphism, and isodimorphism.

We then come to the chemical analysis of minerals in the dry and the wet way; mineral synthesis is next considered. For the products of this process the author prefers the name artificial minerals. He distinguishes between chemical and mineralogical synthesis, the object of the former being merely the production of a compound which agrees with the natural mineral in its chemical attributes, whilst a mineralogical synthesis to be successful must reproduce the product morphologically and physically as well as chemically.

In a chapter on the formation of minerals in nature there are some interesting remarks on the production of minerals by electric currents and by organisms. The decomposing action of plants does not seem to fall within the author's plan.

The last chapter of the work deals with the chemical composition and constitution of minerals.

At the end of the book we find a good index of the authors quoted, in which very few British names occur, a supplement, and an explanation to the fourteen figures.

Students of mineralogy—a subject the popularity of which is far from being on a level with its importance—will find Dr. Doelter's work a valuable guide.

On the Preparation and the Reaction of Ammonium-Mercury Chlorides.—G. André.—Not suitable for abstraction, and not sufficiently important for reproduction in full.—*Comptes Rendus*, cxii., No. 16.

CORRESPONDENCE.

THE COMPOSITION OF WATER.

To the Editor of the Chemical News.

Sir,—I have read with much interest Mr. Morley's account of his experiment on the "Composition of Water," but is there not some mistake in his estimate of the power required to decompose the water? I have always understood that the quantity of water decomposed by a current of electricity was a measure of the quantity of electricity passing through the cell; yet Mr. Morley obtains the same amount of gas with two currents, one thirty times as strong as the other. This surely must be wrong. Of course if the current strength did not alter by increasing the number of voltameters, then the amount of gas evolved in each cell would be the same as if only one were used, but the addition of each voltameter increases the resistance, and consequently the current must be proportionately reduced.—I am, &c.,

W. A. R.

Plymouth, May 10.

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. cxii., No. 16, April 20, 1891.

On Certain Calorimetric Data.—M. Berthelot.—Not available for useful abstraction.

On the Crystalline Form and the Optical Properties of the New Crystalline Variety of Sulphur of M. Engel.—C. Friedel.—M. Engel's sulphur, independently of its physical and chemical properties, is completely differenciated from all known varieties of crystalline sulphur by its crystalline form.

Dissociation of Amylene Hydrobromate at Low Pressures.—G. Lemoine.—The author's conclusions are shown by the graphic method.

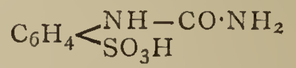
On the Salts of Argentous Oxide.—M. Güntz.—The author has recently shown the existence of a perfectly definite crystalline salt, Ag_2F. By setting out from this product it is easy to obtain the other argentous salts. He has prepared Ag_2Cl, Ag_4S, and Ag_2I.

On Boron Sulphide.—Paul Sabatier.—The author prepares boron sulphide by the action of hydrogen sulphide upon amorphous boron heated to redness. The reaction begins near the temperature at which glass softens and is not complete.

On Hydrogen Boride.—Paul Sabatier.—The hydrogen boride of Jones seems to consist of hydrogen containing a very small quantity of boron hydride. This compound is an exceedingly offensive gas, which burns with a splendid green flame, and is resolved at a red heat into its elements.

On Two New States of Sulphur.—M. Engel.—This paper does not admit of useful abridgment.

Action of Urea upon Sulphanilic Acid.—J. Ville.—The author has obtained a sulphanilicarbamic acid—

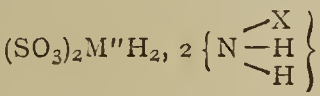


$$C_6H_4{<}\begin{matrix}NH-CO\cdot NH_2\\SO_3H\end{matrix}$$

Determination of Acetone in Denaturated Alcohols.—Leo Vignon.—The acetone may be determined in such alcohols by conversion into iodoform. Iodine must be used in very large excess. The details of the operation may be found in *Comptes Rendus*, cx., p. 534.

The author is studying the form in which sulphanilic acid is eliminated from the animal economy.

New Compounds obtained with Metallic Sulphites and Aromatic Amines.—G. Denigès.—The compounds obtained answer to the general formula—



$$(SO_3)_2M''H_2,\ 2\left\{N\begin{matrix}-X\\-H\\-H\end{matrix}\right\}$$

in which M'' is a bivalent metal (such as Cd, Mn, Fe, Co, or Ni), and X is an aromatic nucleus.

Purification of Industrial Waste Waters and Sewage.—A. and P. Buisine.—The authors venture on the statement that ferric sulphate has not been much used hitherto in the treatment of sewage in default of an economical method for its preparation. They sprinkle burnt pyrites with sulphuric acid at 66° B.

Zeitschrift fur Analytische Chemie.
Vol. xxix., Part 4.

Determination of Tannic Acid in Tanning Materials.—F. Gantter, R. Procter, and E. Guenez.—The former part of this paper will be given in full. The researches of R. Procter will be found in the *Journ. Soc. Chem. Ind.*, and those of E. Guenez have been noticed under the *Comptes Rendus.*

Quantitative Determination of Citric Acid in Vegetable Matter.—Edo Claassen (*Pharm. Rundschau* and *Chemiker Zeitung*).—The plants, &c., are extracted with a very dilute solution of ammonia and ammonium carbonate slightly concentrated, precipitated with lead acetate and filtered. The dry precipitate is extracted at a boil with strong alcohol, suspended in water, treated with sulphuretted hydrogen to remove the lead and filtered. The filtrate is evaporated down to a thin syrup mixed with ammonium chloride, excess of ammonia and calcium chloride, and three times the volume of ammonia is added. The precipitate which is formed is filtered off, washed with a mixture of 3 parts alcohol and 1 part water, and after expelling the alcohol by evaporation to dryness, it is dissolved in hot hydrochloric acid, largely diluted. When cold it is filtered, the filtrate is mixed with an excess of ammonia and filtered again. The filtrate is then evaporated to dryness on the water-bath, the residue is taken up with boiling ammoniacal water, and the precipitate, calcium citrate, is collected on a weighed filter and washed with hot water. As a precaution the filtrate thus obtained is again evaporated to dryness and treated as above, in order to collect further small quantities of calcium citrate which are also collected upon a tared filter.

Methods for the Determination of Starch.—W. Lenz.—This paper will be inserted in full if possible.

Determination of the Diastatic Value of Extracts of Malt.—R. A. Cripps.—From the *Pharm. Journ.* and *Transactions.*

The Impurities of Salicylic Acid.—B. Fischer (*Pharm. Zeit*).—The chief impurities in salicylic acid are kresotic acid, paraoxybenzoic acid, and oxyisophthalic acid. B. Fischer recommends the following simplified process:—3 grms. salicylic are added to 200 c.c. boiling water holding in suspension 1—2 grm. pure calcium carbonate. After the reaction has taken place the liquid is boiled down to 5 c.c. over a free flame, so that there is a plentiful separation of crystals even whilst hot. When cold the mother-liquor and the washings are boiled down to about 1 c.c. in a wide test-tube, and induced to crystallise by rubbing with a glass rod. It is diluted with 1 c.c. of water, filtered through wadding, and again concentrated to 1 c.c. From this liquid hydrochloric acid (if the sample contains 3—5 per cent of the creosotic acids), throws down an acid mixture which melts underneath hot water and collects at the bottom of the tube as a thick, oily drop. Acids containing 0·5 to 1 per cent of creosotic acid do not display this phenomenon. For separating salicylic acid from α-oxyisophthalic acid the mixture must be submitted to distillation along with steam. The non-volatile oxyisophthalic acid remains behind as a light grey powder, and may be shaken out with ether. It is then obtained in snow-white needles by solution in excess of hydrochloric acid and filtration through charcoal. These acicular crystals resemble salicylic acid, but melt with decomposition at 300—305°. The acid is very sparingly soluble in water, easily in alcohol, less readily in ether. It is precipitated by an excess of baryta; the silver salt is sparingly soluble. On separation by calcium salts it remains in the last filtrate.

Determination of Petroleum in Oil of Turpentine.—W. M. Burton.—From the *American Chemical Journal*,

The Examination of Gas Coke.—L. T. Wright (*Society of Chemical Industry*).

Sophistication of Indian Castor Oil with Cocoa-Nut Oil.—M. Conroy.—From the *Pharm. Jour.*

Determination of Morphine in Opium and its Extracts.—A long series of notices from the *Pharm. Central Halle*, the *Archiv. der Pharmacie*, the *American Apotheker Zeitung*, the *American Chemical Journal*, the *Moniteur Scientifique*, &c.

Alkaloidal Reactions of Cubebine. — E. Schär (*Archiv. der Pharmacie*).—For this paper we must refer to the original.

Re-determination of the Atomic Weight of Gold.—J. W. Mallet.—From the *Phil. Trans.* The author concludes in favour of the value 196·762.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 2, No. 535.

Eugène Peligot. — Aimé Girard. — A discourse *in memoriam* delivered at the Annual Meeting of the Société d'Encouragement.

Detection of Impurities Present in Alcohol.—Ed. Mohler.—An examinution of the behaviour of the various alcohols, aldehyds, and ethers present in commercial alcohol according to the colouration which it takes on treatment in heat with sulphuric acid, the colour developed by the action of rosaniline bisulphite, the detection of furfurol by means of aniline acetate, and reduction with potassium permanganate.

The Reactions of Red Prussiate (Potassium Ferricyanide).—M. Prud'homme.—The author examines the action of solutions of ferricyanide with metals and oxides—that of lead nitrate, the ferricyanide, the respective reactions of ferricyanide and potassium chlorate, chromate, and nitro prussiate.

On Bees' Wax.—A. and P. Buisine.—The first portion of an extensive treatise.

Studies on the Tanning Woods.—S. S. Arnaudon.—An account of tanning materials belonging to the family of the Anacardiaceœ, such as the species of Astronium or Urundey, Lythcea or Molle, Schinopnis Laentzii or Quebracho—all natives of South America.

Influence of Silicon upon the Properties of Steel.—R. A. Hadfield.—From the Chemical News.

On Nickel Steel.—J. Hopkinson.—From the *Proc. Roy. Soc.*

Presence of Iron in Zinc obtained from the Dust of Blast Furnaces.—E. Jensch.—The mean proportion of iron present was 22·96 FeO. The finer the dust the more ferrous oxide it contained.

The Obstruction of Gas-Pipes by Naphthaline, and on the Products of the Dry Distillation of Different Coals.—Watson Smith, F.C.S.—From the *Journ. Soc. Chem. Ind.*

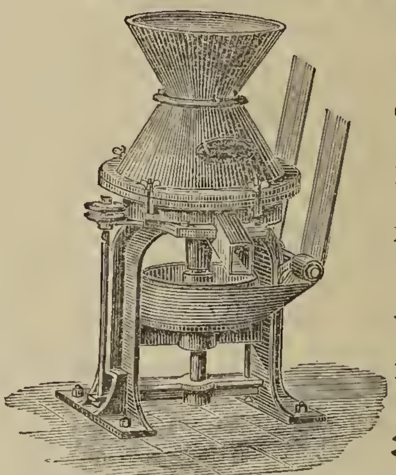
MISCELLANEOUS.

Royal Institution.—Dr. A. C. Mackenzie, Principal of the Royal Academy of Music, will, on Thursday next (May 21st), begin a course of four lectures on "The Orchestra, considered in connection with the Development of the Overture"; and Professor A. H. Church, Professor of Chemistry in the Royal Academy of Arts, will, on Saturday (May 30th), begin a course of three lectures on "The Scientific Study of Decorative Colour."

Detection of Colchicine in Human Remains.—N. Obolonski (*Vierteljahresschrift fur Gerichtlich Medicine and oeffent. Sanitälswesen*).—The intestines, &c., are ground up with glass-powder, the mass is mixed with oxalic acid and digested for 12 hours with alcohol. The liquid is pressed, the dry residue washed twice with alcohol and pressed again. The alcoholic liquids are concentrated on the water-bath at a temperature not exceeding 80°, the cooled residue is again taken up with alcohol to its original volume, filtered, the filtrate concentrated at a gentle heat, the residue re-dissolved, and the filtrate concentrated. These operations are repeated three times, the alcohol is evaporated off, the residue taken up in water, the solution purified by shaking out with petroleum ether, and the colchicine is finally obtained by shaking out with chloroform. In order to distinguish the alkaloid when separated, the author uses the violet colouration with nitric acid, also Erdmann's reagent (nitrosulphuric acid), which gives first a green colour, then deep blue, violet, and yellow, turning raspberry-red on the addition of an alkali, and also Mandelin's test (1 part ammonia vanadate in 200 parts sulphuric acid), which gives a green colour. Colchicine is not readily decomposed on putrefaction. It is most readily found in the kidneys, bladder, and urine.

MEETINGS FOR THE WEEK.

Tuesday, 19th.—Pathological, 8.30. (Anniversary).
— Royal Institution, 3. "The Betterton Period of Stage History," by William Archer.
Wednesday, 20th.—Meteorological, 7.
— Microscopical, 8.
— Pharmaceutical, 11 a.m. (Anniversary).
Thursday, 21st.—Chemical, 8.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "The Orchestra considered in connection with the Development of the Overture," by A. C. Mackenzie, Mus. Doc.
Friday, 22nd.—Royal Institution, 9. "The Molecular Process in Magnetic Induction," by Prof. J. A. Ewing, M.A., F.R.S.
— Physical, 5.
Saturday, 23rd.—Royal Institution, 3. "The Artificial Production of Cold," by H. Graham Harris, M.Inst.C.E.



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THE CHEMICAL NEWS.

Vol. LXIII., No. 1643.

THE VOLUMETRIC COMPOSITION OF WATER.

By EDWARD W. MORLEY.

(Concluded from p. 232).

Determination of Nitrogen contained in the Hydrogen used for Determination of the Volumetric Composition of Water.—The parts p, q, r, were exhausted, filled with hydrogen, from n, and again exhausted. The pressure of the gas in n was then measured by means of m, and its temperature by thermometers at n. From this, with the known volume of n, and its connections, could be computed the reduced volume of the gas in n; then r was heated, and the valve o was opened. When about a litre of hydrogen had been taken from n, o was shut, and the volume remaining was determined. The heating of r was continued till the gas remaining was reduced to some such volume as ten cubic centimetres, when r was cooled, and the gas was extracted by the Sprengel pump. A suitable excess of oxygen was extracted from its store, the two gases were measured, mixed, exploded, and the residue measured. From this was computed the amount of hydrogen found by analysis, whence was learned by difference the amount of nitrogen which was originally contained in the volume known to have been extracted from n.

To illustrate by an actual experiment: In n, before extracting any hydrogen, the temperature and pressure were 766·5 m.m., 20·5 degrees; after, 662·0 m.m. and 20·9 degrees. Hence it was computed that 823 c.c. had been admitted to r. When r was cold, the hydrogen remaining was extracted, and transferred to the apparatus shown in Fig. 3, and found to be 6 722 c.c. at standard temperature and pressure. Oxygen was added, and the sum found to be 17·101 c.c. After explosion there remained 7·019 c.c. Hence the hydrogen found in the 6·722 c.c. taken for analysis was 6·721 c.c. A duplicate analysis agreed well with this; so that this hydrogen was practically free from nitrogen.

Determination of the Volumetric Composition of Water.—Two jars of hydrogen were extracted from n without heating r, and a jar of oxygen from the store of oxygen. I measured a convenient volume of hydrogen; for ease of explanation, suppose it was 180 c.c. About 120 c.c. were transferred after measurement to a jar in the cistern, and the other 60 to a second jar. Then a volume of oxygen either a little smaller or a little larger was measured; suppose it was 175 c.c. After measurement, it was transferred to three jars, 60 c.c. to the jar having 120 of hydrogen, 60 to the other jar of hydrogen, and 55 to a small graduated jar. Another volume of hydrogen was next measured, say 179 c.c. One-third of this was put into the jar into which the smaller quantity of hydrogen had been put before, and the remaining 120 c.c. were left in the eudiometer.

It will be noticed that the three measurements are made at as nearly the same point as is consistent with the fact that there must be a slight excess of either one gas or the other. It would probably have been better to have made the three volumes as nearly equal as possible, and then to have measured a small excess at the point at which the excess was to be measured after the explosion. But this was not thought of in time. As it was, errors of calibration could have no great effect; but they were further made of still less effect on the final mean in two ways. In some experiments, the hydrogen was put in xcess, and in some, oxygen; if in two such experiments the sum of the two gases were the same, the points of measurement of oxygen and of hydrogen would be interchanged, and the errors of calibration would produce contrary effects. Again, the amounts of gas taken were increased from time to time, so that all points from 63 to 75 centimetres were used, by which also accidental errors in calibration were rendered of small influence on the result.

The measured gases were now ready for explosions in fractions. Explosions were always made in the presence of a large volume of inert gas. The ratio of explosive gas to inert was varied within somewhat wide limits, and the same ratio was preserved throughout all the explosions of a given experiment. Suppose that in a given case the ratio desired was that of four to one. To the 120 c.c. of hydrogen left in the eudiometer were added 30 from one of the jars containing hydrogen and oxygen. After this was exploded, a like volume was added again, and so on, till all the gas previously mixed had been consumed. There would still be 120 c.c. of hydrogen in the eudiometer. To this was now added eight c.c. of oxygen from the small graduated jar. The two were mixed by letting mercury drop through the eudiometer, and were exploded. A smaller computed volume of oxygen was added and mixed for the next explosion, and so on, till all the oxygen was finally exploded in presence of fifteen times its volume of hydrogen. But when oxygen was to be finally in excess, a variation was made a little before the last explosion, by adding small quantities of hydrogen to an excess of oxygen in the eudiometer; up to this point, hydrogen was kept in excess. It is obvious that the last explosion of the series is the critical one on whose completeness accuracy depends; sufficient attention was given to this matter.

After the explosion was completed, it cost some trouble to put the eudiometer into condition for good measurement, because so much water had accumulated in it. Then an excess of oxygen or of hydrogen, as the case might be, was added, the mixture was exploded, and the residue was measured. From this was computed the amount of nitrogen in both gases taken together; subtracting the nitrogen known to exist in the hydrogen according to the previous experiment, the remainder was the nitrogen in the oxygen used. The ratio of the volumes of hydrogen to oxygen in water could then be computed. As to the chemistry, consumption of oxygen by oxidation of mercury or of fat, and the possible production of hydrogen dioxide, had to be considered.

When mercury is oxidised in the eudiometer, it is by the oxidation of fine globules on the walls of the eudiometer. In mixing the last third of the oxygen with hydrogen, it was convenient to let a current of mercury run down through the eudiometer, which covered its walls with mercury. In three experiments, some of this mercury was oxidised; two experiments were lost. In the other, it was found possible to reduce the oxidised mercury by a managed explosion, so that the water produced was perfectly clear, as it was in all the other experiments.

There was no carbon in my gases before they were measured. In two experiments, when the eudiometer had not been cleaned, carbon dioxide was produced. This must have come from fat on the walls of the eudiometer forced down by the current of mercury which mixed the oxygen and hydrogen. Since the composition of the lubricant was well enough known, it was possible to add to the oxygen used in producing carbon dioxide the amount used in the combustion of the hydrogen of the fat, and so deduce the value of the ratio sought. As to hydrogen dioxide, in the absence of sufficient knowledge of what might take place in an excess of oxygen, hydrogen was kept in excess till nearly the end of the series of explosions.

To illustrate by an actual experiment, I will give all details of experiment number 6. The first column gives the temperatures, the second the readings of the scale of the eudiometer, the third gives the reduced volume of gas deduced from each measurement, and the fourth gives the adopted mean, with the name of the gas measured.

Temperature.	Pressure.	Volume reduced.	Means.
19·87	688·75	174·333	
19·89	688·76	174·326	174·33 hydrogen.
20·26	680·62	169·954	
20·29	680·65	169·947	169·95 oxygen.
19·44	685·45	172·910	
19·47	685·47	172·905	
19·59	679·98	172·920	172·91 hydrogen.
20·18	137·92	7·797	
20·54	138·08	7·805	7·80 residue.
20·73	255·54	25·271	
21·78	256·02	25·269	25·27 residue and oxygen.
21·80	187·06	13·829	
21·76	187·05	13·830	13·83 residue 2.

1. $\frac{2}{3}(25·27-13·83)=7·62$ c.c., hydrogen in residue 1.
2. 7·80 c. − 7·62 c. = 0·18 c.c., nitrogen in residue 1.
3. 0·18 c.c. − 0·00 = 0·18 c.c., nitrogen in oxygen used.
4. $\dfrac{174·33+172·91-7·62}{169·95-0·18}=2·00047$; ratio sought.

The experiments made divide themselves into groups according to the purity of the gases used. In some, both gases contained nitrogen, in some only the hydrogen, in some only the oxygen, and in some both gases were pure; in some carbon dioxide was produced, although both gases were pure. I give in full the quantities measured or the quantities computed from them in the case of the first experiment of each of these groups; but I selected the eighteenth experiment, rather than the seventeenth, so as to include one in which there was an excess of oxygen.

In the accompanying table I give the approximate temperature and pressure at which the hydrogen and oxygen were measured in each experiment, the amounts of impurities found in each gas, and the amounts of hydrogen and oxygen consumed in the explosion, with the ratio thence deduced. The pairs of determinations which are bracketed together were made one immediately after the other of the pair, with the same stores of gas extracted at the same time, and as nearly as possible under the same conditions, except that different gases were in excess. This will explain why the amounts of impurities found in the oxygen used should show such agreement. The oxygen used in the experiments from the fourth to the twelfth was obviously undergoing slow admixture with air, which was suffered to continue in order to see if the presence of nitrogen affected the ratio found. After a while, the crack in a glass tube which had shown itself was closed by fusion.

Comparison of Results.

Experiment 1 is alone in showing impurity in both gases; its result gives 2·00027 for the value sought.

Experiments 2 and 3 showed nitrogen in the hydrogen; their mean is 2·00029.

Experiments from 4 to 12 showed nitrogen in the oxygen; their mean is 2·00021.

Experiments 13 to 17 and experiment 20 showed no measurable impurity in either gas; their mean is 2·00023.

In experiments 18 and 19 carbon dioxide was produced; their mean is 2·00025.

The mean of the seven experiments where oxygen is in excess is 2·00023, and that of the thirteen in which

Number.	Pressure. C.m.	Temperature. °	Hydrogen taken. C.c.	Oxygen taken. C.c.	Residue. C.c.	Hydrogen in residue. C.c.	Oxygen in residue, C.c.	Nitrogen in hydrogen. C.c.	Nitrogen in oxygen.	Carbon dioxide formed.	Oxygen consumed.	Amount to be subtracted from hydrogen. C.c.	Amount to be subtracted from oxygen. C.c	Hydrogen used.	Oxygen used.	Ratio.
1	64	22	307·89	150·03	8·29	8·015	—	0·11	0·165	—	—	8·12	0·165	299·77	149·865	2·00027
2	64	22	307·29	149·28	8·68	8·57	—	0·11	0·00	—	—	8·68	0·00	298·61	149·28	2·00033
4	66	20	325·36	156·21	13·36	13·21	—	0·00	0·15	—	—	13·21	0·15	312·15	156·06	2·00019
14	72	23	383·30	185·70	11·87	11·87	—	0·00	0·00	—	—	11·87	0·00	371·43	185·70	2·00016
18	75	25	407·98	205·71	1·73	—	1·66	—	—	0·065	0·09	0·00	1·75	407·98	203·96	2·00029

Number.	Temperature.	Pressure.	Nitrogen in hydrogen.	Nitrogen in oxygen.	Carbon diox. produced.	Oxygen consumed.	Hydrogen consumed.	Oxygen consumed.	Ratio.	Gas in excess.
1.	22	64	0·11	0·165	—	—	299·77	149·865	2·00027	Hydrogen.
2.	22	64	0·11	0·00	—	—	298·61	149·28	2·00033	Hydrogen.
3.	19	66	0·12	0·00	—	—	316·45	158·205	2·00025	Hydrogen.
4.	20	66	0·00	0·15	—	—	312·15	156·06	2·00019	Hydrogen.
5.	20	66	0·00	0·15	—	—	325·36	162·67	2·00012	Oxygen.
6.	20	70	0·00	0·18	—	—	339·62	169·77	2·00047	Hydrogen.
7.	20	70	0·00	0·18	—	—	347·24	173·60	2·00024	Oxygen.
8.	20	72	0·00	0·31	—	—	364·58	182·28	2·00011	Hydrogen.
9.	20	72	0·00	0·31	—	—	386·65	193·31	2·00016	Oxygen.
10.	22	72	0·00	0·72	—	—	381·85	190·92	2·00005	Hydrogen.
11.	22	72	0·00	0·82	—	—	389·79	194·87	2·00026	Oxygen.
12.	22	73	0·00	0·82	—	—	395·75	197·85	2·00027	Hydrogen.
13.	23	71	0·00	—	—	—	372·09	186·01	2·00038	Hydrogen.
14.	23	72	0·00	0·00	—	—	371·43	185·70	2·00016	Hydrogen.
15.	23	72	0·00	0·00	—	—	383·30	191·62	2·00031	Oxygen.
16.	26	73	0·00	0·00	—	—	383·51	191·74	2·00016	Hydrogen.
17.	26	73	0·00	0·00	—	—	392·58	196·27	2·00021	Oxygen.
18.	25	75	0.00	0·00	0·065	0·09	399·74	199·85	2·00020	Hydrogen.
19.	25	75	0·00	0·00	0·065	0·09	407·98	203·96	2·00029	Oxygen.
20.	24	75	0·00	0·00	—	—	399 21	199·59	2 00015	Hydrogen.

hydrogen was in excess is also 2·00023. Weights were originally assigned to each result according to the circumstances of each experiment, but they did not change the final mean, and are not given. Four experiments were lost by accident, all others are given. The mean error of a single determination of the ratio is 0·000075, or one part in 26,000. The final mean value of the ratio is 2·0002.

Summary.

Pure hydrogen cannot be obtained from the purest commercial zinc. By the electrolysis of dilute sulphuric acid, with a proper purifying train, I have obtained hydrogen containing less than the hundredth of a c.c. of nitrogen in two litres of hydrogen, and containing no other impurity in amount large enough to be detected. By the use of a fusible metal valve it was possible to obtain any required degree of exhaustion in the part of the apparatus designed to receive hydrogen from the generator. The hydrogen intended to be weighed was not suffered to take up mercurial vapour, nor that intended for analysis to be contaminated with organic matter. A supply of hydrogen sufficient for several experiments was so stored up as to be safe from admixture of air, so that by the apparatus described the amount of nitrogen in it could be determined in duplicate, and other quantities identical in composition could be used for determining simultaneously the amount of nitrogen in the oxygen used, and also the volumetric composition of water. An apparatus for the measurement of gases has been constructed in which the mean error of measurement of the volume of hydrogen and oxygen used in the experiments has been less than one part in fifty thousand. With this, twenty experiments have been made (four others being lost by accident and not completed), which gave a maximum value for the composition of water 2·00047, a minimum value 2·00005, and a mean value 2·00023. Variations in the process gave no corresponding variation in the result. The mean error of a single determination was one part in 26,000.

For the present, then, we may believe that water, when the gases are measured under ordinary temperatures and pressures, is composed of 2·0002 volumes of hydrogen to one volume of oxygen; or that under ordinary conditions the number of molecules in a given volume of oxygen is 1-9000th part greater than the number of molecules in an equal volume of hydrogen.

SILICON FILIMS.

By H. N WARREN, Research Analyst.

In the Chemical News (vol. lviii., p. 215), I published a short account of the production of silicon hydride, noting its peculiar properties; since that period recent investigations upon this and other gases have led to valuable results. Before stating the decomposition of this substance into its component parts, I will give a brief outline of the induction coil employed which was of special construction, the core, or magnet, consisting of two pounds of chemically pure iron wire, upon which was wound about a pound of very thick copper wire, the whole being enclosed in a thick ebonite tube and filled up with pure paraffin wax. This, on being connected to a condenser of 280 sheets of tin-foil, constitutes the primary coil; over this tube was wound in 25 segments, each one being insulated from the other by means of mica disks, 9¾ lbs. of No. 26 copper wire of double silk covering, the object of using so thick a grade being to increase the width of the spark in proportion to its length; the whole was now coated with paraffin, covered with thick vulcanite, and mounted. By the aid of six Bunsen batteries, a spark of six inches in length and of considerable width was thus obtained, the intensity being sufficient to pierce oak planks one quarter of an inch in thickness.

To prepare the silicon hydride, magnesium silicide was obtained by passing over metallic magnesium heated to dull redness a slow stream of silicon fluoride, until half the metal was consumed. The mass was now withdrawn from the tube and melted under a flux composed of a mixture of magnesium, potassium, and sodium chloride, a button of magnesium silicide being thus produced. This was at once introduced into an apparatus for evolving hydrogen gas, and connected to a glass tube through which passed the two electrodes in connection with the induction coil, the apparatus being cleared of the atmospheric air it contained by acting upon metallic magnesium contained therein previous to the introduction of the silicide. When the whole of the atmosphere was thus abstracted, the silicon hydride was evolved by the addition of acetic acid; the current from the coil was now turned on, amorphous silicon being at once deposited upon various parts of the glass tube, but not until the two points were in close proximity to each other did any appearance of a compact filim begin to manifest itself. This, when once started, increased in length upon the withdrawal of the electrodes to a more remote distance, filling up the luminous arc and spreading out towards the furthur electrode; the silicon thus produced was undoubtedly absolutely pure, and when exposed to the flame of a Bunsen burner became converted into a white ash consisting of pure silica.

The gas, in admixture with coal gas, was next treated, and was readily decomposed, yielding a filim consisting of a mixture of silicon and carbon. The idea of utilising these so produced filims for electro-incandescent lamps was naturally one of the first prospects which presented itself; but on account of the silicon appearing mostly as amorphous, it is not sufficient to protect a carbon filim over a certain time. It has nevertheless been the means, however, of carrying out an entirely different, and at the same time efficient and simple process, whereby a dense silicon of peculiar formation has been so produced that several carbon filims that have been thus coated have even withstood the action of the atmosphere for long durations.

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ANALYSIS OF A CHROMITE.*

By H. PEMBERTON, Jun.

On the Pacific Coast of the United States there are several deposits of chromite. As no complete analysis of any of these minerals has, to my knowledge, been published, it may be of interest to place on record an analysis I made some time ago.

According to Wm. Irelan, jun., State Mineralogist of California, throughout the Santa Lucia Mountains and the coast hills of San Luis, Obisbo County, Cal., are found serpentine rocks with beds of chromite, in greater or less masses, existing as loose and fragmentary rocks in the ravines and on the hillsides, ahd as pockets and veins on the mountains. One of the best mines of the neighbourhood is the Pick and Shovel, located on the South Fork of Chorro Creek, at an elevation of 1800 feet.

A sample of the chromite from this mine, selected as free from gangue as possible, gave an analysis in the following results:—

Cr_2O_3	52·68
Al_2O_3	11·40
Fe_2O_3	3·52
MgO	16·23
FeO	11·77
MnO	0·15
SiO_2	3·40
H_2O	0·94
	100·09

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* Read at the Chemical Section of the Franklin Institute, March 17, 1891.

An analysis of the gangue showed it to be serpentine, containing a trace only of ferrous oxide. No other foreign mineral could be detected on a careful examination. Deducting, therefore, the water, silica, and quantity of magnesia (3·26 per cent) combined with the silica (as serpentine) and calculating the remainder to 100 parts, we obtain for the pure mineral :—

Cr_2O_3	56·96	0·374	=0·519
Al_2O_3	12·32	0·121	
Fe_2O_3	3·81	0·024	
MgO..	14·02	0·350	=0·529
FeO	12·73	0·177	
MnO..	0·16	0·002	
	100·00		

R_2O_3 : RO = 519 : 529 = 1·00 : 1·02.

The mineral was decomposed by fusion with sodium carbonate. (Christomanos' process slightly modified). The mixture of ore and Na_2CO_3 is heated over night by a Bunsen burner, the crucible being loosely covered by its lid. Next morning it is heated for one hour over the blast lamp, with frequent stirring. The process has the advantage of giving complete decomposition of the mineral, with the introduction of no bases other than the alkalies.

The ferrous oxide was determined by solution in sulphuric acid in a closed tube, under pressure. According to Francis C. Phillips (*Fres. Zeitschrift*, xii., 189), 1·34 is the specific gravity of the acid that is most favourable to the solution of chromite in this manner.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

May 7th, 1891.

Dr. J. H. Gladstone, F.R.S., Vice-President, in the chair.

Certificates were read for the first time in favour of Messrs. Edward Brown, 32, Courlandsky Street, St. Petersburg; Ernest A. Congdon, Lehigh University, St. Bethlehem, U.S.; W. Porter Draper, 1, Ceal Villas, Ceal Road, Enfield; Thomas Mitchell, c/o E. Mitchell, Crossmount, Bridgend, N.B.; H. J. Marston Mousley, Kingsbury, Portland Road, Edgbaston; Edward Rhodes, Holybank, Frodsham, Cheshire; John Taylor, 15, Lucius Street, Torquay.

The following were elected Fellows of the Society :— Messrs. Edward Arthur Barnes, William Bate, Claude Hooper Bater, Albert Edward Bell, Rhys Pendrilt Charles, Walter Johnson Cooper, Frederick Arthur Evans, Gilbert John Fowler, Joseph Fitze, John Alfred Foster, Berington H. Gibbins, William L. Hiepe, Ph.D., William Beaumont Hart, Walter Herbert Joseland, F. Stanley Kipping, D.Sc., Alexander Lauder, Rev. Edgar Norman Langham, James Leicester, George R Morrison, William Macdonald, Charles Ainsworth Mitchell, Frederick Johnson Merrils, Lewis Ough, Percy Morris Randall, James Ashburner Storey, Albert Searl, James Fowler Tocher, Cecil George Freer Thonger, M.R.A.C., John Wild.

The Chairman announced that since the last meeting of the Society took place a congratulatory address, of which the following is the text, had been forwarded to Professor Stas :—

We, the President, Officers, and Council, on behalf of the Chemical Society, most heartily congratulate you, Professor Jean Servais Stas, on the completion of your fiftieth year of membership of the Royal Belgian Academy of Sciences, Literature, and Arts.

Among the names of the distinguished investigators who have raised chemistry to the dignity of an Exact Science, none either merits or receives a more honoured position than that of Stas. Your researches are universally recognised among men of science as of fundamental importance. By your incomparable determinations of the atomic weights of a large number of the more important elements you have not only placed in our hands numerical data of the utmost value, but your researches are models which must ever serve to show how such determinations should be effected and the innumerable precautions which must be taken. Concerning these precautions comparatively few, even among chemists, fully realise the extent to which they have been shown by you to be necessary: those who have been engaged in similar investigations can only entertain an admiration almost reverential in character for the man who could plan and successfully carry out a prolonged series of such refined, tedious, and delicate operations. A most important result of your inquiries has been the refutation, in its original form at least, of the famous hypothesis of Prout: your marvellously accurate determinations showing that it is no longer possible to believe that the atomic weights of the elements are expressible as a series of multiple whole numbers. With strict logical propriety you have refrained from pronouncing any opinion in explanation of the discrepancy; the data which you have established, however, will surely serve in the future as the groundwork of further discussion of the problem of the mass relationship of the elements. The methods which you have devised for the preparation of pure substances have, in many cases, in themselves been important contributions to chemical science; and the service which you have rendered by teaching the chemist how to prepare pure reagents is of the utmost value. Hence your *Recherches sur les Rapports réciproques des Poids atomiques* must be handed down to future generations as one of the most valuable classics of the Exact Sciences. Apart from the intrinsic value of your work, you have through it exercised a beneficent influence on your colleagues throughout the world, the importance of which cannot be over-estimated; and in the eyes of chemists generally, you are ever regarded as an honour to Science, to your country and to the distinguished Academy of which you have now been an ornament for half a century.

The following papers were read :—

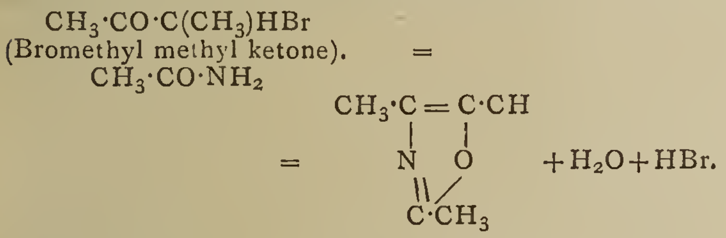
11. *The Action of Alkalis on the Nitro-Compounds of the Paraffin Series.*" By Wyndham R. Dunstan and T. S. Dymond.

The authors have further investigated the conditions and products of the interaction of alkalis and nitroethane, of which they have already given a preliminary account to the Society (*Proc.*, 1888, 117).

Nitroethane attacks alkali carbonates in the cold with formation of carbon dioxide and the alkali derivative of nitroethane which is also obtained when alkali hydroxide is employed. Ammonia combines with nitroethane in the cold to form a crystalline compound analogous to the potassium and sodium derivatives. The action of alkalis does not appear to proceed further at atmospheric temperatures, but on warming, alkali nitrite, acetonitrile, and a new compound, boiling at 170° and freezing to a crystalline solid at 3·5°, are produced. The new compound is a feeble base, which forms unstable salts decomposed by water: the *mercurichloride* has the formula $C_6H_9NO,HgCl_2$, and the *aurichloride* the formula $C_6H_9NO,AuCl_3$. It is remarkable for its great stability, being almost unaffected by heating in closed tubes with strong acids and alkalis. Permanganate oxidises it to acetic acid, and nitric acid to acetic and oxalic acids. It is hard to attack with the usual reducing agents, but is slowly decomposed with formation of ammonia, acetic acid, and secondary butyl alcohol. By acting with sodium on a well cooled moist ethereal solution, a *dihydride* is formed ($C_6H_{11}NO$): this is a crystalline compound (m. p. 110°, corr.), which is resolved by heating with water into ammonium acetate and ethyl methyl ketone.

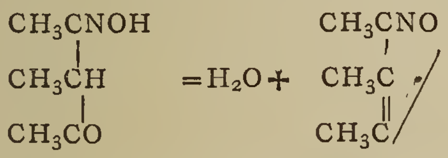
The interactions of the compound prove that it is neither a pyridine nor pyrrol derivative nor a ketocyanide. Most of its properties are consistent with the view that it is either a trimethyloxazole or a trimethylisoxazole.

Trimethyloxazole was produced by the interaction of acetamide and bromethyl methyl ketone.



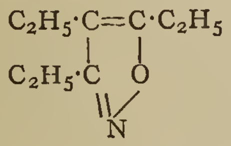
This oxazole was found to have some properties in common with the substance under investigation, but in other respects was entirely different, especially in its physical characters.

Trimethylisoxazole was prepared by acting on the β-diketone, methyl acetyl acetone with hydroxylamine. It may be supposed that the monohydroxime is first formed, and that this then loses water.



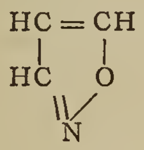
The trimethylisoxazole thus produced is in every respect identical with the compound obtained from nitroethane.

Nitropropane when acted on by alkalis yields triethylisoxazole,



propionitrile, and alkali nitrite, but interaction occurs with greater difficulty than in the case of nitroethane.

Nitromethane is very readily attacked by alkalis with formation of hydrogen cyanide, alkali nitrite, and much resin. The parent isoxazole,



could not be isolated, but the interaction is still being investigated.

Secondary nitropropane is attacked with difficulty by alkalis. Alkali nitrite is produced, but no isoxazole.

12. "*Some New Addition Compounds of 'Thiocarbamide' which afford Evidence of its Constitution.*" By J. Emerson Reynolds, M.D., F.R.S.

In the course of the author's work on silicon compounds, a thiocarbamide derivative containing silicon tetrabromide was obtained which broke up on treatment with ethyl alcohol, affording among other products the fine crystalline substance $(H_4N_2CS)_4H_4NBr$. The same compound was subsequently obtained by direct union of its components as was described in a former paper (*Trans.*, 53, 857). This substance proved to be the first of a series, and the present paper gives an account of their detailed examination of all the members prepared. The following is a summary of the results of the investigation:—

1. Thiocarbamide combines with ammonium bromide, iodide, and chloride at the temperature of boiling alcohol, forming characteristic compounds of the type $(H_4N_2CS)_4H_4NR'$. But no compounds were formed under the conditions specified which contained fewer than four molecular proportions of amide to one of ammonium salt.

2. The following mono- and di-substituted thiocarbamides failed to afford any compounds with ammonium bromide at the temperature of boiling alcohol, viz., methyl-, ethyl-, allyl-, phenyl-, diphenyl-, and acetylphenyl-thiocarbamides.

3. Thiocarbamide combines with tetrethylammonium bromide and iodide, forming well-defined crystalline compounds of the type $(H_4N_2CS)_2Et_4NR'$. No well-defined substance could be isolated under any of the experimental conditions containing more than 2 mols. of the amide and 1 of the tetrethylammonium salt.

4. Thiocarbamide combines with diethylammonium bromide, forming a well-crystallised compound—

$$(H_4N_2CS)_3Et_2H_2NBr.$$

If a tetra-compound be formed in solution, it is certainly broken up on slow crystallisation.

5. Thiocarbamide also unites with triethylammonium bromide, and in presence of excess of amide a somewhat felted mass is obtained, which on re-crystallisation affords two distinct forms of crystals, viz.:—

$$(H_4N_2CS)_3Et_3HNBr \text{ and } (H_4N_2CS)_2Et_3HNBr.$$

6. With methylammonium bromide, thiocarbamide afforded the compound $(H_4N_2CS)_4MeH_3NBr$, which resembles the corresponding ammonium bromide compound in appearance, but melts at a temperature 34° lower. On the other hand, with *ethyl*ammonium bromide, no combination whatever could be effected, and when the amide and salt in the molecular proportions 4 : 1 were heated in a pressure tube to 135° with alcohol, ethyl oxide and *tetrathiocarbamidammonium bromide* were the products.

The author shows that the foregoing facts are not in agreement with the view that thiocarbamide is $CS(NH_2)_2$, but are altogether in favour of the unsymmetrical structure $HN{:}C(SH)NH_2$.

It is pointed out than an interesting practical application of the compound $(H_4N_2CS)_4H_4NBr$ has recently been made by Colonel Waterhouse to the production of *direct positive* photographs. So effective is the agent in securing the reversal of the photographic image, that the presence of only 1-100th of a grain per ounce of "eikonogen" developer causes the negative image that first appears to change into a rich coloured positive.

Discussion.

Referring to the reversed photographs exhibited by Professor Reynolds, Mr. Groves drew attention to the curious fact that the silver deposit which, in the early stage of development, apparently behaved like that forming an ordinary negative image, in the later state became soluble.

13. "*The Action of Acetic Anhydride on Substituted Thiocarbamides; and an Improved Method for Preparing Aromatic Mustard Oils.*" By Emil A. Werner, Assistant Lecturer in Chemistry, Trinity College, University of Dublin.

The present investigation originated from an experiment carried out with the object of obtaining an acetylated diphenylthiocarbamide by the action of acetic anhydride on sulphocarbanilid. The action of the anhydride on diphenyl-, ortho-, meta- and paraditolyl-, metadixylyl, dibenzyl- and diethythiocarbamides has been studied. In the case of the benzenoid derivatives, the results are summed up in the following statements:—

1. No acetylated derivatives of the thiocarbamides were produced.

2. The mere dissolution of the thiocarbamide in acetic anhydride is accompanied by simultaneous decomposition

into "anilid" and mustard oil in accordance with the equation—

$$CS(NHR)_2+(CH_3CO)_2O=CH_3CONHR+\\+R{\cdot}NCS+CH_3COOH.$$

3. *Five minutes* heating at the boiling point of acetic anhydride gives an almost theoretical yield of mustard oil.

4. An extension of the time of heating induces a secondary interaction between the mustard oil and acetic acid, whereby the yield of the former is rapidly diminished, viz.:—

$$R{\cdot}NCS+CH_3COOH=CH_3CONHR+COS.$$

Curves are given in the original paper, showing the influence of time on the rate of fall in the yield of mustard oil.

In the case of the paraffinoid thiocarbamides the results are different.

1. A well defined acetylated thiocarbamide is first produced.

2. Further heating gives rise to the formation of mustard oil, but the yield of the latter is never high, on account of the secondary interaction proceeding simultaneously with the generation of the mustard oil.

3. Prolonged heating gives a substituted amide as final product.

Acetyldibenzylthiocarbamide—

$$CS(NH{\cdot}CH_2Ph)(NAc{\cdot}CH_2Ph),$$

prepared from dibenzylthiocarbamide, crystallises from alcohol in prisms; m. p. 93° C. The alcoholic solution is not desulphurised by boiling with alkaline lead tartrate. With $AgNO_3{\cdot}2NH_3$ it gives a white precipitate. It decomposes partly on distillation, yielding between 175—180° an oil rich in sulphur, and between 180—190° the distillate solidifies to a substance which after purification forms colourless crystals melting at 60—61° and free from sulphur.

Acetylbenzylthiocarbamide—

$$CS(NH{\cdot}CH_2Ph)(NH{\cdot}CO{\cdot}CH_3),$$

was incidentally prepared from acetic anhydride and monobenzylthiocarbamide. It crystallises from alcohol in thin rhombic prisms; m. p. 129—130°. The alcoholic solution, unlike that of the previous compound, desulphurises alkaline lead solution on boiling, and with $AgNO_3{\cdot}2NH_3$ gives a white precipitate which darkens on standing, and is immediately blackened on boiling. On distillation, the urea decomposes partly into CH_3CONCS and benzylamine and partly into benzylthiocarbimide and acetamide.

14. "*The Decomposition of Silver Chloride by Light.*" By Arthur Richardson, University College, Bristol.

The author describes experiments which have been made with a view to determine whether silver chloride which has been darkened by exposure to light under water contains oxygen. The nature of the change which occurs during decomposition of the chloride was also studied with reference to the part played by water.

Pure silver chloride was prepared by addition of dilute chlorhydric acid to a solution of pure silver nitrate, the precipitate being washed by decantation till free from acid. The following facts were observed during exposure:—

(1.) Oxygen was evolved, a part of which was present as ozone.

(2.) When small quantities of water were present, chlorine and hydrogen chloride were found in solution.

(3.) When a large volume of water was taken, hydrogen chloride but no chlorine was detected.

The influence of hydrogen chloride in retarding the decomposition of silver chloride is considered, and is explained from experimental results given, which show that even minute quantities of hydrogen chloride exercise a marked influence on the stability of chlorine water when exposed to light, he rate of decomposition of the silver chloride being dependent on the readiness with which the chlorine in solution and water interact to form hydrogen chloride. Thus, when silver chloride was exposed to light in a solution of hydrogen chloride containing 0·9 part per 100 of solution, the total chlorine liberated was 0·201 grm., of which 13·7 per cent represented free chlorine, whilst for the same weight of silver salt in pure water the total chlorine found was 0·276 grm., of which 0·9 per cent was present as free chlorine.

In the examination of the darkened product for oxygen, a portion of the substance was taken which had lost 8 per cent of its total chlorine during exposure. After it had been dried at 110° C. till it ceased to lose weight, it was heated in a current of pure hydrogen, the gaseous products of the reduction being passed through a weighed phosphorus pentoxide tube. Before using this substance as an absorbent of moisture, it was ascertained that hydrogen chloride was not absorbed by it after contact for a few hours only, as the weight of the tubes remained unaltered in contact with the dry gas. The hydrogen was prepared by the action of steam on sodium, numerous precautions, which are described in full in the paper, being taken to preclude errors.

The results show that the gain in weight of the drying tubes after the decomposition of the silver compound, which lasted from 7—8 hours, is so small as to preclude the possibility of the presence of an oxygen compound in the darkened product. The darkening of the carefully dried chloride was also observed to take place when exposed to light in a tube containing dry carbon tetrachloride from which all air had been removed by boiling. From these facts the author concludes that the darkened silver compound is of the nature of a subchloride rather than an oxychloride.

15. "*The Addition of the Elements of Alcohol to the Ethereal Salts of Unsaturated Acids.*" By T. Purdie, Ph.D., B.Sc., and W. Marshall, B.Sc.

In this paper the authors record the results of further experiments on the addition of the elements of alcohol to ethereal salts of fumaric and maleic acids by the agency of small quantities of sodium alkylate; they also describe a series of similar experiments with other ethereal salts, the object of which was to ascertain if the ethereal salts of unsaturated acids in general are capable of undergoing the same additive change.

By the action of small quantities of sodium methylate in the cold on a mixture of methyl alcohol and methylic fumarate, the latter is converted, almost quantitatively, into methylic methoxysuccinate, which crystallises in very large and perfectly developed crystals melting at 28°. Methylic methoxysuccinate from methylic maleate is identical with that obtained from methylic fumarate. Methoxysuccinamide, from the action of alcoholic ammonia on the ethereal salts, melts at 175°.

From the product of the action of alcoholic sodium methylate on methyl fumarate aided by heat, an amorphous substance was obtained, the composition of which agreed with that of a compound having the formula $C_{11}H_{12}O_7$, formed by the abstraction of 3 mols. of methyl alcohol from 2 mols. of methylic methoxysuccinate.

By the action of small quantities of sodium methylate on a mixture of methylic acrylate and methyl alcohol, methylic methoxypropionate was obtained.

Methylic and ethylic crotonate gave, in a similar manner, methylic methoxybutyrate and ethylic ethoxybutyrate respectively. The metallic salts of these acids are mostly gums or resins, but the acid amines are crystalline; the methoxybutyramide melts at 69°, and the corresponding ethoxy-derivative at 75°. The authors think that in the interaction under consideration, the alkoxy-group attaches itself to the β-carbon atom, but the evidence on this point is not conclusive.

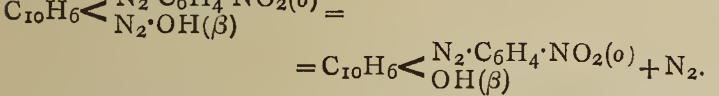
Ethylic methacrylate seems also to be capable of combining with the elements of alcohol, but pure products were not obtained.

Ethylic angelate, ethylic allylacetate, methylic and ethylic cinnamate, and ethylic o-(β-)ethylcumarate were found incapable of the additive change under investigation. Similar experiments were made with ethylic phenylpropiolate, but no additive product was obtained.

The ethereal salts of unsaturated acids differ greatly in respect of their capability of combining with the elements of alcohol under the agency of sodium alkylate. This capability is, no doubt, affected by the position of the doubly-linked carbon atoms and by the nature of the atomic groups with which they are united. It is, however, impossible at present to draw any general conclusion regarding the influence of these factors.

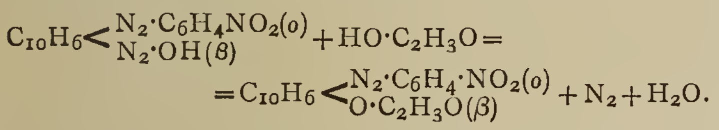
16. "*Notes on the Azo-derivatives of β-naphthylamine.*" By RAPHAEL MELDOLA, F.R.S., and FRANK HUGHES.

The authors have completed the series of azo-derivatives obtainable from the nitranilines and β-naphthylamine by preparing orthonitrobenzeneazo-β-naphthylamine. This compound crystallises in bronzy scales; m. p. 198°. When acted on by sodium nitrite in a warm glacial acetic acid solution, it gives orthonitrobenzeneazo-β-naphthol—



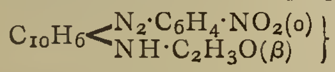
$$C_{10}H_6{<}\begin{matrix}N_2{\cdot}C_6H_4{\cdot}NO_2(o)\\N_2{\cdot}OH(\beta)\end{matrix} = \\ = C_{10}H_6{<}\begin{matrix}N_2{\cdot}C_6H_4{\cdot}NO_2(o)\\OH(\beta)\end{matrix} + N_2.$$

The latter forms bright red needles; m. m. 209—210°. When the interaction is effected in a cold acetic acid solution, the naphthyl acetate is formed—

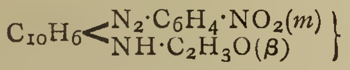


$$C_{10}H_6{<}\begin{matrix}N_2{\cdot}C_6H_4NO_2(o)\\N_2{\cdot}OH(\beta)\end{matrix} + HO{\cdot}C_2H_3O = \\ = C_{10}H_6{<}\begin{matrix}N_2{\cdot}C_6H_4{\cdot}NO_2(o)\\O{\cdot}C_2H_3O(\beta)\end{matrix} + N_2 + H_2O.$$

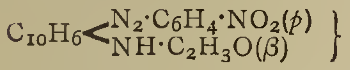
The latter is a deep red oil, from which the acetyl group is easily removed by alkalis. Acetyl derivatives of the ortho-, meta-, and para-nitroazo-derivatives of β-naphthylamine have also been prepared—



$C_{10}H_6{<}\begin{matrix}N_2{\cdot}C_6H_4{\cdot}NO_2(o)\\NH{\cdot}C_2H_3O(\beta)\end{matrix}$ } Dull orange needles; m. p. 154°.

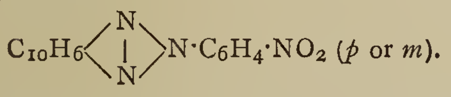


$C_{10}H_6{<}\begin{matrix}N_2{\cdot}C_6H_4{\cdot}NO_2(m)\\NH{\cdot}C_2H_3O(\beta)\end{matrix}$ } Bright orange needles; m. p. 192°.



$C_{10}H_6{<}\begin{matrix}N_2{\cdot}C_6H_4{\cdot}NO_2(p)\\NH{\cdot}C_2H_3O(\beta)\end{matrix}$ } Dull red needles; m. p. 227—228°.

The pseudazimides from the para- and meta-nitro-compounds have been prepared by Zincke's method of oxidation with chromic acid in glacial acetic acid solution. The first of these crystallises in flat, colourless needles, m. p. 236°, and the second in whitish needles of m. p. 224°. The ortho-compound gives but a very small quantity of pseudazimide on oxidation. The formula of these compounds is—



The action of aldehyds on these β-naphthylamine azo-derivatives gives rise to the formation of triazines, which are being investigated. Fuming nitric acid in the cold converts the azo-compounds into orange, amorphous products which are apparently definite but difficult to purify and explosive.

17. "*The Estimation of Nitrates.*" By G. MCGOWAN, Ph.D.

The author describes a method of estimating nitrates based on the interaction

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

The nitrate is warmed together with an excess of concentrated chlorhydric acid in an apparatus from which air has been expelled by CO_2, and the gaseous products are led into a solution of potassium iodide; an amount of iodine is liberated equivalent to the whole of the chlorine carried forward, nitric oxide escaping, *i.e.*, $HNO_3 = 3Cl$.

18. "*New Benzylic Derivatives of Thiocarbamide.*" By AUGUSTUS E. DIXON, M.D.

A re-examination of "monobenzylthiocarbamide" has shown that the substance hitherto bearing this name is really benzylamine thiocyanate; the latter can be converted into the isomeric thiocarbamide by heating for a short time at 150—160°. The melting-point recorded for symmetrical dibenzylthiocarbamide also requires correction; it lies between 146° and 147°, and not at 114°, as stated.

The following compounds are described:—

Benzylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH_2$, small white prisms; m. p. 161—162°.

Benzylorthotolylthiocarbamide—

$$Ph{\cdot}CH_2{\cdot}NH_2{\cdot}CS{\cdot}NH\mathit{o}To,$$

white, rhombic prisms; m. p. 138—139°.

Benzylmetatolylthiocarbamide,—

$$Ph{\cdot}CH_2.NH{\cdot}CS{\cdot}NH\mathit{m}To,$$

glassy clear rhombs, m.p. 113—114°.

Benzylparatolylthiocarbamide,—

$$Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}\mathit{p}To,$$

glassy rhombic crystals; m. p. 120—121°.

Benzylmetaxylylthiocarbamide,—

$$Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_3Me_2,$$

large colourless monoclinic prisms; m. p. 84—85°.

Benzylalphanaphthylthiocarbamide,—

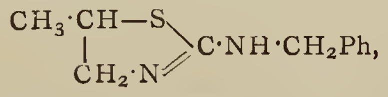
$$Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7,$$

micaceous-looking rhombs; m. p. 172—173°.

Benzylbetanaphthylthiocarbamide rhombic plates; m. p. 165—166°.

Allylbenzylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}All$, colourless rhombic crystals; m. p. 93—94°. Converted by heating with HCl at 100° into—

Benzylpropylene-ψ-thiocarbamide,—



fine white needles; m. p. 65—66°.

Acetylbenzylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NHAc$, thin pearly plates; m. p. 128—129°.

Benzylmethylphenylthiocarbamide,—

$$Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NMePh,$$

white prisms; m. p. 84—85°.

Methylphenylbenzylthiocarbamide,—

$$MeNH{\cdot}CS{\cdot}NPh{\cdot}CH_2Ph,$$

shining white prisms; m. p. 120—121°.

Benzylethylphenylthiocarbamide,—

$$Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NEt{\cdot}Ph,$$

long slender oblique prisms; m. p. 90—91°.

Ethylbenzylphenylthiocarbamide,—

$$Et{\cdot}NH{\cdot}CS{\cdot}NPh{\cdot}CH_2Ph,$$

short thick rectangular prisms; m. p. 90·5—91°.

Benzylphenylbenzylthiocarbamide,—

$$Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NPh{\cdot}CH_2{\cdot}Ph,$$

white pointed prisms; m. p. 102—103°.

Benzylpiperidylthiocarbamide,—

$$Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}N{:}C_5H_{10},$$

waxy-looking prisms; m. p. 85—88°.

19. "*Interaction of Phenylthiocarbimide and Acetic Acid.*" By EMIL A. WERNER, Trinity College, Dublin.

This interaction was originally made the subject of an experiment by Professor von Hofmann, and later on by Claus and Völtzkow; the former considered diacetanilid to be the product, while the latter simply mention acetanilid as being formed.

In neither case was the examination of the products exhaustive. The author has made a careful re-investigation of the subject, and wishes to state his results at once, as an abstract of a paper, by Messrs. Cain and Cohen, on the same interaction, appeared in the last *Proceedings*. The author agrees with Messrs. Cain and Cohen, that diacetanilid is not formed, but his results oblige him to differ entirely from these gentlemen with respect to the course of the change.

The influence of water on the nature of the interaction is very marked. With *pure anhydrous* acetic acid and phenylthiocarbimide, interaction takes place, *quantitatively*, at 130—140°, in accordance with the equation, $C_6H_5NCS+CH_3COOH=CH_3CONHC_6H_5+COS$.

If the acid *contain water*, H_2S, CO_2, and diphenylurea are formed as products of a secondary change, viz., $2C_6H_5NCS+3H_2O=CO(NHC_6H_5)_2+CO_2+2H_2S$.

At a higher temperature, 160—170°, the diphenylurea disappears, through interaction with acetic acid, thus:

$$CO(NHC_6H_5)_2+2CH_3COOH= \\ =CH_3CONHC_6H_5+CO_2+H_2O,$$

the extent to which this change takes place increases, within certain limits, with the proportion of water present in the acid.

Propionic acid and phenylthiocarbimide interact in a similar manner, but with formic acid a secondary interaction takes place, which appears to be independent of the presence of water.

Research Fund.

Fellows desiring grants are requested to forward their applications to the Secretaries, in order that they may be considered at a meeting early in June.

PHYSICAL SOCIETY.

April 17th, 1891.

Visit of the Physical Society of London to Cambridge.

On Saturday, the 9th inst., the Society varied its ordinary procedure by paying a visit to the ancient seat of learning situated on the banks of the Cam.

Assembling at Liverpool Street Station, members and visitors to the number of about one hundred were conveyed in saloon carriages by the 11 o'clock express direct to their destination, the whole journey being accomplished in about seventy-five minutes.

Amongst those present were Dr. E. Atkinson, Prof. Ayrton and Mrs. Ayrton, Mr. Walter Bailey, Mr. Shelford Bidwell and Mrs. Bidwell, Mr. D. T. Blaikley, Mr. T. H. Blakesley and Mrs. Blakesley, Mr. J. T. Bottomley, Mr. C. V. Boys, Prof. Carey Foster, Mr. Conrad W. Cooke, Prof. Fitzgerald, Dr. E. Frankland and Mrs. Frankland, Dr. W. R. Hodgkinson, Prof. O. J. Lodge, Prof. Meldola, Prof. Perry and Mrs. Perry, Prof. Rücker, Dr. Sumpner, Prof. S. P. Thompson and Mrs. Thompson, Mr. A. P. Trotter and Mrs. Trotter, and Mr. G. M. Whipple.

On arriving at the historic town the party became the guests of the Cambridge members, and proceeded to Emmanuel College, where they were received by Mr. W. N. Shaw, M.A. Various groups visited "The Cloisters," chapel, and gardens, and at 1 o'clock lunch was provided in the College Hall.

At 2.30 a meeting of the Society was held in the Lecture Room of the Cavendish Laboratory. The papers read were all by authors resident in Cambridge, and the abstracts given below will sufficiently indicate the variety of the subjects brought before the Society. After the meeting, the visitors inspected the Cavendish Laboratory. Amongst the many interesting instruments and apparatus to be seen, specially noticeable were Prof. J. J. Thomson's 50 feet vacuum tube glowing from end to end with a luminous discharge; Mr. Shaw's pneumatic bridge, by which the pneumatic resistance or conductivity of various shaped orifices and channels can be compared; and the new air condensers to be used by Mr. Glazebrook as standards.

The Cambridge Scientific Instrument Company had an interesting exhibit, including a dividing engine, Boys' radio-micrometer, electrically-driven tuning-forks, and various recording instruments, amongst which was Galton's apparatus for registering the growth of plants.

Other things which attracted attention were Glazebrook's spectrophotometer; Lord Rayleigh's coils and apparatus used in his determination of the ohm; a collection of models, medals, and instruments formerly belonging to Professor Maxwell; the resistance standards of the British Association, together with the historic rotating coils and electrodynamometer used in the determination of the B.A. unit.

Tea was served in the combination Room of Trinity College, and a majority of the visitors returned to town by the 8 o'clock express, greatly pleased with the day's outing. Others, however, prolonged their visit until Monday, and had opportunities of discussing important physical problems with the Cambridge members.

The meeting was in every sense a great success, and will long be remembered as a red-letter day in the history of the Society.

At the Science meeting held in the Cavendish Laboratory, Prof. Ayrton, F.R.S., President, in the Chair, the following communications were made:—

"*Some Experiments on the Electric Discharge in Vacuum Tubes.*" By Prof. J. J. Thomson, M.A., F.R.S.

The phenomena of vacuum discharges were, he said, greatly simplified when their path was wholly gaseous, the complication of the dark space surrounding the negative electrode and the stratifications so commonly observed in ordinary vacuum tubes being absent. To produce discharges in tubes devoid of electrodes was, however, not easy to accomplish, for the only available means of producing an electromotive force in the discharge circuit was by electromagnetic induction. Ordinary methods of producing variable induction were valueless, and recourse was had to the oscillatory discharge of a Leyden jar, which combines the two essentials of a current whose maximum value is enormous and whose rapidity of alternation is very great.

The discharge circuits, which may take the shape of bulbs or of tubes bent in the form of coils, were placed in close proximity to glass tubes filled with mercury, which formed the path of the oscillatory discharge. The parts thus corresponded to the windings of an induction coil, the vacuum tubes being the secondary and the tubes filled with mercury the primary. In such an apparatus the Leyden jar need not be large, and neither primary or secondary need have many turns, for this would increase the self-induction of the former and lengthen the discharge path in the latter. Increasing the self-induction of the primary reduces the E.M.F. induced in the secondary, whilst lengthening the secondary does not increase the E.M.F. per unit length. Two or three turns in each were found to be quite sufficient, and on discharging the Leyden jar between two highly polished knobs in the primary circuit a plain uniform band of light was seen to pass round the secondary. An exhausted bulb containing traces of oxygen was placed within a primary spiral of three turns, and on passing the jar discharge a circle of light was seen within the bulb in close proximity to the primary circuit, accompanied by a purplish glow which lasted for a second or more. On heating the bulb the duration of the glow was greatly diminished, and it could be instantly extinguished by the presence of an electromagnet. Another exhausted bulb surrounded by a primary spiral was contained in a bell-jar, and when the pressure of air in the jar was about that of the atmosphere, the secondary discharge occurred in the bulb, as is ordinarily the case. On exhausting the jar, however, the luminous discharge grew fainter, and a point was reached at which no secondary discharge was visible. Further exhaustion of the jar caused the secondary discharge to appear outside the bulb. The fact of obtaining no luminous discharge either in the bulb or jar, the author could only explain on two suppositions, viz., that under the conditions then existing the specific inductive capacity of the gas was very great, or that a discharge could pass without being luminous. The author had also observed that the conductivity of a vacuum tube without electrode increased as the pressure diminished until a certain point was reached, and afterwards diminished again, thus showing that the high resistance of a nearly perfect vacuum is in no way due to the presence of the electrodes.

One peculiarity of the discharges was their local nature, the rings of light being much more sharply defined than was to be expected. They were also found to be most easily produced when the chain of molecules in the discharge were all of the same kind. For example, a discharge could be easily sent through a tube many feet long, but the introduction of a small pellet of mercury in the tube stopped the discharge, although the conductivity of the mercury was much greater than that of the vacuum. In some cases he had noticed that a very fine wire placed within a tube on the side remote from the primary circuit would present a luminous discharge in that tube.

"*Some Experiments on the Velocities of the Ions.*" By Mr. W. C. D. Whetham, B.A.

In studying electrolysis, the question as to whether there is any transference of solvent when a porous wall is absent presented itself to the author. The ordinary methods of testing for transference, such as by increase of pressure or by overflow, not being available when there was no diaphragm, the author used different coloured solutions of the same salt, such as cobalt chloride in water and in alcohol, the former of which is red and the latter blue. By putting the solutions into a kind of U-shaped tube any change in the position of the line of junction of the two liquids could be measured. Two aqueous solutions in which the anion was the same were also tried, one combination being cupric chloride and common salt, and in this case the line of demarcation traversed about seven inches in three hours. The results hitherto obtained by this method agreed fairly with those found by Kohlrausch.

"*On the Resistance of some Mercury Standards.*" By Mr. R. T. Glazebrook, M.A., F.R.S.

In 1885 M. Benoit, of Paris, supplied the author with three mercury standards nominally representing the Paris Congress ohm, now commonly known as the legal ohm. Tests of these standards were described in a paper read before the Physical Society in 1885 by the present author. Recently he had occasion to compare two of the standards with the British Association coils. The mean of many concordant results gave the resistance of one of the mercury standards (No. 37) as 1·01106 B.A.U., whilst that of the other (No. 39) was 1·01032 B.A.U. Expressing them in legal ohms, the present resistances are (No. 37) 0·99986 and (No. 39) 0·99913, whilst in 1885 the values obtained were (No. 37) 0·99990 and (No. 39) 0·99917. This shows that within the limits of experimental error the ratios of the mercury standards to the B.A. coils have remained practically unchanged during six years. The numbers given above are based on Lord Rayleigh's determination of the specific resistance of mercury, which differs appreciably from that found by Mascart and other observers. Taking the mean of the later concordant determinations, the value of the mercury standards expressed in legal ohms become (No. 37) 1·00033 and (No. 39) 0·99959. The values given by the maker were 1·00045 and 0·99954 respectively, showing a very close agreement. The author also found that refilling No. 37 from the same sample of mercury produced no appreciable change in its resistance, whilst No. 39 was somewhat affected by a similar operation.

Experiments on the coefficient of increase of resistance of mercury with temperature gave the value 0·000872 as the mean coefficient between 0° and 10° C., a number rather less than that obtained by Kohlrausch.

"*On an Apparatus for Measuring the Compressibility of Liquids.*" By Mr. S. Skinner, M.A.

The apparatus consisted of a large spherical flask with a long narrow neck containing the liquid to be experimented upon, the lower part of which was in communication through a stop-cock and flexible tube with an adjustable reservoir. By raising or lowering the latter, the flask could be easily filled or emptied, or the quantity of liquid adjusted. The flask was enclosed in a bell-jar whose interior was in communication with a pump and barometer guage. So sensitive was the arrangement that the compression of water produced by blowing into the jar caused the liquid to descend about 1 centimetre in the neck of the flask. This movement corresponded with a change of volume of about half a millionth. The coefficient of compressibility had been tested at different temperatures, and the results were not very different to those obtained by Tait and others. The influence of salts in solution in changing the compressibility had also been tested, and a great difference in this respect found between electrolytes and non-electrolytes.

"*Some Measurements with the Pneumatic Bridge.*" By Mr. W. N. Shaw, M.A.

The action of the apparatus is analogous in many respects to the Wheatstone's Bridge, and its object is to compare the pneumatic resistances or conductivities of various orifices, channels, tubes, &c. The proportional arms are represented by two circular holes in thin plates of mica, the third arm by an aperture provided with a sliding shutter adjustable by a screw, and the fourth might consist of any aperture or tube whose conductivity was to be determined. The several apertures are pneumatically connected by large wooden boxes. The battery takes the form of a Bunsen burner with a long chimney, whilst the galvanometer is represented by a glass tube connecting opposite chambers and containing a vane which sets itself at right angles to the tube when no air-current is passing. The apparatus is remarkably sensitive to movements of the shutter, and on starting or stopping the draught after balance had been obtained, effects analogous to those produced by self-induction are observed. By its use it has been found that bevelling off one side of a hole in a thin plate increases the pneumatic conductivity of the aperture very considerably, particularly when the bevel is on the egress side. Another interesting result is that for square-ended tubes of given size the conductivity first increases as the length is made greater, and afterwards diminishes with further increase of length. Putting a flange on the outlet end reduces the anomalous effect, whilst a bevelled mouthpiece similarly placed causes it to disappear.

In the discussion on Prof. Thomson's paper, Prof. Fitzgerald said the beautiful experiments were likely to lead to very important results. He did not quite understand how placing a fine wire in a vacuum tube could prevent the luminous discharge, for if the wire was on the side remote from the primary, and if there was any great increase in specific inductive capacity, he would have expected the air to screen the wire.

Prof. Lodge asked for further information as to the action of the magnet in preventing the afterglow, and in some cases precipitating a luminous discharge. The experiment with the exhausted bulb within the bell-jar was also difficult to understand, and he did not see why one of Prof. Thomson's two suppositions must necessarily be true.

The President enquired whether Prof. Thomson had tried Mr. Crookes's experiment, in which the electric pressure necessary to produce a discharge was greatly lessened by putting a phosphorescent material in the tube.

Prof. Thomson, in reply, said he had not tried the experiment, but the phosphorescence he had observed was of quite a different character to that produced in Mr. Crookes's tubes. To Prof. Fitzgerald he said the action of the wire was probably a question of time, and thought the whole field was in some way thrown on the wire and thus discharged. In reply to Prof. Lodge, he had not ascertained the true nature of the effect of a magnet on the glow, but he believed the glow to be due to a combination which might be prevented or facilitated by the action of the magnet causing the density to be different in different parts of the bulb.

M. **Guillaume**, in discussing Mr. Skinner's paper, described the methods used by Sabine, Jamin, and others in determining the compressibility of liquids, and pointed out their defects. The chief difficulty in such experiments was in finding the compressibility of the reservoir. Numbers expressing the compressibility of mercury obtained by different observers were given, the best values varying between 0·0000039 and 0·0000040.

On the motion of Prof. **Ayrton**, seconded by Prof. **Rücker**, a hearty vote of thanks was accorded to the authors for their valuable and interesting communications, and for the kind manner in which the Society had been received and entertained by the Cambridge members.

Prof. **Thomson** and Mr. **Glazebrook** acknowledged the vote.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, May 4, 1891.

Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following Vice-Presidents for the ensuing year were announced:—Sir Frederick Abel, K.C.B., D.C.L., F.R.S., Sir Dyce Duckworth, M.D., LL.D., William Huggins, Esq., D.C.L., LL.D., F.R.S., David Edward Hughes, Esq., F.R.S., Hon. Rollo Russell, F.M.S., Basil Woodd Smith, Esq., F.R.A.S., F.S.A., Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer, Sir Frederick Bramwell, Bart., D.C.L., F.R.S., Hon. Secretary.

Professor Edmond Becquerel, F.R.S. (of Paris), Prof. Marcellin Berthelot, F.R.S. (of Paris), Professor Alfred Cornu, F.R S. (of Paris), Professor E. Mascart (of Paris), Professor Louis Pasteur, F.R.S. (of Paris), Prof. Robert Wilhelm Bunsen, F.R.S. (of Heidelberg), Prof. H. L. F. von Helmholtz, F.R.S. (of Berlin), Prof. August Wilhelm Hofmann, Ph.D., F.R.S. (of Berlin), Prof. Rudolph Virchow, F.R.S. (of Berlin), Prof. Josiah Parsons Cooke (of Cambridge, U.S.), Prof. James Dwight Dana, LL.D., F.R.S. (of Newhaven, U.S.), Prof. J. Willard Gibbs (of Newhaven, U.S.), Prof. Simon Newcomb, F.R.S. (of Washington, U.S.), Prof. S. Cannizzaro, F.R.S. (of Rome), Prof. P. Tacchini (of Rome), Prof. Julius Thomsen, Ph.D. (of Copenhagen), Prof. Tobias Robert Thalén (of Upsal), Prof. Demetri Mendeleef, Ph.D. (of St. Petersburg), Prof. Jean C. G. de Marignac, F.R.S. (of Geneva), Prof. J. D. Van der Waals (of Amsterdam), Prof. Jean Servais Stas, F.R S. (of Brussels), were unanimously elected Honorary Members of the Royal Institution, in commemoration of the Centenary of the birth of Michael Faraday (born 22nd September, 1791).

Charles Davis, Esq., John Douglas Fletcher, Esq., Felix Semon, M.D., F.R.C.P., Frederick Anthony White, Esq., were elected Members of the Royal Institution.

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

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. cxii., No. 17, April 27, 1891.

The Late M. Cahours.—This savant has left to the Academy of Sciences the sum of 100,000 francs, the interest on which is to be distributed yearly among men who have already made themselves known by interesting work, to encourage and assist them in the prosecution of their researches, especially in chemistry. A commission of five members is to be appointed to distribute the prizes, three at least of whom must be members of the Chemical Section.

Researches on the Humic Substances.—MM. Berthelot and André.—The substances in question are known as ulmine and ulmic acid, and for the purpose of examination have been obtained from cane-sugar. Their experiments throw a new light on the part played by humic matters in the fixation of nitrogen and of alkalis. Humic anhydride participates at once in the properties of the acid and the alcoholic anhydrides. A vacancy having occurred among the correspondents of the Section of Geography and Navigation, the Prince of Monaco received 38 votes, against 2 given to Fritjoff Mansen and 1 to Herr Schreinfurth!

Quantitative Studies on the Chemical Action of Light.—The author's results are given in formulæ and tables.

Action Exerted by the Haloid Salts of Potassium on the Solubility of Neutral Potassium Sulphate.—Ch. Blarez.—The precipitating action of the potassium haloid salts upon saturated solutions of neutral potassium sulphate is proportionate to the equivalent of the salt added.

On Isocinchonine.—E. Jungfleisch and E. Leger express the opinion that Hesse's isocinchonine is not identical with cinchonigine.

On a Carbide of the Terpene Series contained in the Oils of Compressed Gas.—A. Etard and P. Lambert.—The body in question, pyropentylene, $C_{10}H_{12}$, becomes polymerised in the cold. It melts at 8°, and has the specific gravity 100·30. It is neither identical with valylene nor with perylene.

On Trehalose.—M. Maquenne.—Trehalosic anhydride is an octoatomic alcohol, an isomer of the saccharoses, and approximating in its constitution to maltose.

Action of Oxyhydrocarbides upon the Nitrides and Hydronitrides.—Raymond Vidal.—The action of phospham upon the alcoholic hydrates is not an isolated fact.

The Constitution of the Aqueous Solutions of Tartaric Acid.—M. Aignan.—Tartaric acid in solution in water exists as a polymer partially dissociated according to the law indicated by a discussion of the experiments of Biot.

The Artificial Production of Hyalite at Common Temperatures.—Stanislas Meunier.—Not adapted for useful abstraction.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 2, No. 535.

The Part Played by Sulphur in the Metallurgy of Zinc.—F. Orgler (*Zeit. Angewandt. Chemie*).—If lime is deficient each atom of sulphur keeps back an atom of zinc.

The Dismore Process for the Manufacture of Lighting Gas.—Isaac Carr.—From the *Journ. Soc. Chem. Ind.*

The Presence of Coumarone in Coal Tar.—C. Kramer and A. Spilker.—Coumarone has been obtained from the light oils of coal tar, which pass over between 175—178° after the phenols and the pyridic bases have been removed. The authors have also obtained from coumarone a polymer which they designate as paracoumarone.

Purification of the Heavy Oils of the Lignite Tars.—E. V. Boyen.—This paper does not admit of useful abstraction.

Considerations on the Mode of Formation of Coal and other Combustibles.—W. A. Dixon.—From the *Proceedings of the Australian Association for the Advancement of Science.*

Determination of Fatty Acids in Alizarin Oil.—F. Guthrie, Rowland Williams, and Arthur Wilson.—From the Chemical News.

New Process for the Volumetric Determination of Sulphates.—L. W. Andrews.—From the *Amer. Chem. Journ.*

Determination of Free Hydrochloric Acid in Solutions of Tin Chloride.—W. Minor (*Zeit. Angew. Chemie*).—Ten c.c. of the solution are diluted with water, and it is treated in heat with a current of hydrogen sulphide until all the tin is thrown down. The liquid is filtered and diluted to 1 litre. Of this solution 500 c.c. are taken (corresponding to 5 c.c. of the original liquid), the H_2S is expelled by boiling, and the acid is determined with a solution of soda. On the other part the tin is determined, *e.g.*, by titration with a solution of iodine. From it we deduce the weight of the combined acid, which is then subtracted from the total acid.

The Citrate Method for the Determination of Phosphoric Acid.—O. Reitmair (*Zeit. Angew. Chemie*).—The precipitation of P_2O_5 by the citrate method is always imperfect however the process is modified. Even in presence of lime, iron, alumina, and manganese, a compensation is possible only on using a large excess of the magnesia mixture. An excess of citrate is always necessary, and in this case the weight of the precipitate is augmented. If lime is previously eliminated there is always an error in minus if we do not use at least twice the necessary quantity of magnesia.

Reaction of Ammonium Molybdate on the Hypophosphites.—J. Millard.—From the *Pharm. Journ.*

New Process for the Volumetric Determination of Bromine in Presence of Chlorine and Iodine.—Norman McCulloch.—From the Chemical News.

Journal fur Praktische Chemie.

New Series, Vol. xlii., Parts 2 and 3.

The Action of Phenylhydrazine upon the Anhydrides of Pyrocinchonic Acid, α-Dichlor-ς-dimethylsuberic Acid, and α-Dichlorpropionic Acid as well as upon the Pyrocinchonic Acid Chloride—R. Otto and G. Holst.—The most important results of these investigations are that by the action of two mols. phenylhydrazine upon one mol. of pyrocinchonic anhydride there is first formed as an addition product the phenylhydrazine salt of pyrocinchonylphenyl hydrazinic acid, which is then further converted into β-pyrocinchonylphenylhydrazine by the abscission of one mol. each of water and phenylhydrazine. There is probably formed pyrocinchonyldiphenylhydracid as an intermediate product. In the reaction between 3 mols. of phenylhydrazine and 1 mol. pyrocinchonchloride there is formed α-pyrocinchonylphenylhydrazine along with 2 mols. phenylhydrazine hydrochlorate. In the combination of phenylhydrazine with α-dichlor-ς-dimethylsuccinic anhydride, 4 mols. of hydrazine and 1 mol. anhydride enter into reaction; and besides phenylhydrazine hydrochlorate, nitrogen and probably benzol, there is formed β-pyrocinchonylphenylhydrazine. On the other hand, in the action of phenylhydrazine upon dichlorpropionic anhydride, 8 mols. of phenylhydrazine enter into reciprocal action with one mol. of the anhydride with both an allocation of the monovalent phenylhydrazine residue $-NH-NH-C_6H_5$ to the radicle of the bivalent phenylhydrazine residue $=N-NH-C_6H_5$, for both chlorine atoms, forming besides 1 mol. water and 4 mols. phenylhydrazine hydrochlorate.

Action of Chlorbenzoyl upon Sodium Cyanide in Presence of Ethyl-Ether.—W. Buddens.—Benzoylchloride (1 mol.), and sodium cyanide (2 mols.), in presence of ether yield sodium benzoyl-cyamide, cyanamide, and sodium chloride. Mineral acid but not organic acids precipitate benzoyl cyamide from its salts. Benzoyl cyamide, if heated alone, is resolved into carbon dioxide, benzonitrile, and dicyandiamide. It is not polymerised if heated either alone or in liquids which boil at high temperatures. If heated with alcohols it is decomposed into the corresponding benzoic esters and cyanamide. With the exception of the silver salt its salts are readily soluble in water and in alcohol. The barium salt on heating, is decomposed into benzonitrile, carbon dioxide, and barium cyamide. Sodium cyamide (1 mol.), with chlorbenzoyl (1 mol.), in presence of ether yield as ultimate products, carbon dioxide, hydrocyanogen, benzonitrile, cyanamide, sodium chloride, dibenzoylcyamide, α-symmetric dibenzoylurea, and two isomeric bodies of the formula $(C_7H_4N_2)x$. Dibenzoyl cyamide may also be formed directly from silver cyamide and benzoylchloride and is converted into dibenzoylurea by taking up water.

Communications from the Laboratory of the University of Freiburg.—These communications consist of a paper by Ad. Claus and Runschke on the location of the dichlormetaxylol (4—6), obtained by direct chloration and on some of its derivatives, and a memoir by C. Willgerodt and B. Hermann on derivatives of ortho-para dinitrophenylhydrazine.

The Influence of the Filling of Space upon the Chemical Process.—Fr. Kehrmann.—This paper is not adapted for useful abstraction.

On Dimethylacetylen and its Tetrabromide.—Al. Faworsky.—The author determines the boiling-point of dimethylacetylene. At the beginning of the distillation the thermometer stood at 10° in the dephlegmator. The distillation began at 27°, and ended at 28°. The tetrabromide has the compostion $C_4H_6Br_4$.

On the Geometrical Isomerism of the Bromine Derivatives of Pseudobutylene.—Al. Faworsky and C. Debout.—The authors consider that their results show that Wislicenus and Hölz have operated upon ordinary mixtures, and not upon geometric isomers.

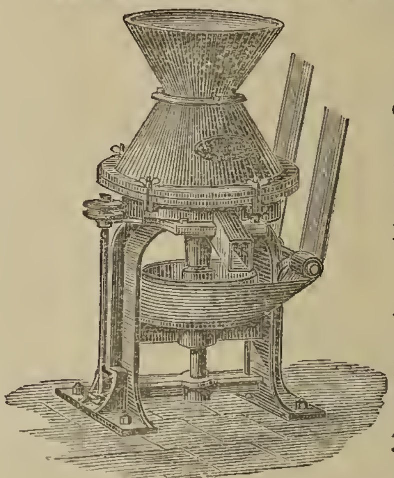
Some Small Communications from the Laboratory of E. von Meyer.—These consist of papers by M. Schmidt on the action of sulphurous acid upon nitroso-compounds, by W. Knebel on the derivatives of salol, and by J. T. Carrick on a product of the condensation of cyanacetic ether and benzaldehyd.

Detection of Sugar or Treacle in Roasted Coffee.—A. Stutzer and O. Reitmair (*Zeit. Angew. Chemie*).—The authors put 20 grms. of unground coffee into a litre flask, covers them with ½ litre water, and shakes them violently for five minutes in a mechanical agitating apparatus. The flask is filled up to the mark with water, and the liquid is immediately filtered. 50 c.c. are evaporated in a platinum capsule upon the water-bath, dried for two hours at 95—99°, weighed, incinerated, and weighed again. In this manner there was obtained from pure coffee-beans from different sources from 0·44—0·72 per cent, or as the mean of five determinations 0·598 per cent. The samples when shaken up in cold water gave off no colouring-matter. Samples of coffee roasted with sugar coloured water more or less deeply, and yielded, when treated as above, 1·81—8·18 per cent of extractive matter.

Detection and Estimation of Starch in Liquids containing Dextrin.—G. Burkard (*Chemiker Zeitung*).—The cold liquid containing starch and dextrin is cautiously mixed whilst being shaken with exactly so much alcohol as to cause a slight milky turbidity. The solution is then heated until the turbidity disappears; a little solution of tannin is then added and the mixture is let cool, when all the starch present is deposited as a thinly flocculent precipitate.

MEETINGS FOR THE WEEK.

Tuesday, 26th.—Royal Institution, 3. "The Cibber Period of Stage History," by William Archer.
— Institute of Civil Engineers, 8. (Anniversary).
— Royal Medical and Chirurgical, 8.30.
Wednesday, 27th.—Geological, 8.
Thursday, 28th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Orchestra considered in connection with the Development of the Overture," by A. C. Mackenzie, Mus. Doc.
— Society of Arts, 4.30. "The Study of Indian History," by C. L. Tupper, B.A.
Friday, 29th.—Royal Institution, 9. "An Astronomer's Work in a Modern Observatory," by David Gill, LL.D., F.R.S.
Saturday, 30th.—Royal Institution, 3. "The Scientific Study of Decorative Colour," by Prof. A. H. Church, M.A., F.R.S.



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THE CHEMICAL NEWS.

VOL. LXIII., No. 1644.

ON A NEW METHOD OF MEASURING THE GLYCERIN YIELDED BY THE FATS.

By J. ALFRED WANKLYN and WILLIAM JOHNSTONE.

THE amount of glycerin given by different fats has been measured by the direct method, in which a given weight of fat is saponified, the soap decomposed by means of acid, and the glycerin extracted, purified, and finally weighed. This procedure has the advantage of conclusiveness, but it is slow and very troublesome, and is wanting in precision. There is a quicker and easier process founded upon the observation that alkaline permanganate resolves one molecule of glycerin into one molecule of oxalic and one molecule of carbonic acid. This method is of very limited applicability, inasmuch as there are many other substances besides glycerin which furnish oxalic acid on being submitted to this process of oxidation. It has, therefore, the defect of inconclusiveness, and has, we believe, led analysts into error.

There is a demand for a method of measuring the glycerin which shall have the conclusiveness of the direct estimation, and at the same time shall be rapid and precise. The method which we bring forward appears to meet these requirements.

Thirty years ago the discovery was made that glycerin and hydriodic acid react thus—

$$C_3H_8O_3+5HI=3H_2O+2I_2+C_3H_7I.$$

Our method takes advantage of this reaction and measures the glycerin by means of the iodide of isopropyl which it yields.

That such a method must be conclusive, if it can be worked at all, must be obvious. That it furnishes accurate results is quite practicable and comparatively quick (in one of its forms it may be completed within three hours, starting with the fat in its ordinary condition), is shown by the experiments which we have made.

ON THE GLASER OR ALCOHOL METHOD FOR THE DETERMINATION OF OXIDE OF IRON AND ALUMINA IN PHOSPHATES.

By H. H. B. SHEPHERD, F.I.C., F.C.S.

THIS method has recently been brought very prominently before the notice of English chemists by the action of the Chemical Manure Manufacturers' Association, at whose instance two influential meetings have been held for the purpose of discussing, among other subjects, the determination of oxide of iron and alumina in phosphates. At these meetings a very general opinion was expressed that, with certain modifications, the Glaser process could be recommended as a reliable and useful addition to the means at our disposal for the analysis of phosphates, and one less likely than the older method to yield inaccurate results in inexperienced hands. Exception was, however, taken to the following points, all of which form part and parcel of the method as adopted on the Continent:—

1. To working upon a solution representing so little as 0·4 grm. of phosphate.
2. To employing nitrohydrochloric acid as the solvent for the raw phosphate, and consequently including in the oxide of iron and alumina any iron present in the form of pyrites.
3. To the plan of dividing the phosphates of iron and alumina found by 2 to obtain the oxide of iron and alumina, instead of determining the amount of the phosphoric acid in the precipitate and deducting this from the total.

As this method seems likely now to come into general practice, at any rate as an alternative one, it may be useful to those chemists connected with the manure trade who have not as yet had any experience of it to place before them some practical working details embracing modifications introduced to meet the objections referred to.

Alcohol Method.

Two and a half grms. of phosphate are dissolved in 10 c.c. hydrochloric acid, evaporated to dryness, taken up with hydrochloric acid, raised to the boil, washed out into a 250 c.c. flask with as little water as possible, 10 c.c. strong sulphuric acid added, and the solution allowed to stand for about five minutes with frequent shaking. Alcohol (95 per cent) is now added, the mixture cooled, made up to the mark with alcohol and well shaken. Owing to the contraction in volume which takes place, it must again be made up to 250 c.c. and mixed. It is now allowed to stand for one hour, filtered, 200 c.c. of the filtered solution (equal to 2 grms. of phosphate) taken, and gently evaporated to a small bulk in a basin. It is desirable when organic matter is present to carry the evaporation to pastiness, that the acid may effect its partial destruction. It is then washed into a beaker with about 50—100 c.c. water, boiled for a short time with bromine or other oxidising agent, ammonia added in excess, again boiled for about half-an-hour, cooled, a little more ammonia added to make sure a slight excess is present, filtered, washed with hot solution of ammonium chloride, ignited, and weighed. Unless ammonium chloride solution is used, the precipitate is very apt to wash through even a very close filter.

When the weight of the phosphates of iron and alumina has been obtained, the precipitate is re-dissolved and the phosphoric acid contained therein determined—the amount so found, deducted from the total weight of the phosphates of iron and alumina, giving the oxide of iron and alumina by difference. Of course, if the oxide of iron is required apart from the alumina, a separate iron determination must be made; but this, in any case, has to be done by whatever method the separation of the phosphates of iron and alumina is effected.

The following postscript has been suggested by Messrs. TESCHEMACHER and SMITH:—

Should the phosphate under examination contain *magnesia*, the phosphates of iron and alumina obtained in the foregoing process must be freed from this impurity by washing the precipitate off the filter and boiling with water and a little nitrate of ammonia, repeating the treatment if, after the first application, the filtrate still shows any magnesia.

ON THE PERIODIC TABULATION OF THE ELEMENTS.

By JAMES WALKER, D.Sc., Ph.D., F.R.S.E.

THE best tabular expression for the periodic law is to be found in the arrangement given by Mendeléeff, who writes the elements in periods in order of their atomic weights, and thus separates the odd from the even series by the transition elements of the eighth group. Lothar Meyer's spiral and the tables based on it do not show the relations of the elements amongst themselves to the same advantage. What is to be aimed at in such a tabulation is evidently that elements which are analogous in their chemical and other properties should be found together in the table, and apart from elements to which they bear little or no resemblance. Mendeléeff's arrangement is at once justified by the fact that certain general statements can be made concerning the elements of odd series as contrasted with those of even series, and *vice versâ*. It also, however, gives expression to generalisations of a somewhat more limited character, but still of considerable interest. In his table, here reproduced, we see, for example, that the metals of the rare earths are found together in the even series, and may be enclosed in a rectangle, as is indicated by the dotted lines in the upper part of the diagram.

EVEN SERIES.

Group.		2.	4.	6.	8.	10.	12.
I.		Li	K	Rb	Cs	—	—
II.		Be	Ca	Sr	Ba	—	—
III.		B	Sc	Y	La	Yb	—
IV.		C	Ti	Zr	Ce	—	Th
V.		N	V	Nb	Di	Ta	—
VI.		O	Cr	Mo	—	W	U
VII.		F	Mn	—	—	—	—
			Fe	Ru	—	Os	
VIII.			Co	Rh	—	Ir	
			Ni	Pd	—	Pt	
I.	H	Na	Cu	Ag	—	Au	
II.		Mg	Zn	Cd	—	Hg	
III.		Al	Ga	In	—	Tl	
IV.		Si	Ge	Sn	—	Pb	
V.		P	As	Sb	—	Bi	
VI.		S	Se	Te	—	—	
VII.		Cl	Br	I	—	—	
	1.	3.	5.	7.	9.	11.	

ODD SERIES.

Again, the "metallurgical" metals are all to be found in the lower rectangle marked off in the table; and immediately adjoining these we have the technically important light metals sodium, magnesium, and aluminium, as well as the half metals arsenic, antimony, and bismuth. These relations are not clearly apparent in Meyer's table, although they come out well in his curve of atomic volumes, corresponding parts of which contain analogous elements; the metals of the rare earths, for example, lying on the lower part of the descending portions of the curve in the great periods, and the useful heavy metals at or close after the minima. In the above diagram the various periods are brought alongside each other, so that elements on corresponding parts of the curve become neighbours in the table.

One of the distinctions between elements of odd and those of even series is that only elements belonging to the former are capable of forming compounds with the alcohol radicals and with hydrogen (the transitional eighth group being here, and in what follows, left out of account). We see at once, however, that this statement is not strictly true, for the elements of the *second* series *do* form compounds with the alcohol radicals and with hydrogen. Again, it may be stated that the elements of even series do not occur in the free state in nature. But this also is manifestly untrue of carbon, nitrogen, oxygen, and, as it would seem, of fluorine—all members of Series 2. This exceptional position of the second series was from the first recognised by Mendeléeff, who named the elements which constitute it (and also sodium) "typical" elements. Would it not be more rational to remove Series 2 from its present position, and place it before Series 3, calling it then the first series—a name at present monopolised by hydrogen? It would thus appear amongst the odd series, and the above generalisations would apply practically without exception. By so moving Series 2, we should also be spared classifying oxygen with chromium, molybdenum, &c., and fluorine with manganese. The table in its modified form is given below:—

EVEN SERIES.

Group.			4.	6.	8.	10.	12.
I.			K	Rb	Cs	—	—
II.			Ca	Sr	Ba	—	—
III.			Sc	Y	La	Yb	—
IV.			Ti	Zr	Ce	—	Th
V.			V	Nb	Di	Ta	—
VI.			Cr	Mo	—	W	U
VII.			Mn	—	—	—	
			Fe	Ru	—	Os	
VIII.			Co	Rh	—	Ir	
			Ni	Pd	—	Pt	
I.	Li	Na	Cu	Ag	—	Au	
II.	Be	Mg	Zn	Cd	—	Hg	
III.	B	Al	Ga	In	—	Tl	
IV.	C	Si	Ge	Sn	—	Pb	
V.	N	P	As	Sb	—	Bi	
VI.	O	S	Se	Te	—	—	
VII.	F	Cl	Br	I	—	—	
	1	3.	5.	7.	9.	11.	

ODD SERIES.

Here oxygen is in its proper place beside sulphur; and fluorine beside chlorine, bromine, and iodine. Lithium, too, is near its analogue magnesium, beryllium near aluminium, and boron near silicon. Now, also, it can be stated that all the non-metals are in the odd series, and indeed it is possible to draw a fairly sharp line of demarcation between them and the metals. By a glance at the modified table it will be seen that all the non-metals lie in the lower left-hand corner of the diagram, and may be separated from the metals by a diagonal straight line.

The advantages gained by this modification seem to me to outweigh any slight alterations which it may be necessary to make in such rules relating to odd and even series as were laid down by the late Prof. Carnelley. The table as it stands is still far from perfect; we have still, for instance, lithium and sodium classed with copper, silver, and gold, whilst their place is evidently with potassium, rubidium, and cæsium; but discrepancies such as these are much less numerous than before.

In his last paper on the Periodic Law (*Phil. Mag.*, xxix., 97), Prof. Carnelley advanced a formula which represents in a fairly close manner the atomic weight of the elements as a function of their position in the periodic system. The formula is $A=c(m+\sqrt{v})$, A being the atomic weight, m a member of an arithmetical progression depending on the series to which the element belongs, v (valency) the number of the group in which the element is found, and c a constant. After fixing the form of the expression and the numerical values in the arithmetical series, he found that the constant c was equal to 6·6, a number at once suggesting the constant 6·4 of Dulong and Petit's Law. The coincidence, however, is purely accidental. Dulong and Petit's Law expressed in corresponding algebraical form is—

$$A=c'\left(\frac{1}{\text{specific heat}}\right)$$

where c' is a constant. Now the numerical values of c and c' evidently depend on the units in which the various magnitudes in the equations are measured; and if instead of taking the atomic weight of hydrogen, and the specific heat of water at the ordinary temperature as units, we adopted some other system, then c and c' would no longer in general be even approximately equal. Thus there is no real connection between the atomic heat of the elements and Prof. Carnelley's constant, their identity depending on the form of expression chosen and the accidental circumstance that the atomic weight of hydrogen and the specific heat of water of 18° are the most convenient units to employ in ordinary measurements of these two magnitudes.

With reference to Dulong and Petit's Law, it may not be out of place again expressly to call attention to the fact frequently overlooked, that the specific heat of the elements in the solid state is an excellent example of a property of the elements which is *not* periodic.

University of Edinburgh,
March 20, 1891.

THE ELECTROLYTIC METHOD AS APPLIED TO PALLADIUM.

By EDGAR F. SMITH and HENRY F. KELLER.

Our knowledge bearing upon the behaviour of this metal towards the current is limited and rather indefinite. In 1868, Wöhler published in the *Annalen*, 143, 375, an article, entitled "Ueber das Verhalten einiger Metalle im elektrischen Strom," from which the following facts are taken:—Palladium, as the positive pole of a battery, consisting of two Bunsen cells, was immersed in water acidulated with sulphuric acid, when the metal immediately became coated with a deposit having a bright steel-like colour. This deposit is doubtless palladium dioxide, as it liberates chlorine when treated with hydrochloric acid, and carbon dioxide whem warmed with oxalic acid. At the same time, black, amorphous metal separated upon the negative pole. Its quantity was slight. In the second edition of "Classen's Quantitative Electrolysis, p. 72 (American edition), it is stated that a feeble current will deposit palladium in a beautiful metallic state from an acid solution. One Bunsen cell is given as sufficient for this purpose. A more energetic current produces a spongy deposit. Ludwig Schucht has communicated (*Berg- und Huttenmännische Zeitung*, 38, 121; also *Zeit. fur Anal. Chem.*, 22, 240), that from an aqueous solution of palladious nitrate, acidulated with a few drops of nitric acid, the current precipitated upon the negative pole a bronze-coloured deposit, which, as it grew more dense, became darker, and finally black in colour. At the positive pole there was a simultaneous deposition of oxide, showing a reddish colour. In alkaline palladic solutions the precipitation of metal was much retarded; the deposition of oxide was also observed.

Our first experience in the electrolysis of palladium salts was acquired from the double cyanide in an excess of potassium cyanide. In such solution a current, generating 1 c.c. oxyhydrogen gas per minute, failed to cause metallic deposition until after the expiration of thirty-six hours; in other words, not until the excess of potassium cyanide had been completely converted into alkaline carbonates. Then the deposit was black in colour, but the precipitation was not at all complete. No deposition of oxide was noticed upon the positive pole. The conduct of the metal in cyanide solution led to the trial of certain separations, the results of which will be given in a later communication. The action of the current (feeble) was also tried upon a solution of palladious chloride, in the presence of a large excess of potassium sulphocyanide. In this case the deposition of metal was exceedingly rapid. Spongy spots were noticeable. The deposit was black is colour. The experiment was made with this solution in the hope that possibly a separation of copper from palladium might be found; but, as these metals separate with equal rapidity from their sulphocyanides, the results are valueless for this purpose.

The next attempt was made with palladammonium chloride, $Pd(NH_3)_2Cl_2$, in just sufficient ammonium hydroxide to retain it in solution. The total dilution of the solution was 125 c.c.; the acting current gave 0·9 c.c. OH gas per minute. The poles were distant from each other about two inches. Just as soon as the circuit was completed, a yellowish-brown coating appeared upon the spiral of the positive pole; while upon the dish, in connection with the negative pole, a deposit of metal closely resembling the platinum itself in colour made its appearance. After acting through the night the current was interrupted, the metal deposit carefully dried and weighed. The precipitation was incomplete. It was, however, discovered that the deposition at the positive pole, which gradually increased in mass and assumed a black colour, had entirely disappeared. In all instances where the ammonium hydroxide was in decided excess, the precipitation of oxide on the positive pole was not observed. This behaviour is similar to that of nickel when its ammoniacal solutions are electrolysed. In subsequent experiments the course was somewhat modified. From solutions such as just described, the palladium thrown out upon the platinum dish was extremely slow in dissolving, even in fuming nitric acid, so that it was deemed expedient to first coat the platinum dishes employed in the electrolysis with a layer of silver, varying in weight from 0·1 to 0·3 grm. This was done in the experiments recorded below, and was found to be decidedly advantageous. The layer of silver seemed to hasten the deposition of the palladium.

Experiment I.

A quantity of palladammonium chloride (=0·2228 grm. Pd) was dissolved in ammonium hydroxide; to this solution were added 20 to 30 c.c. of the same reagent (sp. gr. 0·935) and 75 c.c. water. The current allowed to act upon this ammoniacal liquid gave 0·9 c.c. oxyhydrogen gas per minute. The decomposition continued through the night. At no time was there any oxide deposition upon the anode. The palladium gradually assumed a bright metallic appearance. After drying, the deposit showed about the same appearance as is ordinarily observed with this metal in sheet form. The washing was limited to hot water, and when the deposit was perfectly dry, the dish containing it was covered with a watch-glass and exposed to a temperature ranging from 110° to 115° C. This was done to expel any hydrogen that might possibly have been retained by the palladium.

Weight of silvered dish + Pd = 61·9575 grms.
" " " − Pd = 68·7350
0·2225 Pd

Experiment II.

In every respect similar to Experiment I. gave—

Weight of silvered dish + Pd = 71·9540 grms.
" " " − Pd = 71·7315
0·2225 Pd

The filtrates from these deposits were warmed for eight hours with ammonium sulphide without showing any formation whatever of palladium sulphide.

In several experiments, with conditions unlike those just described, and where consequently an incomplete precipitation of metal occurred, the digestion with ammonium sulphide produced in every instance, in a very short time, a reddish-brown flocculent sulphide, carrying with it quite a considerable quantity of free sulphur.

In a second series of two experiments, in each of which there was the same amount of palladium as in the previous trials, the quantity of ammonium hydroxide in excess was made 30 c.c., while the current (giving 0·8 c.c. oxyhydrogen gas per minute) was allowed to act fo sixteen hours. The results were quite concordant:—

Experiment III.

Weight of silvered dish + Pd = 72·1055 grms.
" " " − Pd = 71·8825
Weight Pd = 0·2230

Experiment IV.

Weight of silvered dish + Pd = 62·0512 grms.
" " " − Pd = 61·8280

Weight Pd = 0·2232

It may be remarked that in filling the silvered platinum dishes a rather large surface of silver was allowed to remain above the electrolysed liquid, so that by merely adding water it was possible to ascertain when the palladium was fully precipitated. When the deposition was not finished, the new silver surface soon showed streaks of metal.

A third series of two experiments, in which the added amount of palladium was double that recorded in the preceding examples, the same conditions were observed as before, with the exception that as the current was only giving 0·70 c.c. oxyhydrogen gas per minute, the time of precipitation was extended to eighteen hours. The results were as follows:—

Experiment V.

Weight of silvered dish + Pd = 72·3555 grms.
" " " − Pd = 71·9100

Weight Pd = 0·4455

Experiment VI.

Weight of silvered dish + Pd = 62·2600 grms.
" " " − Pd = 61·8138

Weight Pd = 0·4462

Curiously enough, upon warming the liquid poured off from the palladium in Experiment V., with ammonium sulphide there appeared a very slight sulphide precipitate after some hours. The liquid from Experiment VI. showed no trace of unprecipitated metal.

The deposits in the experiments just recorded were bright, metallic, and very dense. In none was there the slightest tendency to sponginess. To show the accuracy of the method, the results may be tabulated as follows:—

Experiment.	Found Pd.	Calculated Pd.
I.	0·2225	0·2228
II.	0·2225	0·2228
III.	0·2230	0·2228
IV.	0·2232	0·2228
V.	0·4455	0·4456
VI.	0·4462	0·4456

If the percentage differences be calculated, it will be found that they are quite within the limit of error occurring in almost any ordinary gravimetric determination.

The behaviour of ammoniacal palladium solutions, when exposed to the action of the electric current, will be further studied as time permits, and, if possible, the attempt will be made to re-determine the atomic weight of the metal by this method in a somewhat modified form. —*Proceedings of the Chemical Section of the Franklin Institute*, Vol. ii., 1890.

ON THE DETECTION OF MERCURY IN TOXICOLOGICAL INVESTIGATIONS.

By MARCO T. LECCO.

It is universally assumed that mercury is readily soluble in hydrochloric acid on the addition of potassium chlorate. It is also expected with certainty that in the destruction of mercuriferous organic substances by means of hydrochloric acid and potassium chlorate the entire quantity of mercury present will pass into solution. Observations made by the author during the examination of a human stomach containing mercury do not agree with this assumption.

In the stomach in question minute metallic globules could be distinctly seen, which when separated were recognised with certainty as mercury.

In order to test the stomach for other mineral poisons, and to determine the mercury it was exposed to the action of hydrochloric acid and potassium chlorate. After the destruction of the organic matter the product of the reaction was worked up in the ordinary manner. But on examining the solution it was scarcely possible to find the slightest trace of mercury. In consequence the residue which had remained undissolved in hydrochloric acid and potassium chlorate was examined more closely, when the author found that the mercury sought for had remained in the insoluble residue.

A further portion of the mercuriferous stomach was submitted to the action of hydrochloric acid and potassium chlorate. The operation was conducted in a glass dish. After a short time small globules of mercury were deposited at the bottom of the vessel, so that they were distinctly seen. After the destruction of the organic matter and the expulsion of the chlorine by heating in the water-bath, the globules of mercury remained unaltered at the bottom of the dish.

The author further convinced himself of the sparing solubility of mercury on treatment with hydrochloric acid and potassium chlorate by experiments on pure mercury. These experiments were conducted both with concentrated and dilute acid, at common temperatures with prolonged action and on the water-bath, and in all cases the result was that mercury is with difficulty soluble in hydrochloric acid and potassium chlorate.

It is, therefore, alsolutely necessary in the destruction of organic matter by means of hydrochloric acid and potassium chlorate to keep this property of metallic mercury in mind, and to prolong the action of the acid and the chlorate for several hours with the application of heat and with frequent stirring.—*Berichte der Deutsch. Chem. Gesellsch.*, Vol. xxiv., No. 6, p. 928.

SEPARATION AND DETERMINATION OF NICKEL AND COBALT.

By CONSTANTIN KRAUSS.

The author re-examines the methods hitherto proposed:—

A.—*Methods Founded upon the Different Behaviour of the Two Metals in their Higher Stages of Oxidation.*

1. A. Jorissen proposes to oxidise the solution of the metallic salts with potassa-lye and bromine, and then to add in the cold without filtration 1 to 2 c.c. solution potassium cyanide, and then to filter. Nickel is said to pass into solution, whilst cobalt remains undissolved. Jorissen considers the method inapplicable if the nickel is in large excess. Krauss rejects the method completely, as a part of the cobalt dissolves if too much potassium cyanide is used, and if too little cyanide is employed a part of the nickel remains undissolved.

2. Terreil's method (*Comptes Rendus*, lxii., p. 139) gives quite unsatisfactory results. The separation of the cobalt as roseo-cobaltic chloride was very uncertain; the precipitate was generally very trifling, and the precipitation was never complete.

In the separation of manganese from nickel a small quantity of nickelous oxide was always carried down by the manganic peroxide.

3. M. G. Delvaux's method (*Comptes Rendus*, xcii., 723) was found to give a deficiency of cobalt which contained ponderable quantities of nickel. The precipitate of nickel was largely contaminated with cobalt, and especially with manganese.

4. G. Vortmann uses as an oxidising agent sodium hypochlorite. He takes a solution of cobalt and nickel

containing ammonium chloride, renders it ammoniacal, and adds hypochlorite. Complete oxidation takes place even in the cold, but is more rapid at ebullition. The solution which contains the cobalt as a luteo-salt is diluted with water when cold, and the nickel is precipitated with potassa-lye as nickelous hydrate. The cobalt was always too low, and was still not free from nickel; the values found for nickel were always too high. Krauss pronounces the results as not satisfactory even for technical purposes.

5. O. Popp boils a solution of a nickelous and cobaltous salt with sodium acetate and hypochlorite in order to obtain the nickel as oxide, whilst the cobalt remains in solution. This method also was found useless.

6. W. Gibbs and H. Rose separate the two metals by boiling the neutral sulphates with lead peroxide.

Krauss after boiling for several hours with freshly prepared lead peroxide, found that ponderable quantities of cobalt remained in the solution.

7. E. Fleischer divides the solution of both metallic salts into two equal parts. After both the halves have been rendered alkaline with potassa-lye they are boiled with hypochlorite or bromine water until all escape of gas has ceased. In one of the halves the cobalt and nickel sesquioxides are filtered off, and the precipitate is added to an excess of a ferrous salt of known strength containing sulphuric acid. By titrating back with permanganate the ferrous oxide which remains unoxidised there is found the quantity of cobalt *plus* nickel. The precipitate filtered from the second half is boiled with ammonia, when all the nickel is reduced to nickelous oxide, whilst cobalt remains unchanged, and is determined volumetrically in the manner mentioned above.

In testing this method the author established the fact that in the oxidation of a cobalt salt with alkali and a hypochlorite a stage of oxidation is reached higher than R_2O_3; whilst the oxidation product obtained from a nickel-salt always remains below R_2O_3. In a mixture of both metals the error may be in part compensated, and the results obtained may suffice for practical purposes.

The second part of Fleischer's process, the reduction of nickel sesquioxide with ammonia, titration of the cobalt sesquioxide, and determination of nickel from the difference, must be rejected, because an excess of cobalt is always obtained at the expense of the nickel. Besides, the reduction of nickel sesquioxide with ammonia is very slow.

8. E. Donath and Jas. Mayrhofer modify the Fleischer process by precipitating the metals in one half of the solution with potassa-lye as hydrated oxides (nickelous and cobaltous), and adding solid iodine or strong solution of iodine, whereby the cobalt is converted into sesquioxide, whilst the corresponding nickel compound remains unchanged. In the second half of the solution both metals are precipitated as sesquioxides by means of hypochlorite or of bromine water. The quantity of the sesquioxides produced is in either case obtained iodometrically.

This method also suffers from the defect that the precipitation of both metals does not yield a product of constant composition. The cobalt oxide obtained by oxidation with iodine and potassa does not answer to the formula Co_2O_3; but on iodometric determination yields too high results.

Experiments to obtain in one or other manner a constant oxidation product of both metals lead to a favourable result only in case of cobalt.

In this manner a determination of cobalt is easily executed. The solution is mixed with potassa-lye and hydrogen peroxide, boiled until there is no escape of gas, let cool, and a little solid potassium iodide is added. As soon as it dissolved hydrochloric acid, or preferably sulphuric acid, is added, and the vessel is well stoppered. When all the cobalt oxide is dissolved the liberated iodine is titrated with sodium thiosulphate.

9. C. Wicke precipitates the nickel sulphate with excess of potassa-lye, boiled with a copious addition of sodium hypochlorite until the escape of gas has ceased, and hypochlorous acid can no longer be detected. A standard solution of arsenious acid is then added in excess, and heat is applied until the nickel hydroxide is again converted into the pure green nickelous hydroxide. The latter is completely dissolved by heating with tartaric acid mixed with sodium carbonate until the reaction is slightly alkaline, and the excess of arsenious acid is titrated back with normal iodine.

As in the former methods, a nickel sesquioxide of constant composition is not obtained, whence the method gives no accurate results for the determination of nickel. According to the experiments of Krauss, the method is available for the determination of cobalt, where, however, the oxidation is better effected with hydrogen peroxide.

(To be continued).

ON A NEW QUANTITATIVE SEPARATION OF MANGANESE AND ZINC.

By PAUL JANNASCH and J. F. McGREGORY

The new method of separating manganese and zinc described below depends on the easy and complete conversion of the former metal into manganese hydroperoxide, whilst the zinc compounds undergo no changes. Carnot was the first who precipitated the manganic salts alone by hydrogen peroxide, and thus determined the manganese quantitatively.

As one of the writers more than two years ago made numerous preliminary experiments concerning the oxidising action of hydrogen peroxide, and has recognised it as a remarkably efficient oxidising agent in his new method for the determination of sulphur, he thought it advisable not to delay any longer to commence a series of quantitative separations by means of this reagent. The first of these separations is here communicated.

In their first experiments they set out with solutions of the mixed sulphates, acidulated with dilute hydrochloric acid (5—10 c.c.), adding a moderate excess of strong ammonia, and then effecting the precipitation with hydrogen peroxide with prolonged heating on the water-bath. Here considerable quantities of zinc oxide were invariably found accompanying the manganese precipitate. In an especial case where the manganese precipitate had been left covered upon the water-bath for more than four hours, the manganese separated was found to contain 0·0822 grm. ZnO. (The quantities taken had been 0·5380 grm. $MnSO_4,5H_2O$, and 0·5602 grm. $ZnSO_4,7H_2O$.) That precipitations of zinc were connected with the expulsion of the excess of ammonia appeared from the solutions filtered from the manganese precipitate, which, on concentration, soon became turbid from the separation of white flocks, which subsequently, however, re-dissolved.

When we afterwards heated on the water-bath for a very short time only (the other conditions remaining as before), the results were considerably better, so that the mean proportion of manganous oxide was found by 2·5 per cent too high, a value which could be reduced by 0·5 per cent by washing the manganese precipitate with dilute ammonia. Thoroughly satisfactory results were only obtained by considerably increasing the proportion of ammonium chloride and ammonia in the liquid to be precipitated with hydrogen peroxide, and working afterwards exactly according to the following directions—a mixture of 0·5 grm. manganese sulphate, and the same weight of zinc sulphate are placed in a Berlin-ware capsule in 75—100 c.c. water. The capsule must be large enough to hold conveniently 600 c.c. water. The solution is acidified with a little dilute hydrochloric acid, and a large quantity (at least 100 c.c.), of a solution of ammonium chloride at 15—20 per cent is added. Finally, the liquid is rendered strongly alkaline by the addition of 60—100 c.c. strong ammonia, when no brown colouration of manganic hydroxide ought to take place.

The solution thus prepared and covered with a glass capsule is at once mixed with an excess of hydrogen peroxide (50—60 c.c. free from barium chloride), and all the manganese is thus completely precipitated. It must here be noted that at the end of the precipitation the liquid suddenly boils up and spirts in consequence of the oxygen gas liberated. The precipitate thus obtained is heated for 10—15 minutes on a boiling water-bath until the precipitate settles well after stirring. It is then collected upon a roomy filter. The residue of manganic oxide adhering to the porcelain is removed from the capsule by means of a feather and rinsing with hot water and a little ammonia, and at last the precipitate is washed with boiling ammoniacal water and afterwards with hot water alone until a drop of the filtrate evaporated upon platinum foil leaves no trace of a residue. The manganese precipitate can be incinerated in a platinum or porcelain crucible without previous desiccation, and is then ignited in the blast flame until the weight is constant. A repetition of the precipitation is perfectly unnecessary. Nor is it necessary to dissolve the precipitate in hydrochloric acid and re-precipitate the manganese as a carbonate.

For the determination of the zinc in the filtrate after removal of the manganese, there is the choice of two methods. In one, the boiling ammoniacal solution is precipitated with ammonium sulphide, and the precipitate is filtered after heating for an hour on the water-bath. As the washing of the precipitated zinc sulphide involves much inconvenience it is advisable to pour through the filter only the liquid in the beaker, and then return the filter with the unwashed precipitate into the beaker which contains only small quantities of zinc sulphide. The precipitate is then dissolved in dilute hydrochloric acid with the aid of heat, and the zinc is precipitated by sodium carbonate in presence of only a small quantity of ammoniacal salt. It must be noted that zinc carbonate precipitated in this manner may contain a small impurity of silica.

In the other method the zinc solution is evaporated to dryness on the water-bath in a large platinum capsule (stirring is not necessary towards the end); the residual saline mass is heated to 125—150° in the air-bath for about an hour, and the ammoniacal salts are expelled by heating on an asbestos plate over the gas-flame. The saline masses which adhere to the sides must be occasionally pushed down to the bottom of the capsule with a stout platinum wire. An exposure of the ammonium salts directly over the flame is not admissible, as losses of zinc might possibly happen. The non-volatile residue is dissolved in hot water and a couple of drops of hydrochloric acid, the solution is filtered and precipitated at a boil with sodium carbonate in a Berlin-ware capsule.

This method of separating manganese and zinc possesses various advantages. The manganese is rapidly precipitated, and the filtration and washing are so easy that a determination of manganese in presence of zinc can be easily carried out within two hours. The weighing of the zinc does not involve any circumstantialities. These distinguishing properties of manganese precipitated with hydrogen peroxide have already induced the authors to attempt other separations in the same manner. They are already in a position to announce that manganese and nickel, and probably cobalt, can be separated in the same manner. As they are at present examining the behaviour of the alkaline potassium cyanides of cobalt, nickel, and manganese with hydrogen peroxide, they will give full reports on all these possible separations of manganese, zinc, cobalt, and nickel.—*Journ. für Prakt. Chemie*, New Series, Vol. xliii., p. 402.

Oxides of Salts of Chrome.—M. Prud'homme.—An examination of chromium hydroxide, chloride, chlorates, and sulphites from a tinctorial point of view.—*Mon. Sci. Ques.*, No. 584.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending April 30th, 1891.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

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

London May 8th, 1891.

Sir,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

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

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

Of the 182 samples examined, the whole were found to be clear, bright, and well filtered.

Throughout the month of April the condition of the water supply to the Metropolis continued to be entirely satisfactory, in respect alike to freedom from turbidity, from colour-tint, and from excess of organic matter. Thus, in the case of the Thames-derived supply, the mean ratio of brown to blue tint was as 13·9 to 20; the mean amount of oxygen required for oxidation, 0·055 grain per gallon; the mean amount of organic carbon, 0·155 part in 100,000 parts; and the maximum amount in any single sample examined, 0·190 part in 100,000 parts of the water,—numbers which, it will be seen, correspond very closely with those recorded as expressing the results furnished by the previous month's supply.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

ON CERTAIN POINTS IN THE ESTIMATION OF BARIUM AS THE SULPHATE.*

By F. W. MAR.

In the received mode of precipitating barium as barium sulphate, three conditions are carefully observed—absence of excess of acid, slow mixing of the reagents and rest, before filtration, of twelve hours, or until the precipitate has completely subsided. Usually in this process, the precipitate is thrown out in a finely-divided, milky condition, and settles very slowly. My observation that the precipitate, under certain circumstances, is formed in a more crystalline condition and settles rapidly, led me to investigate the conditions of so rapid a precipitation. These quickly settling precipitates were noticed in the first instance, in the action of sulphuric acid upon solu-

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* *American Journal of Science*, vol. xli., April 1891. Contributions from the Kent Chemical Laboratory of Yale College.—VI.

tions containing a very large amount of potassium chloride with hydrochloric acid in excess. In the course of five or ten minutes the precipitate had completely settled and was found to be in a distinctly crystalline condition, and much coarser than the usual form of precipitated barium sulphate.

At the time it was thought that the cause of this rapid subsidence was the alkaline salt present, and accordingly, a series of experiments was made in which potassium, sodium and ammonium hydroxides were added in varying amounts to about 400 c.m.^{3} of water, hydrochloric acid added to more than acidity (but not in measured amount), 0·5 grm. of barium chloride introduced, and precipitation brought about by adding dilute sulphuric acid. Sometimes these precipitates settled rapidly, but as often came down in the familiar milky condition. Later, another series of experiments, in which the different conditions were more carefully regulated, was made thus: in 400 c.m.^{3} of water were dissolved 0·5 grm. of barium chloride, 10 c.m.^{3} of strong hydrochloric acid, and amounts of the alkaline chlorides varying from 5 grms. to 0·05 grm., the whole being precipitated with 10 c.m.^{3} of a solution of sulphuric acid made by diluting the concentrated acid with three parts of water. These precipitates all settled rapidly, and the variation in the amounts of alkali seemed to exert no very marked influence. Finally, these experiments seeming to point to hydrochloric acid as the influential factor, a series of experiments was made to test the effect of varying the amount of this acid. From a solution containing in 400 c.m.^{3} 0·5 grm. of barium chloride and amounts of hydrochloric acid varying from 1 c.m.^{3} to 50 c.m.^{3}, the barium was thrown out by means of 10 c.m.^{3} of dilute sulphuric acid. This series showed that the hydrochloric acid had a very marked effect upon the precipitation of the barium sulphate. When only one or two c.c. of hydrochloric acid were present, the precipitate appeared immediately, in a milky condition, and settled slowly; as the amount of acid was increased, a point was soon reached where the precipitate was not so quickly apparent, but settled out much more quickly and in a coarser condition. With 10—15 c.m.^{3} of strong hydrochloric acid in the solution, the precipitate settled clear in ten or twelve minutes, and was in excellent condition for filtration. When the solution contained 50 c.m.^{3} of the acid, the precipitate settled clear in five minutes. Upon adding the sulphuric acid to such very acid solutions, no precipitate shows for a moment, but then it separates in beautiful crystalline condition and falls almost immediately. It can be safely filtered with or without pressure in ten minutes. In one instance, in the course of the experiments just detailed, 2 grms. of barium chloride were precipitated in the presence of 30 c.m.^{3} of hydrochloric acid, the precipitate was allowed to settle clear, and was then filtered and washed, the whole operation being completed in seven minntes. This rapid subsidence of the precipitate is seen in hot solutions only —75° C. being the lowest temperature compatible with the attainment of good results, and 85—90° better.

To ascertain whether small amounts of barium would be precipitated in like manner from these acid solutions, a series of experiments was made with solutions containing in 400 c.m.^{3}, 10 c.m.^{3} of hydrochloric acid, and 5, 10, 15, 20, 25, 30, and 50 m.grms. of barium chloride, precipitation being brought about as in the experiments above. These solutions remained clear a few minutes, and then a very transparent precipitate appeared, but in no case was it as pronounced, as the more finely-divided precipitate produced in a neutral solution containing 5 m.grms. of barium chloride by the same amount of sulphuric acid. However, by giving a circular motion to the solution in the beaker, after about 20 minutes a small conical heap of barium sulphate was collected in each case in the centre of the beaker.

Experiments were next undertaken to ascertain whether barium is completely thrown out of solution when precipitated under the conditions related above. The barium salt used in all the experiments described below was obtained by finely powdering selected crystals of barium chloride and drying by pressure between blotting papers. Portions of the same sample were used throughout. The hydrochloric acid used was the chemically pure article of commerce and had a specific gravity of 1·20. The sulphuric acid used was obtained by diluting the pure concentrated acid with three parts of water, and had a specific gravity of 1·28.

In the first series the barium salt was dissolved in about 400 c.m.^{3} of water, 15 c.m.^{3} of hydrochloric were added, and precipitation was brought about by adding 10 c.m.^{3} of the dilute sulphuric acid. The precipitates were filtered, after standing about ten minutes, upon asbestos felts in perforated platinum crucibles.

	$BaCl_2 \cdot 2H_2O$ taken. Grm.	$BaSO_4$ found. Grm.	Error. Grm.
1.	0·5002	0·4760	0·0016—
2.	0·5042	0·4812	0·0006—
3.	0·5038	0·4786	0·0025—
4.	0·5002	0·4760	0·0016—
5.	0·5046	0·4812	0·0006—
6.	0·5038	0·4804	0·0006—

The results of these determinations indicate plainly a loss of barium sulphate, but inasmuch as the felts used had been made very thin and it had been subsequently observed that a small quantity of the sulphate could be collected in one of the filtrates of the series by giving a circular motion to the water, it was thought that the thinness of the felts might offer an explanation of the loss and of the varying results of the series. The following series was, therefore, made in exactly the same manner, except that care was taken to have the felts carefully made and reasonably thick.

	$BaCl_2 \cdot 2H_2O$ taken. Grm.	$BaSO_4$ found. Grm.	Error. Grm.
7.	0·5014	0·4785	0·0004—
8.	0·2227	0·2122	0·0005—
9.	0·5003	0·4773	0·0004—
10.	0·5046	0·4814	0·0004—

These results are uniform, and indicate a trifling loss only; though in the filtrates of these experiments also a very slight, but, as it proved upon re-filtering, unweighable amount of the sulphate could be collected. The precipitate in the last of these experiments was filtered off almost immediately after precipitation, and before it had completely subsided. In another case the whole operation, including the three weighings necessary, was conducted to a finish in forty-five minutes.

In spite of the appearance of the trifling deposit in the filtrate, the deficiency in barium sulphate in these determinations was not greater than should be expected from the accepted solubility of that salt in water. To ascertain the effect of strongly acid solutions upon the solubility of barium sulphate, the following determinations were made:—

In experiment 11 the same amounts of the sulphuric and hydrochloric acids, 10 c.m.^{3} and 15 c.m.^{3} respectively, were used as before, but the total volume was reduced to 100 c.m.^{3}. In 12 and 13 the same total volume as before, 400 c.m.^{3}, was used, but this volume contained 150 c.m.^{3} of the strong hydrochloric acid instead of 15 c.m.^{3}, as in the preceding experiments.

	$BaCl_2 \cdot 2H_2O$ taken. Grm.	$BaSO_4$ found. Grm.	Error. Grm
11.	0·5016	0·4888	0·0002—
12.	0·5004	0·4779	0·0000—
13.	0·5001	0·4776	0·0000—

It appears from these experiments that, as in the preceding series, the solubility of barium sulphate in solutions constituted as described is not increased by the free hydrochloric acid, and that the effect upon the solubility when this acid is present in great strength is to make the precipitate rather more insoluble, if anything, than it is in water. In this connection, it should be remarked that experiments of Fresenius,* together with somewhat similar experience gained by the writer in another line of work not included in this account, point to the fact that the presence of an excess of sulphuric acid is an important condition of this high degree of insolubility. The exact amount of such excess has not been determined, but the amount used in the foregoing experiments seems to be sufficient.

In the preceding experiments barium chloride was used in considerable quantity. The following determinations were made to ascertain whether very much smaller quantities of barium would come down as completely and as soon, or whether it is necessary to let the precipitations stand longer before filtration. In these experiments the barium salt was measured from a standard solution containing 200 m.grms. of the chloride to the litre. The amounts of hydrochloric and sulphuric acids, 15 c.m.³ and 10 c.m.³ respectively, and the whole volume of the solution was the same as in the former experiments.

	$BaCl_2 \cdot 2H_2O$ taken. Grm.	$BaSO_4$ found. Grm.	Time in minutes between precipitation and filtration.	Error. Grm.
14.	0·0030	0·0024	120	0·0004 −
15.	0·0050	0·0046	150	0·0002 −
16.	0·0050	0·0023 0·0043	5 60	0·0025 − 0·0005 −
17.	0·0050	0·0031	5	0·0016 −
18.	0·0050	0·0040	10	0·0007 −
19.	0·0100	0·0078	10	0·0017 −
20.	0·0100	0·0085	15	0·0010 −
21.	0·0100	0·0083	30	0·0012 −
22.	0·0100	0·0087	60	0·0007 −

From these results it would appear that the precipitation, in the presence of hydrochloric acid to the amount indicated, does not take place so rapidly when the amount of the barium salt is small, but that two or three hours are sufficient for reasonably complete separation of the precipitate in any case.

In all the experiments described above there was no attempt at a gradual admixture of the reagents, but they were measured out and at once added to the solutions, the whole being well stirred. From the results obtained it appears to be established, as regards the usual precautions in precipitating barium by means of sulphuric acid, that, contrary to former usage, it is highly advantageous to have the solution strongly acid with hydrochloric acid; that it is not necessary to add the reagents drop by drop, but that the whole quantity required to complete the reaction may be added at once; that ordinary quantities of barium salts, in presence of a considerable excess of sulphuric and hydrochloric acids, are precipitated completely and at once, but that when only a few m.grms. are present the precipitate requires more time to separate under the same conditions. Two or three hours are, however, sufficient, and in no case is the excessive time of twelve hours required.

In the light of the fact demonstrated in the preceding account, that hydrochloric acid may be introduced freely, and without detriment to the quantitative exactness of the precipitation of barium in the form of sulphate from pure solutions, it seemed desirable to look somewhat into the question as to what the influence of a large excess of hydrochloric acid might be upon the well-known contaminating effect of alkaline salts present during precipitation, especially as it is customary to attempt the purification of barium sulphate thrown down in the reverse of this process—the determination of sulphuric acid by means of a soluble barium salt—by digestion of the washed precipitate in hydrochloric acid. The following series of experiments was undertaken with this end in view. The details are shown in the tabular statement, precipitation being effected in the presence of free acid and the alkaline salt.

	$BaCl_2 \cdot 2H_2O$ taken. Grm.	$BaSO_4$ found. Grm.	Error. Grm.	HCl in solution. C.m.³.	Alkaline salts present. Grms.
23.	0·5092	0·5032	0·0169 +	110	$KClO_3$ 3
24.	0·5027	0·4907	0·0107 +	10	,, 3
25.	0·5026	0·4944	0·0154 +	100	KCl 5
26.	0·5045	0·4939	0·0122 +	10	,, 5
27.	0·5020	0·4931	0·0137 +	10	,, 5
28.	0·5013	0·4849	0·0061 +	10	NaCl 5

From the results it is plain that, whatever may be the effect of digesting the washed precipitate in hydrochloric acid, the presence of this acid in large excess during precipitation in the presence of alkaline salts, does not prevent contamination of the precipitate. On the contrary, the greatest contamination seems to have occurred in those cases in which the acid was present to the largest degree, but in view of the slight variation in contamination as compared with the great differences in the amount of acid employed, it does not appear probable that the increase of acid has very much to do with the amount of contamination.

It likewise seemed to be a matter of some interest in this connection, to investigate the process by which it is currently supposed (Fres. "Quant. Anal.," vol. i., p. 547) that barium sulphate carrying alkaline salts may be effectually purified, viz., by the solution of the washed precipitate in strong sulphuric acid and re-precipitation by water. Accordingly the determinations of the following series were undertaken. The barium sulphate, precipitated from solutions containing 5 grms. of potassium chloride and 10 c.m.³ of hydrochloric acid, was collected upon a filter, either paper or asbestos, and, after burning the paper or removing the precipitate from the asbestos (by tapping the crucible which held it and brushing out with a camel's hair brush), was dissolved by warming with concentrated sulphuric acid in a large porcelain crucible and, after cooling, poured into water containing 15 c.m.³ to 20 c.m.³ of hydrochloric acid. The water into which the solutions in strong acid was poured was warmed with a view to diminish the milkiness of the precipitate, but care must be taken to keep the temperature below 60° C. to avoid danger of spattering on the addition of the sulphuric acid. In the last two of the experiments recorded a large amount of ammonium chloride was added to the water into which the solutions in acid were poured, but this appears to be without influence upon the purification or the character of the precipitation. The precipitates, after settling clear, were filtered upon asbestos, ignited, and weighed, the original felts being employed in those cases in which asbestos was used in the first instance. Those marked with an asterisk were gathered in the first filtration upon paper, the paper being burned in the crucible in which solution of the precipitate was subsequently effected. The remainder were filtered originally upon asbestos.

	$BaCl_2 \cdot 2H_2O$ taken. Grm.	$BaSO_4$ found. Grm.	Error. Grm.
29.	0·5026	0·4746	0·0044 −
30.	0·5035*	0·4830	0·0022 +
31.	0·5016	0·4767	0·0024 −
32.	0·5025	0·4804	0·0050 +
33.	0·5046*	0·4829	0·0010 +
34.	0·5004	0·4825	0·0047 +

These results show, evidently, that this process of purification is not satisfactory. It is possible that the losses observed may have been mechanical, and due to the violent action of the strong acid upon the water, but the excess in weight which is noticed in the majority of the determinations can only be attributed to residual contamination.

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* *Zeit. für Anal. Chem.*, vol. ix., p. 62.

Certain experiments, on the other hand, in which the solvent action of sulphuric acid upon barium sulphate is utilised in a different manner resulted more favourably. When a solution of barium sulphate in sulphuric acid is evaporated to dryness, the salt, as is well known, is deposited in large crystals, which can be filtered off as readily as sand. The following series of experiments show the result of an attempt to utilise this property of comparatively slow and large crystallisation in purifying the precipitate. Solution of the precipitate was effected as in the experiments described above, and the evaporation of the acid was effected over a matting of asbestos, or by means of a ring burner, in porcelain, which is preferable to platinum when the evaporation is carried on as slowly as is necessary. After the acid was completely evaporated, the crystals were washed upon a felt of asbestos, ignited, and weighed. Five grms. of potassium chloride and 10 c.m.^{3} of hydrochloric acid were added to the solution of barium chloride in each case.

	$BaCl_2 \cdot 2H_2O$ taken. Grm.	$BaSO_4$ found. Grm.	Error. Grm.
35.	0·5029	0·4796	0·0006 −
36.	0·5008	0·4783	0·0001 +
37.	0·5038	0·4810	0·0001 −
38.	0·5087	0·4861	0·0003 +
39.	0·5025	0·4795	0·0006 +

These results are plainly good and satisfactory so far as concerns the purification of the salt, but, when the evaporation is conducted in the manner described, several hours are needed for the evaporation, and great care must be exercised to obviate the danger of snapping which becomes manifest in the later stage of the evaporation.

By the aid, however, of a Hempel evaporating burner (*Ber. d. Deutsch. Chem. Ges.*, xxi., p. 900) the operation can be finished safely, and with but little care, in the course of half an hour. The following determinations were made exactly like those of the last series, with the exception that the evaporation was effected by means of the Hempel apparatus :—

	$BaCl_2 \cdot 2H_2O$ taken. Grm.	$BaSO_4$ found. Grm.	Error. Grm.
40.	0·5050	0·4824	0·0002 +
41.	0·5069	0·4838	0·0000
42.	0·5041	0·4825	0·0021 +
43.	0·5021	0·4812	0·0018 +
44.	0·4033	0·4801	0·0005 −

Though not an absolutely perfect process, the purification of barium sulphate by this method of solution and evaporation is evidently better by far than the old method of solution and re-precipitation by dilution.

The writer gratefully acknowledges his indebtedness to Prof. F. A. Gooch for many helpful criticisms and suggestions during the course of this investigation.

NOTICES OF BOOKS.

Bibliography of the Chemical Influence of Light. By ALFRED TUCKERMAN, Ph.D. Smithsonian Miscellaneous Collections, No. 785. Washington City, 1891, iii.—22 pp., 8vo.

DR. TUCKERMAN is already known to us as the author of valuable indexes to the "Literature of the Spectroscope," and to the "Literature of Thermodynamics," and now he places chemists and physicists under further obligations by his indefatigable zeal in bibliography. His latest production above named contains the titles of over 250 works and papers relating to the chemical influence of light; the whole is simply arranged in a few sections and alphabetically under each.

The Smithsonian Institution continues in this to publish aids for research, and to place them at the disposal of men of science. Unfortunately, however, most librarians treat the independent treatises issued by the Smithsonian Institution as if they formed numbers of a periodical, and they fail to catalogue separately the several parts of each volume of the "Miscellaneous Collections." Thus these admirable treatises are practically buried, and are less known and used than they deserve. This applies also to the "Contributions," a separate series in quarto form. The treatise before us bears the number 785, and will form part of a volume yet to be issued. Meanwhile it is available for the use of chemists and physicists interested. H. C. B.

A History of Chemistry from Earliest Times to the Present Day; being also an Introduction to the Study of the Science. By ERNST VON MEYER, Ph.D., Professor of Chemistry in the University of Leipzig. Translated, with the author's sanction, by GEORGE McGOWAN, Ph.D., Demonstrator in Chemistry, University College of North Wales, Bangor. London and New York: Macmillan and Co.

A HISTORY of chemistry adapted to the requirements of the present day has been a desideratum in English literature. The work of Thomson is decidedly obsolete, and the treatises of Kopp and Hoefer no longer meet the wants of the student.

We therefore welcome Professor von Meyer's work, the more especially from the broad and luminous character of its views.

We no longer find here the erroneous theory that alchemy was the mother, or, as the Comteans would put it, the theological stage of chemistry. We now find it presents us merely with "a certain disjointed knowledge of chemical processes acquired accidentally," and applied "for their practical results alone, and not with the object of deducing any comprehensive scientific explanation from them."

But the earliest authentic writings touching on chemistry, such as the "Book of the Balance of Wisdom," the "Papyrus Ebers," &c., are perfectly free from the mystical gibberish of the alchemists. The alchemical period, which our author supposes as extending from at least the fourth century of our era to the first half of the sixteenth, was only incidentally contributory to the progress of the science by largely extending the area of our knowledge of chemical facts.

The next stage, according to Professor von Meyer, was the iatro-chemical, expounded by Paracelsus, Helmont, Sylvius, and their colleagues. Technical chemistry, though being ably elaborated by Georgius Agricola, was, in the author's opinion, of little influence on the prevailing tendency of the science of that age.

The author very justly considers that the history of chemistry, properly speaking, begins with Robert Boyle. He points out the general disinclination of the Ancients towards experiment and their preference for the deductive method. But we think that the mischievous influence of the Socratic school has scarcely even yet been brought into sufficient relief.

We find the destruction of the Alexandrian library still assigned to the Arabs. Both external and internal evidence seem to indicate that the sack of the Serapeion and the destruction of the library were due to Bishop Cyril.

As an instance of the untrustworthy character of the history of these times we may mention Raymund (Ramon) Lully, one of the most celebrated alchemists of the fourteenth century, and a pupil of Roger Bacon. It is not certain whether he is or is not identical with a grammarian and dialectician of the same name (*Doctor Illuminatissimus*). The most eminent chemist of this epoch was undoubtedly Basil Valentine. The history of alchemy in its later stages presents a humiliating picture. But before looking back with pity upon the men of the seventeenth and eighteenth century we must remember that minds of the same calibre are accumulating wealth by means of "patent" medicines and systems of medical treatment.

Among the more prominent iatro-chemists we find mention of Sir Turquet de Mayerne (spoken of in old English medical works as Monsieur Mayhorn), Court Physician and, it is whispered, poisoner to James I.

The dominance and the ultimate subversion of the phlogistic theory are very clearly treated, but without the exaggerations which we encounter in the writings of Dumas and Wurtz.

The author pronounces it unjustifiable to assert that chemistry was to the end of the phlogistian period "no science," so that it was created by Lavoisier out of what was previously no science.

It is remarkable that, despite the daring assertion that "*La Chemie est une Science Francaise*," the doctrine of "caloric," a transformation of phlogiston, lingered long in France.

Our author speaks with just indignation of the judicial murder of Lavoisier. It would seem that whilst some of his colleagues, such as Guyton de Morreau and Monge, did not dare to offer any opposition, Fourcroy went further.

But whilst Lavoisier must be acquitted of the frivolous charges on which he was condemned, his behaviour to Scheele, Black, Priestley, and Cavendish, whose results he appropriated without acknowledgment, merits the sternest condemnation.

In the author's survey of the Lavoisierian nomenclature it is much to be regretted that the generic term "metalloids" for non-metallic elementary simple bodies should have been retained.

Passing attention must be given to the labours of a school which interfered with the healthy development of chemistry, physics, and biology in the earlier part of the century. We refer to the *Naturphilosophen*, Shelling, G. H. von Schubert, H. Steffens, Winterl, and others. This school Professor von Meyer speaks of as the "natural philosophy current of that day." "Physiophilosophy" would have been the happier term, since "natural philosophy" has in English a quite distinct meaning. Liebig complains with some bitterness that his studies under Shelling at Erlangen had cost him "two precious years of his life."

We regret that we cannot extend our survey of this most valuable and important work save by warmly recommending it to the student.

Elementary Chemistry for Beginners. By W. Jerome Harrison, F.G.S. London: Blackie and Son.

We are compelled to ask sorrowfully, when will authors and publishers arrive at the conclusion that elementary treatises on chemistry have been already produced in superfluity? Why this should be the case in Britain more than in other civilised countries we are quite unable to explain. But we feel convinced that, pending some capital discovery which shall demand a re-organisation of chemical science, such works, however accurate, lack a *raison d'être*. Mr. W. J. Harrison is a writer of recognised ability, and might, we submit, have employed his time and talents better.

On page 94 we find a statement which is scarcely in harmony with the latest discoveries. We are told that "plants cannot take in nitrogen directly from the air by which they are surrounded." It is now concluded that plants of the leguminous class, by means of the little nodules to be found on their roots, are able to fix and utilise atmospheric nitrogen. Hence they are not benefitted by nitrogenous manures.

On the same page we find it declared that "fortunately" the sulphurous acid gas poured into the atmosphere in consequence of the consumption of pyritic fuel, "is very soluble in water, so that every shower which falls, sweetens and freshens the air." This is perfectly correct, but every such shower inevitably moistens the trees, the ground, as well as all metal articles exposed to the weather, with a dilute solution of sulphurous acid. Under such circumstances, vegetable life quickly succumbs.

The Metallurgy of Gold: a Practical Treatise on the Metallurgical Treatment of Gold-bearing Ores, including the Processes of Concentration and Chlorination, and the Assaying, Melting, and Refining of Gold. By M. Eissler. Third Edition, Revised and greatly Enlarged. With 187 Illustrations. London: Crosby Lockwood and Co. Small 8vo., 518 pp.

The fact that this work has already reached its third edition since 1888 is sufficient truth that it meets a recognised want, and that it is fully appreciated among metallurgists and gold miners. The author is decidedly a practical man, with prolonged and extensive experience in California and North-Western America, and he is now engaged in studying the deposits of South Africa and the methods there in use. To the present edition there have been added four new chapters and about fifty new illustrations. Among the additional matter is an account of the Gates Rock Breaker, of the Globe Mill, which is said to be an improvement on the stamps and the Cornish rollers. Several improvements in the appliances for amalgamation and chlorination are also described. The author describes Greenwood's electrolytic method of obtaining chlorine from solutions of salt, and the successful smelting of auriferous pyrites.

Sea-Sickness: Cause, Prevention, and Cure. Voyaging for Health, with an Appendix on Ship Surgeons. A Concise Practical Treatise. By Thomas Dutton, M.D. (Durham). Second edition. London: Baillière, Tindall, and Cox.

This little work treats of a very important subject, but one which lies most distinctly outside the pale of chemical science. The author's views can be judged, favourably or unfavourably, by the practical physician only. Dr. Dutton thinks that sea-sickness "has prevented many from knowing what pleasure can be derived from a trip on the sea." But a far more important fact is the misery which it inflicts upon the multitudes who are compelled to undertake voyages for purposes of business or when emigrating. The author thinks that nothing is to be hoped from improved constructions of steamers. But it has been found possible to build vessels which aggravated the ordinary risks of sea-sickness. Such were those ununhappy ten-gun brigs, one of which, the notorious "Beagle" was thought good enough for a scientific exploring expedition, and rendered Charles Darwin an invalid for life. How little the tendency to sea-sickness is overcome even in seafaring life may be gathered from the author's own experience, no less than from that of Lord Nelson. Dr. Dutton seems to hold that if there is a specific for sea sickness it is ammonium bromide taken regularly for some days before going on board.

A somewhat distinct subject is the very unsatisfactory position in which the ship's surgeon is placed. If he does his duty he becomes a "black sheep" and imperils his position. The author thinks that the surgeon should be perfectly independent of the captain. He thinks that the Board of Trade should form a medical marine department, and should make the appointments. It is said—and, we believe, with too much truth—that many captains and owners like incompetent, idle surgeons, as they give no trouble and never write to the Board of Trade. This, however, is a subject which belongs to medical authorities. It is curious that whilst on railways the wide distinction which formerly existed between the first class and the third class passenger in fading away, on passenger steamers the movement is in the contrary direction. Invention is racked to find increased luxuries for the first class, whilst the third class are treated little better than convicts, and are denied even that ordinary civility which is generally considered a cheap boon.

CORRESPONDENCE.

ELECTROLYTIC ASSAY OF COPPER.

To the Editor of the Chemical News.

SIR,—Happening to look over some back numbers of the CHEMICAL NEWS, I notice a query by an inquirer who signs himself "Deposit" on "Electrolytic Assay of Copper" (CHEMICAL NEWS, vol. lxii., p. 25). Having had the same trouble as your inquirer has had, I think it may perhaps relieve him to know he is (or was) suffering from a current which was too strong for the solution; with a weaker current of electricity, and also possibly a weaker solution of the copper, the deposit on the cathode would be firm, and either shiny or of a rosy appearance. —I am, &c.,

JOHN RUFFLE.

Rape Oil.—Reimer and Will (*Deutsch. Chem. Gesell.*). —According to the authors, rape oil consists of the glycerides of three distinct fatty acids, one of which, melting at 75°, occurs only in very small quantities. The other two, erucic acid and a liquid acid which the authors name rapinic acid, are present in equal quantities. Lead erucate is readily soluble in hot ether. The zinc salts of the fatty acids can be separated by means of ether.

Detection of Cotton Oil in Lard.—A. Bujard and J. Waldbauer (*Zeit. Ange. Chemie*).—The authors use Bechi-Hehner's silver nitrate test and Labiche's lead acetate reaction. For the former test 10 grms. of the filtered anhydrous lard are heated with 5 c.c. of silver nitrate solution (1 part silver nitrate, 200 alcohol, 40 ether, and 0·1 part nitric acid) in the water-bath for fifteen minutes, shaking continually. The mixture, according to its proportion of cotton-seed oil, turns more or less deeply reddish brown to black. Pure lard, poppy, olive, and sesame oils are not affected. For the Labiche test, 25 grms. of the clear melted sample are mixed with a 25 c.c. of a solution of lead acetate, heated to 35°, and well mixed after the addition of 5 c.c. ammonia. The emulsion thus obtained, if cotton oil is present, soon shows a yellowish red colour, which becomes more intense after standing for a day. Poppy-rape, sesame oils, and pure lard are not affected.

Determination of Resin Oil in Mineral Lubricants. —L. Storch (*Chemiker Zeitung*).—10 to 15 grms. of the lubricant containing resin oil, but no fatty oils, is gently heated on the water-bath in a small flask with 5 vols. alcohol at 96 p.c., shaken up, and let cool down to the temperature of the room. The alcohol is then placed in a small Erlenmeyer flask about 7 c.m. in height; the mineral oil which remained in the first flask is rinsed round (not shaken) with a few c.c. of 90 per cent alcohol, the solution poured into the second flask and heated upon a water-bath which is slightly simmering, enclosing it within a beaker with the bottom cut off to avoid too rapid condensation on the sides of the vessel. The heat is continued until the residue in the flask is free from bubbles. It is weighed when cold, and the residue is covered with ten parts by weight of alcohol at 96 per cent. If the residue consists entirely of resin oil this quantity of alcohol will suffice for its solution. The alcoholic solution is treated as above, and the residue contains small quantities of mineral oils.

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. cxii., No. 18, May 4, 1891.

Quantitative Studies on the Chemical Action of Light. Reactions with Different Thicknesses and Different Forms of Vessels.—George Lemoine.—This memoir does not admit of useful abstraction.

Certain Compounds Formed by Mercuric Chloride. —G. André.—The author has obtained double zinc and mercury ammonium chlorides by dissolving in ammonium chloride either the two oxides or an oxide and a chloride. Aniline also acts upon mercuric chloride, giving, like ammonia, two kinds of compounds—the first, a well-known addition compound, $C_6H_5(NH2)_2HgCl_2$, and the second a substitution compound, $C_6H_5NH{\cdot}HgCl$. With benzylamine the results are more definite.

Announcement of a General Law determining as a Simple Function of the Chemical Constitution of Bodies the Temperatures of their Changes of Conditions under all Pressures.—G. Hinrichs.—A purely mathematical paper.

On Boron Selenide.—Paul Sabatier.—The author has succeeded in obtaining this compound by causing vapours of selenium or a current of hydrogen selenide to pass over amorphous boron heated to redness. Boron selenide is less fusible and volatile than the corresponding sulphide. Its odour is exceedingly irritating.

On the Action of Hydriodic Acid upon Boron Bromide.—A. Besson.—The compounds produced are the bromoiodide, BBr_2I—a colourless liquid distilling about 125°; and $BBrI_2$, also a colourless liquid which distils about 180°.

On Basic Magnesium and Zinc Chromites and on Neutral Cadmium Chromite.—G. Viard.—The author has obtained magnesium chromite, $2MgOCr_2O_3$, by calcining magnesium chromate. At higher temperatures there is formed $MgOCr_2O_3$. By the action of potassium bichromate upon magnesia there is obtained an intermediate product, $3MgO,2Cr_2O_3$. The action of alkaline chromates upon magnesium chloride does not seem to furnish pure products. The calcination of zinc chromate yields a violet-black compound, $3ZnO,2Cr_2O_3$. Cadmium gives results much less complex than do magnesium and zinc, producing only one compound, CdO,Cr_2O_3.

Preparation of Disodium Erythrate.—M. de Forcrand.—It results from these researches that whilst we may easily replace the first and second equivalent of alcoholic hydrogen of erythrite by sodium, the two others resist this action even in presence of an excess of soda.

Formation of Dimethylacrylic Acid in the Preparation of the Acid Amides of Isovaleric Acid.—E. Dunllier.—In preparing the amidic acids of isovaleric acid the author has followed the ordinary method, which consists in calling bromoisovaleric acid to react upon an ammonia. But after having decomposed the ammoniacal salts of baryta, expelled the ammonia by ebullition, and precipitated the baryta by sulphuric acid, in place of setting the amidic acid at liberty by silver oxide, he previously submitted the liquid to distillation. He collected an acid product which, after saturation with soda, evaporation to dryness, and treatment with sulphuric acid, yielded a notable quantity of an oily acid, very sparingly soluble in water, distilling at 175—195°, absorbing bromine and iodine and partly crystallising, The crystals have the composition and the properties of dimethylacrylic acid.

Discussion of the Experiments of Biot relating to Aqueous Solutions of Tartaric Acid in Presence of Potassa or Soda.—M. Aignan.—This memoir does not admit of useful abstraction.

Methylmethylcyanosuccinate; Methylethenyltricarbonic Ether.—L. Barthe.—The author, under a pressure of 0·06 m.m., and at a temperature of 195—200°, obtains a homogeneous, colourless, oily liquid, the composition of which may be expressed by the formula $C_8H_4NO_4$.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 2, No. 584.

Camille Kœchlin.—P. Schutzenberger.—An obituary notice of the illustrious tinctorial chemist of Mulhouse, followed by a list of his researches.

The Chemical Revolution. — M. Lavoisier. — An abstract of M. Berthelot's paper compiled by Hippolyte Stupuy. We can merely quote the epigrammatic utterance of Lagrange: "It took them (the terrorists), merely a moment to cause this head to fall, but a century will perhaps not suffice to produce such another."

On Beer-Yeast.—H. Bungener.—This paper requires the ten accompanying figures.

Action of Mineral Acids in Saccharification by Malt, and in the Fermentation of Starch.—Dr. J. Effront.—A detailed study of the action of hydrofluoric acid, and of the soluble fluorides, upon diastase upon yeast, and upon the fermentation of solutions of cane sugar and of worts. The industrial use of the fluorides in distilleries has been made the subject of a Belgian patent.

MISCELLANEOUS.

Royal Institution.—An extra evening meeting will be held on Tuesday, June 2nd, at 9 o'clock, when Dr. Chas. Waldstein will give a discourse on "The Discovery of the 'Tomb of Aristotle.'"

Institution of Naval Architects.—At a meeting of the Council of the Institution of Naval Architects held on the 15th inst., it was unanimously resolved to award the Gold Medal of the Institution to Prof. V. B. Lewes, F.C.S., F.I.C., for his paper on "Boiler Deposits," read at the recent Annual General Meetings of the Institution.

MEETINGS FOR THE WEEK.

Monday, June 1st.—Society of Chemical Industry, 8. "Gum Arabic and its Modern Substitutes," by Dr. S. Rideal and W. E. Youle. "On the Quantitative Analysis of Light and Colour, founded on the Tintometer Colour Scales," by J. W. Lovibond.
—— Royal Institution, 5. General Monthly Meeting.
Tuesday, 2nd.—Royal Institution, 3. "The Garrick Period of Stage History," by William Archer.
Thursday, 4th.—Royal, 4.30.
—— Royal Institution, 3. "The Orchestra considered in connection with the Development of the Overture," by A. C. Mackenzie, Mus. Doc.
—— Chemical, 8. "Observations on the Molecular Refraction and Dispersion of Various Substances in Solution," by Dr. J. H. Gladstone, F.R.S. "The Nature of Solution as Elucidated by a Study of the Densities, Heat of Dissolution, and Freezing-points of Solutions of Calcium Chloride," and "A Reply to a Recent Criticism of the Conclusions drawn from a Study of Various Properties of Sulphuric Acid Solutions," by S. U. Pickering, F.R.S. "On Volatile Platinum Compounds," by W. Pullinger.
Friday, 5th.—Royal Institution, 9. "On the Discovery of the 'Tomb of Aristotle,'" by Charles Waldstein, Ph.D.
—— Quekett, 8.
—— Geologists' Association, 8.
Saturday, 6th.—Royal Institution, 3. "The Scientific Study of Decorative Colour," by Prof. A. H. Church, M.A., F.R.S.

THE CHEMICAL NEWS.

Vol. LXIII., No. 1645.

THE WAR AGAINST CRAM.

It is very satisfactory to find that the protest against "cram" in education, which was so ably and forcibly raised by Mr. Auberon Herbert, is not being allowed to die out. We therefore take the opportunity of meeting some of the pleas still urged in favour of examinationism.

Says a contemporary, the prospect of the abolition or the mitigation of the present tests is exciting the hopes of students. This is a complete misapprehension. No idle or incompetent youth will find degrees and honours easier of attainment. If the new movement is successful the very contrary will be the case. Nothing but sterling work—successful research in some department of science or literature—will open the gate to the candidate. Our senior wranglers, double first men, Fellows of colleges, &c., will be the men who have proved themselves able to make some addition to the existing sum total of human knowledge. They will emphatically not be the men who prove themselves the most apt in re-absorbing and reproducing—however intelligently—the knowledge of others. They will not be mere "secondary batteries," which, when charged, merely give off what has been put into them with a certain percentage of loss. Without any wish to be offensive, we cannot help saying that the emptier a vessel the greater is its receptive power. This fact, in its bearing upon their pupils, is not overlooked by university "coaches." "Such a one," said a member of this prosperous and influential fraternity, "would do very well, only he thinks!" Now we wish to bring to the front a quite different class of men from those who now take honours, men who cannot be easily crammed because their mental condition is that of a plenum, not a vacuum, men of suggestive fruitful minds, full of resources, as distinguished from mere walking text-books.

We must never forget that in the country which is our most formidable rival in science, pure or applied, examination plays a very slight part, and competition no part at all. If we look through its copious scientific literature we note the total absence of books compiled for the use of students preparing for one or the other examination, or adapted to some newly-devised syllabus. The German professor aims at qualifying his students, not to "pass," but to know. His reputation rises with the number of successful researches conducted in his class-rooms. Now it is self-evident that before a student can do good work in any science, he must be well grounded in the general laws of such science, and be more particularly acquainted with all that has been done in the subject he takes in hand.

This method of teaching any science—say chemistry—by leading the student as rapidly as possible into the fields of original research, is not an untried experiment, but a method which has been successfully adopted on the largest scale.

When a man has once shown himself capable of conducting a research, we cannot be mistaken as to his intellectual calibre. But by no examination yet devised or even conceivable can we gauge his power of accurate and thorough observation, and of drawing right conclusions from the facts ascertained. The examiner may find out what a student *knows*, but not what he can *do*. The coach may convey into his memory information without end, but he cannot give the pupil mental resources. Hence examinations really tell us little as to the value of a candidate. We have heard it said that the ability to play a good game of whist is in reality a better test than any which the Civil Service Commissioners have invented.

EARLY STUDIES ON THE METALS OF THE RARE EARTHS.

It is not generally known in this country that one of the earliest workers in this interesting and delicate department of analytical chemistry was H.I.H. Prince Louis Lucien Bonaparte. We have recently received from the author a copy of a pamphlet, reprinted from the *Gazetta Toscana delle Scienza Medicofisiche* of April 15th, May 1st, and September 1st, 1843, containing articles by H.I.H. on the rare earths.

Although half a century has thus elapsed since the publication of these researches, we think that their reproduction will be found not merely of historical interest, but even suggestive for chemists engaged in such investigations.

The subjects more particularly discussed in the pamphlet before us are the separation of cerium from didymium by means of the action of valerianic acid upon the mixed nitrates. He obtained didymium oxide so free from cerium that no trace of cerium could be detected in the concentrated and neutralised solution. He further finds that benzoic acid is quite as effective for the separation of cerium and didymium as is valerianic acid, cerium benzoate being precipitated, whilst the didymium salt remains in solution in the acid liquid. The author suggests, also, the use of phocenic or of butyric acid, but points out that they would present no advantage except from an economical point of view. He shows that the substance, which at that time was generally regarded as cerium sesquioxide, obtained by calcining the nitrate, is a mixture of cerium, didymium, and lanthanum oxides.

The pure cerium dioxide, as obtained by Prince L. L. Bonaparte, is described as insoluble in dilute acids and not easily soluble even in concentrated and boiling acids. If didymium or lanthanum is present it is more soluble. It is light yellow in colour, without any approach to a brick-red, and if finely triturated it becomes nearly colourless. The salts and the hydrate are yellow. The hydrate dissolves in nitric acid, and the solution, if prepared in the cold, is not rendered turbid by a further addition of nitric acid. If the solution is rendered perfectly neutral and boiled, it becomes turbid, and deposits an isomeric nitrate, insoluble in acidulated liquids, but soluble in pure water. The author puts on record that the solution of this salt becomes very turbid on the addition of a solution of potassium sulphate.

The pure cerous salts were found colourless and not precipitable by the valerianic, benzoic, or succinic acid, as are the ceric salts. They are precipitated by oxalic acid and with potassium sulphate. They form the well-known double sulphate.

On carefully reading this pamphlet we are led to the belief that, had the Prince been able to continue his studies with a larger supply of material, and, above all, with the spectroscope at command, he would have anticipated much that has since been done by others.

In one sense we are happy to learn that the illustrious author has supplemented the philological studies in which he has achieved so much by a return to the science of chemistry. Still we must all regret the immediate occasion—the necessity for economising his failing eyesight.

Thermic Data on Propionic Acid and the Potassium and Sodium Propionates.—G. Massol.—Propionic acid, when combining with potassa and soda, liberates as much heat as its higher and lower homologues—the acetic and the butyric acids.—*Comptes Rendus*, cxii., No. 20.

SEPARATION AND DETERMINATION OF NICKEL AND COBALT.

By CONSTANTIN KRAUSS.

(Continued from p. 255).

10. P. Gucci (*Gazz. Chim.*) evaporates the solution of both metals to dryness, heats the residue with saltpetre until it is in quiet flux, takes up in warm water, filters, and washes with hot water. The residue is rinsed into a beaker, the chief part of the water is poured off, and mixed with double its volume of nitric acid at 1·2 sp. gr. The beaker is then plunged for a minute into boiling water, let cool, and the contents are filtered. All the nickel is said to be in the filtrate, whilst the cobalt oxide remains undissolved.

This method does not effect a complete separation of the two metals. The result is too much nickel and too little cobalt.

11. H. Rose (*Handb.*, 6th edition) mixes the neutral solution of the metals with hydrochloric acid, and passes into the strongly diluted liquid chlorine gas until it is completely saturated. Recently precipitated barium carbonate is then added in excess, and the mixture is allowed to stand in the cold for twelve to eighteen hours, with frequent shaking. The cobalt is supposed to be separated as cobaltic hydroxide, whilst the nickel remains in solution. Henry proposes the use of bromine-water in place of chlorine, and Denham Smith recommends a solution of chloride of lime, which has been completely decomposed by the addition of sulphuric acid.

According to the author, this method gives approximately satisfactory results if it is carried out according to Henry's modification and with the aid of refrigeration. The cobalt oxide eliminated contains then in most cases merely a trace of nickel, which is scarcely ponderable. But the results are quite useless if the experiments are made at the ordinary temperature of the work-room. If the solution is heated all the nickel is deposited as a blue-black oxide.

12. Liebig (*Annalen der Chemie*) mixes the solution of the two metals with hydrochloric acid in decided excess, and adds potassium cyanide until the precipitate of nickelous and cobaltous cyanides formed is re-dissolved. A little more potassium cyanide is then added and the liquid is boiled for some time, adding gradually hydrochloric acid, but not in such a quantity that the reaction becomes acid. The liquid is then boiled in a flask with an excess of hydrochloric acid until, on a further addition of hydrochloric acid, no escape of hydrocyanic acid can be traced. The cobaltous cyanide passes into the state of a cobaltic cyanide, whilst the nickelous cyanide is decomposed with a formation of nickelous chloride. The nickel can then be precipitated with potassa-lye and determined as nickelous oxide. The filtrate is evaporated to dryness with nitric acid, and the residue is fused for a considerable time in a porcelain crucible. On treatment with hot water cobaltic oxide remains undissolved.

According to H. Rose, this method gives accurate results if carefully executed, but is inferior to the process with chlorine gas (No. 11).

Krauss contests this opinion, as, according to his experiments, if a sufficient quantity of potassium cyanide is used and the ebullition duly prolonged with a very gradual addition of hydrochloric acid, Liebig's method gives decidedly better results than that of Rose. The cobaltic oxide separated from the melt requires, however, as Rose observes, to be re-dissolved and again precipitated.

Liebig modifies his method as follows:—The solution of the metallic salts is mixed with hydrocyanic acid and potassa-lye and heated until everything is dissolved. After the excess of hydrocyanic acid has been expelled by boiling, the nickel (present as nickelous cyanide) is separated with elutriated mercuric oxide, partly as nickelous oxide and partly as cyanide. The cobalt, which is present as potassium cobalticyanide, remains in solution, and can be precipitated from the filtrate (after acidulation with acetic acid) as copper cobalticyanide by the addition of copper sulphate. The precipitate is decomposed with potassa-lye, and the quantity of the cobalt is calculated from that of the copper oxide separated out. If it is thought preferable to determine the cobalt directly the precipitate of copper cobalticyanide after ignition is dissolved in hydrochloric acid, with the addition of a few drops of nitric acid, the copper is precipitated with hydrogen sulphide, and the cobalt is determined in the filtrate according to one of the well-known methods.

This modification gives surprisingly accurate results if the directions are accurately followed, and if the ebullition is sufficiently prolonged. But the precipitation of the cobalt with copper sulphate cannot be recommended, since the precipitate, as Rose has observed, either becomes slimy and retains potassa, or is so finely crystalline that a clear filtrate cannot be obtained.

Wöhler has simplified Liebig's method. After precipitating the nickel with mercuric oxide he neutralises the solution with nitric acid, precipitates mercury cobalticyanide by means of mercurous nitrate, ignites the precipitate strongly, and determines the residual cobalt oxide in the known manner.

With this modification Krauss obtains very satisfactory results. For determining the cobalt in the mercury cobalticyanide the following volumetric process was found very advantageous:—The precipitate, which has been previously heated with dilute nitric acid, is decomposed with alkali, free from any haloid, and the black mercurous oxide is filtered off. The filtrate is supersaturated with nitric acid, a measured quantity of a standard solution of silver is added, and the excess of silver is determined in the filtrate by Volhard's method with ammonium sulphocyanide and iron-alum.

(To be continued).

THE PRICE OF HIGH CLASS PHOSPHATES.

By ALEX. BUCHAN, F.I.C.

THESE are usually sold at so much per unit, with a rise of, say, one-fifth of a penny per unit for each unit over, say, 70 per cent, calculated on the dry sample, and an allowance of 2 units of phosphate for each excess unit of iron and alumina over, say, 4 per cent after the unitary price has been fixed.

These terms are very unfair to the manufacturer, and with the object of drawing their attention to the subject this article has been written.

The percentage is calculated on the dry sample. Now this may be fair enough in the case of rock phosphates, which require to be dried anyway before grinding, but it is manifestly unfair in the case of ground phosphates, like Somme, which sometimes contain as much as 5 per cent moisture.

It is weighed and delivered in the moist state and used without any drying, so why introduce an altogether foreign element into the question, and raise the price but certainly not the value something like 4 per cent? If the seller wants to be paid on the dry sample let him deliver it in this more valuable condition.

The allowance for iron and alumina is made after the unitary price has been fixed. Now it is quite evident that the iron and alumina reduce the value, else why the allowance of 2 units of phosphate for each excess unit? Consequently the allowance should be made before the unitary price is fixed. The present regulation seems to show that the iron and alumina do not reduce the value of each unit, but only the number of them, which is absurd.

An example will make this contention clearer;—

100 tons Somme phosphate, testing—

Phosphate of lime	80 per cent
Iron and alumina	6 ,,
Moisture	5 ,,

at 12 pence per unit on 70, rising ⅕d., calculated on the dry, with an allowance of 2 units of phosphate of lime for each excess unit of iron and alumina over 4 per cent,

The dried sample would test—

Phosphate of lime ..	84·21 per cent
Iron and alumina ..	6·31 ,,

The seller's way of invoicing this would be—

Phosphate delivered	100 tons
Less 5 per cent for moisture	5 ,,
	95 ,,

$$84{\cdot}21 \text{ units} - 2\,(6{\cdot}31 - 4) = 79{\cdot}59 \text{ units.}$$
$$\text{at } 12 + \tfrac{1}{5}\,(84{\cdot}21 - 70) = 14{\cdot}84 \text{ pence per unit.}$$
$$79{\cdot}59 \text{ units at } 14{\cdot}84 \text{ pence} \times 95 \text{ tons} = £467\ 10\text{s.}$$

The fair and just way would be—

$$80 - 2\,(6-4) = 76 \text{ units at } 12 + \tfrac{1}{5}\,(76-70) = 13{\cdot}2 \text{ pence per unit.}$$
$$76 \text{ units at } 13{\cdot}2 \text{ pence} \times 100 \text{ tons} = £418.$$

A difference of 10 per cent against the seller.

Laboratory,
Port Dundas Chemical Works,
Glasgow, May 18, 1891.

ON THE BASES (ORGANIC) IN THE JUICE OF FLESH. Part I.*

By GEORGE STILLINGFLEET JOHNSON, M.R.C.S., F.C.S., F.I.C.

The author has endeavoured to ascertain by careful experiments how far the substances hitherto prepared from flesh are true "*educts*," and really present in the flesh itself, or merely products, due to (1) the action of chemical or physical agencies applied in the course of extraction, or (2) to bacterial action modifying the composition of the flesh before it comes into the hands of the operator.

Preliminary experiments are first described bearing chiefly upon the first-named source of error.

Liebig's process for extracting kreatine from the juice of flesh was modified by omitting the use of baryta-water, with the result that abundance of kreatine was obtained, mixed with acid potassium phosphate (KH_2PO_4). In Liebig's process potassium chloride is obtained after the kreatine has been separated.

A preliminary experiment has been described in which the author precipitated the albumenoid matters from the watery extract of fresh butchers' beef by means of solution of mercuric chloride, the filtrate depositing on standing a spherical precipitate, consisting of the mercury salt of the sarcous kreatinin, from which a tabular kreatinin was obtained isomorphous with the tabular kreatinin obtained by the author from human urine in 1887.

The special advantages of the method adopted by the author in isolating the kreatinin of urine are next detailed, after which a series of experiments are described in which muscle substance in different stages of freshness was extracted with water, the extracts treated by the mercuric chloride method, and the products compared.

Among these products is sarcous kreatinin, whose properties are fully described and carefully compared with those of urinary kreatinins previously investigated (vide *Roy. Soc. Proc.*, vol. xliii., pp. 493—534).

The final conclusion drawn is that sarcous kreatine is not present in fresh muscle, but results from bacterial action, whereas sarcous kreatinin is probably a true "educt."

JUSTUS von LIEBIG:
An Autobiographical Sketch.*

[At the recent celebration of the Jubilee of the Chemical Society, reference was made to the wonderful energy and ability of Liebig, to the great work which he did in founding organic chemistry, and to the immense stimulus which he gave, alike in his own country and in England, to scientific investigation in pure chemistry and in its applications to agriculture, physiology, and pathology.

Very opportunely a portion of an autobiographical sketch in Liebig's own handwriting has just come to light, in which he gives a most interesting account of the formation of his habits of thought, and of the development of his scientific activity. He also gives an amusing description of the lectures given in his student days by professors of the deductive method.

In his sixtieth year, we are told, Liebig wrote some biographical sketches which were laid aside and could not be found when he wished to resume them. They were never finished. A portion of the manuscript was found among some other papers in Liebig's handwriting by his son Dr. Georg Baron von Liebig, and has been published by the latter in the *Deutsche Rundschau* for January, 1891. Mr. E. K. Muspratt has been good enough to lend me a copy which he received from his friend the present Baron.

I have endeavoured to render it into English as literally as the difference in the idiom and modes of expression in the two languages will permit; and it is now made public in England by the kind permission of the *Deutsche Rundschau.*

His method of teaching and its remarkable success are worthy of attention at the present time, when technical education is occupying so much of the public mind.]

My father, who had a colour warehouse, frequently occupied himself in making some of the colours in which he dealt, and for that purpose had fitted up for himself a small laboratory to which I had access, and where I sometimes enjoyed the privilege of helping him. He made his experiments as prescribed in works upon chemistry, which were, with great liberality, lent to the inhabitants of Darmstadt from the rich Court Library.

The lively interest which I took in my father's labours naturally led me to read the books which guided him in his experiments, and such a passion for these books was gradually developed in me that I became indifferent to every other thing that ordinarily attracts children. Since I did not fail to fetch the books from the Court Library myself, I became acquainted with the librarian Hess, who occupied himself successfully with botany, and as he took a fancy to the little fellow, I got, through him, all the books I could desire for my own use. Of course the reading of books went on without any system. I read the books just as they stood upon the shelves, whether from below upwards, or from right to left was all the same to me; my fourteen-year-old head was like an ostrich stomach for their contents, and amongst them I found side by side upon the shelves the thirty-two volumes of Macquer's "Chemical Dictionary," Basil Valentine's "Triumphal Car of Antimony," Stahl's "Phlogistic

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* Abstract of a Paper read before the Royal Society, May 28, 1891.

* Read at a joint Meeting of Societies in the Chemical Laboraties, University College, Liverpool, on Wednesday evening, March 18, 1891, by Prof. J. Campbell Brown, D.Sc.

Chemistry"—thousands of essays and treatises in Göttling's and Gehlen's periodicals, the works of Kirwan, Cavendish, &c.

I am quite sure that this manner of reading was of no particular use so far as acquisition of exact knowledge is concerned, but it developed in me the faculty, which is peculiar to chemists more than to other natural philosophers, of thinking in terms of phenomena; it is not very easy to give a clear idea of phenomena to anyone who cannot recall in his imagination a mental picture of what he sees and hears, like the poet and artist for example. Most closely akin is the peculiar power of the musician, who, while composing, thinks in tones which are as much connected by laws as the logically arranged conceptions in a conclusion or series of conclusions. There is in the chemist a form of thought by which all ideas become visible to the mind as the strains of an imagined piece of music. This form of thought is developed in Faraday in the highest degree, whence it arises that to one who is not acquainted with this method of thinking, his scentific works seem barren and dry, and merely a series of researches strung together, while his oral discourse when he teaches or explains, is intellectual, elegant, and of wonderful clearness.

The faculty of thinking in phenomena can only be cultivated if the mind is constantly trained, and this was effected in my case by my endeavouring to perform, so far as my means would allow me, all the experiments whose description I read in the books. These means were very limited, and hence it arose that, in order to satisfy my inclination, I repeated such experiments as I was able to make a countless number of times, until I ceased to see anything new in the process, or till I knew thoroughly every aspect of the phenomenon which presented itself. The natural consequence of this was the development of a memory of the sense, that is to say of the sight, a clear perception of the resemblances or differences of things or of phenomena, which afterwards stood me in good stead.

One will easily understand this if one imagines, for instance, a white or coloured precipitate which is produced by mixing two liquids; it is formed either at once or after some time, it is cloudy or of a curdy or gelatinous character, sandy or crystalline, dull or bright, it deposits easily or slowly, &c.; or if it is coloured it has a certain tint. Among the countless white precipitates each has something peculiar to itself; and when one has experience in this sort of appearances, whatever one sees during an investigation at once awakens the remembrance of what one has seen. The following example will make clear what I mean by sight or eye memory. During our joint research on uric acid, Wöhler one day sent me a crystalline body which he had obtained by the action of peroxide of lead upon this acid: I immediately thereupon wrote to him with great joy, and without having analysed the body, that it was allantoin. Seven years before I had had this body in my hands; it had been sent to me by C. Gmelin for investigation, and I had published an analysis of it in *Poggendorff's Annalen*; since that time I had not seen it again. But when we had analysed the substance obtained from uric acid there appeared a difference in the amount of carbon, the new body gave 1½ per cent carbon less, and since the nitrogen had been determined by the qualitative method a corresponding quantity (4 per cent) of nitrogen more; consequently it could not possibly be allantoin. However, I trusted my eye memory more than my analysis, and was quite sure that it was allantoin, and the thing now to be done was to find the remains of the substance previously analysed in order to analyse it afresh. I could describe the little glass in which it was with such precision that my assistant at last succeeded in picking it out from amongst a couple of thousand other preparations. It looked exactly like our new body, except that examination under the lens showed that Gmelin, in the preparation of his allantoin, had purified it with animal charcoal, some of which having passed through the paper in the filtration had become mixed with the crystals.

Without the complete conviction which I had that the two bodies were identical, the allantoin produced artificially from uric acid would undoubtedly have been regarded as a new body, and would have been designated by a new name, and one of the most interesting relations of uric acid to one of the constituents of the urine of the fœtus of the cow would perhaps have remained for a long time unobserved.

In this manner it came to pass that everything I saw remained intentionally or unintentionally fixed in my memory with equal photographic fidelity. At a neighbouring soap boiler's I saw the process of boiling soap, and learned what "curd soap" and "fitting" are, and how white soap is made; and I had no little pleasure when I succeeded in showing a piece of soap of my own making, perfumed with oil of turpentine. In the workshop of the tanner and dyer, the smith and brass founder, I was at home, and ready to do any hand's turn.

In the market at Darmstadt I watched how a peripatetic dealer in odds and ends made fulminating silver for his pea-crackers. I observed the red vapours which were formed when he dissolved his silver, and that he added to it nitric acid, and then a liquid which smelt of brandy, and with which he cleaned dirty coat collars for the people.

With this bent of mind it is easy to understand that my position at school was very deplorable; I had no ear-memory and retained nothing or very little of what is learned through this sense; I found myself in the most uncomfortable position in which a boy could possibly be; languages and everything that is acquired by their means, that gains praise and honour in the school, were out of my reach; and when the venerable rector of the gymnasium (Zimmermann), on one occasion of his examination of my class, came to me and made a most cutting remonstrance with me for my want of diligence, how I was the plague of my teachers and the sorrow of my parents, and what did I think was to become of me, and when I answered him that I would be a chemist, the whole school and the good old man himself broke into an uncontrollable fit of laughter, for no one at the time had any idea that chemistry was a thing that could be studied.

Since the ordinary career of a gymnasium student was not open to me, my father took me to an apothecary at Heppenheim in the Hessian Bergstrasse; but at the end of ten months he was so tired of me that he sent me home again to my father. I wished to be a chemist, but not a druggist. The ten months sufficed to make me completely acquainted alike with the use and the manifold applications of the thousand and one different things which are found in a druggist's shop.

Left to myself in this way, without advice and direction, I completed my sixteenth year, and my persistent importunity at last induced my father to give me permission to go to the University of Bonn; whence I followed to Erlangen the Professor of Chemistry, Kastner, who had been called to the Bavarian University. There arose at that time at the newly-established University of Bonn an extraordinary quickening of scientific life; but the degenerate philosophical methods of investigation, as they had been embodied in Oken, and still worse in Wilbrand, had a most pernicious influence on the branches of natural science, for it had led alike in lecture and in study to a want of appreciation of experiment and of an unprejudiced observation of nature, which was ruinous to many talented young men.

From the professional chair the pupil received an abundance of ingenious contemplations; but, bodiless as they were, nothing could be made of them.

The lectures of Kastner, who was considered a most eminent chemist, were without order, illogical, and arranged just like the jumble of knowledge which I carried about in my head. The relations which he discovered between phenomena were somewhat after the following pattern :—

"The influence of the moon upon the rain is clear, for as soon as the moon is visible the thunder-storm ceases," or "the influence of the sun's rays on water is shown by the rise of the water in the shafts of mines, some of which cannot be worked in the height of summer." That we see the moon when the thunderstorm is dispelled, and that the water rises in the mine when the brooks which drive the pumps dry up in summer, was, of course, too blunt an explanation for a clever lecture.

It was then a very wretched time for chemistry in Germany. At most of the universities there was no special chair for chemistry; it was generally handed over to the professor of medicine, who taught it, as much as he knew of it, and that was little enough, along with the branches of toxicology, pharmacology, materia medica, practical medicine, and pharmacy.

Many years after this in Giessen, descriptive and comparative anatomy, physiology, zoology, natural history, and botany were in one single hand.

While the labours of the great Swedish chemist, the English and French natural philosophers, Humphry Davy, Wollaston, Biot, Arago, Fresnel, Thenard, and Dulong opened up entirely new spheres of investigation, all these inestimable acquisitions found no soil in Germany where they could bear fruit. Long years of war had undermined the well-being of the people, and external political pressure had brought in its train the desolation of our universities, filled men with painful anxiety for many years, and turned their desires and their strength in other directions. The national spirit had asserted its freedom and independence in ideal spheres, and by the destruction of belief in authority had brought rich blessings in many ways—for example, in medicine and philosophy; only in physiology it had broken through its natural limits, and wandered far beyond experience.

The goal of science and the fact that it has value only when it is useful to life had almost dropped out of sight, and men amused themselves in an ideal world which had no connection with the real one. It was considered an almost debasing sentiment, and one unworthy of an educated person, to believe that in the body of a living being the crude and vulgar inorganic forces played any part. Life and all its manifestations and conditions were perfectly clear. Natural phenomena were clothed in bewitchingly lovely dress, cut out and fitted by clever men, and this was called philosophical investigation. Experimental instruction in chemistry was all but extinct at the universities, and only the highly-educated pharmacists, Klaproth, Hermbstädt, Valentin Rose, Trommsdorff, and Buchholz, had themselves preserved it, but in another department.

I remember at a much later period, Professor Wurzer, who held the chair of chemistry at Marburg, showing me a wooden table drawer, which had the property of producing quicksilver every three months. He possessed an apparatus which mainly consisted of a long clay pipe stem, with which he converted oxygen into nitrogen by making the porous pipe stem red hot in charcoal, and passing oxygen through it.

Chemical laboratories, in which instruction in chemical analysis was imparted, existed nowhere at that time. What passed by that name were more like kitchens filled with all sorts of furnaces and utensils for the carrying out of metallurgical or pharmaceutical processes. No one really understood how to teach it.

I afterwards followed Kastner to Erlangen, where he had promised to analyse some minerals with me; but unfortunately he did not himself know how to do it, and he never carried out a single analysis with me.

The benefit which I gained through intercourse with other students during my sojourn in Bonn and Erlangen was the discovery of my ignorance in very many subjects which they brought with them from school to the university, and since I got nothing to do in chemistry I laid out all my energies to make up for my previously neglected school studies.

In Bonn and Erlangen small numbers of students joined with me in a chemico-physical union, in which every member in turn had to read a paper on the question of the day, which, of course, consisted merely in a report on the subjects of the essays which appeared monthly in *Gilbert and Schweigger's Journal*.

In Erlangen, Schelling's lectures attracted me for a time, but Schelling possessed no thorough knowledge in the province of natural science, and the dressing up of natural phenomena with analogies and in images, which was called exposition, did not suit me.

I returned to Darmstadt fully persuaded that I could not attain my ends in Germany.

The dissertations of Berzelius, that is to say, the better translation of his handbook, which had a large circulation at that time, were as springs in the desert.

Mitscherlich, H. Rose, Wöhler, and Magnus had then repaired to Berzelius, in Stockholm; but Paris offered me means of instruction in many other branches of natural science, as, for instance, physics, such as could be found united in no other place. I made up my mind to go to Paris. I was then seventeen and a half years old. My journey to Paris, the way and manner in which I came in contact with Thenard, Humboldt, Dulong, and with Gay-Lussac, and how the boy found favour in the sight of those men, borders on the fabulous, and would be out of place here. Since then it has frequently been my experience that marked talent awakens in all men, I believe I may say without exception, an irrepressible desire to bring about its development. Each helps in his own way, and all together as if they were acting in concert; but talent only compels success if it is united with a firm indomitable will. External hindrances to its development are in most cases very much less than those which lie in men themselves; for just as no one of the forces of nature, however mighty it may be, ever produces an effect by itself alone, but always only in conjnnction with other forces, so a man can only make valuable that which he learns without trouble, or acquires readily, for which, as we say, he has a natural gift, if he learns many other things in addition, which perhaps cost him more trouble to acquire than other people.

Lessing says that talent really is *will and work*, and I am very much inclined to agree with him.

(To be continued).

THE SEPARATION OF TITANIUM, CHROMIUM, ALUMINUM, IRON, BARIUM, AND PHOSPHORIC ACID IN ROCK ANALYSIS.

By THOMAS M. CHATARD.

Having to examine some magnesian silicate rocks, containing, in addition to iron and aluminum, small quantities of titanium, chromium, barium, and phosphoric acid, the methods for the decomposition of such rocks and the separation of their constituents were studied and compared so as to determine the most advisable manner of procedure. After repeated trials the following course, combining a number of well-known methods, has been found to be the most satisfactory.

The silica and bases are determined by the ordinary sodium carbonate fusion method, in which the hydrates of titanium, chromium, iron, and aluminum, together with the phosphoric acid, are precipitated together, and, after weighing, fused with sodium bisulphate, dissolved, the small amount of silica separated, and the solution, after reduction of the ferric oxide, titrated for total iron.

To separate these oxides, and at the same time to determine the barium, 2 grms. of the finely pulverised mineral are put into a platinum crucible or dish, moistened with water, dilute sulphuric acid (1 : 1) and pure strong hydrofluoric acid added in considerable excess, the vessel put on a radiator to evaporate, and stirred from time to time. When the solution is so far evaporated that fumes of sulphuric acid begin to come off, there should still be so much acid present as to form a solution or emulsion, and not a paste, since the paste is liable to bake on the bottom of the vessel and form the difficultly-soluble anhydrous sulphates produced by overheating, especially when magnesia is present in quantity. At this point it is well to add a few drops of nitric acid to oxidise the ferrous oxide, and a little more hydrofluoric acid to ensure the complete expulsion of the silica. The evaporation is then continued until the sulphuric acid fumes strongly and no odour of hydrofluoric acid can be detected when the solution is cooled below the point at which the sulphuric acid fumes.

About 25 c.c. of dilute hydrochloric acid (1 : 5) is now added, the stirring being continued, and the material is then evaporated on the water-bath until most of the hydrochloric acid has been driven off. The material is then washed into a beaker, and any residue adhering to the vessel can be removed by a few drops of hot, strong hydrochloric acid, the vessel being rubbed with a bit of paper if necessary. If the solution be very turbid it can be digested on the water-bath for some time, but ultimately it is diluted with hot water to 250—300 c.c., allowed to stand for several hours, and then filtered.

The residue contains the barium as sulphate, and sometimes the small amounts of chromite or other minerals of the same class. It is washed, ignited, and thoroughly fused with sodium carbonate in a small crucible, the fused mass being then digested with hot water and leached. The well-washed residue is dissolved on the filter with dilute hydrochloric acid, and this solution filtered through the same filter, which, after washing, is burned, the ash fused with a little sodium carbonate, the mass dissolved in dilute hydrochloric acid and added to the leachings, which are now acidified and added to the main solution, after reduction of the chromic acid. The hydrochloric acid solution containing the barium is evaporated to a few drops to get rid of the excess of acid, diluted, the barium precipitated, and the filtrate from the barium sulphate added to the main solution.

This main solution, which should be perfectly clear and contain the iron and chromium as sesquioxides, is now made alkaline by ammonia and the precipitate re-dissolved by dilute hydrochloric acid. A few drops of acetic acid are added, the liquid brought to a boil, ammonia added in very slight excess, the boiling continued for a few minutes, and the precipitate filtered and washed. As the sole reason for this precipitation is to get rid of the magnesia and the accumulation of other salts, the washing need not be thorough, but the filtrate must be tested and the precipitation proved complete.

The precipitate is dissolved in hot dilute hydrochloric acid. The filter, after washing, is burned in a large platinum crucible, into which the solution, concentrated to a small bulk, is put and evaporated on the water-bath till it becomes pasty. Just enough water is now added to dissolve the salts, and then dry sodium carbonate is added in small portions, with continual stirring, till a comparatively dry mass results. This must be carefully done, for if too much soda is added at a time, and each addition is not thoroughly stirred into the mass, the after fusion is apt to be "lumpy" and unsatisfactory.

When a good excess of carbonate has thus been added, the mass is dried and gradually brought to clear fusion, which should be continued for half an hour. If lumps form, which is, however, rarely the case if lime and magnesia are absent and the foregoing directions are followed, they can be broken up by shaking the crucible with a circular motion to detach them from its walls. When the fusion is complete the mass is spread around the walls of the crucible and slightly cooled. A small quantity of sodium nitrate is now added, the whole rapidly fused and carefully boiled for not more than five minutes; it is then again spread over the crucible and rapidly cooled with a blast of air. The mass is boiled with water till completely disintegrated, and then leached: repeated tests have shown that the residue which contains the titanium is, when well washed, free from chromium and phosphoric acid.

The washed residue is dissolved in hot dilute hydrochloric acid, the filter burned, the ash fused with sodium bisulphate, dissolved in water, and added to the solution. The titanium in this solution is separated by the excellent method of Dr. Gooch,* all the details as laid down by him being followed. I have, however, found it convenient, after the destruction of the tartaric acid by potassium permanganate, and the clearing of the solution by sulphurous acid, to add ammonia in slight excess, then at once acetic acid in excess, and boil with addition of sulphurous acid. The precipitate of titanium hydrate, mixed with some alumina, is filtered and washed with water containing sulphurous acid and a little acetic acid. It is thus freed from manganese and brought into a small compass, rendering the after work easier. Before the final precipitation of the titanium, the platinum generally in the solution should be removed by hydrogen sulphide.

The filtrate containing the chromic and phosphoric acids is heated, and ammonium nitrate cautiously added till no further precipitation of alumina occurs. The precipitation of the aluminum phosphate seems to be complete, but some alumina always remains in solution. The precipitate is allowed to settle, the supernatant liquid decanted, and the precipitate washed with a solution of ammonium nitrate until the yellow tinge disappears; it is then dissolved in dilute nitric acid, and the phosphoric acid precipitated by molybdate solution.

The filtrate containing the chromic acid is acidified, boiled, neutralised with ammonia, and the chromium precipitated by freshly prepared ammonic sulphide. The precipitate, after some washing, is dissolved in hot dilute nitric acid, and, after concentration, potassium chlorate is added, the solution boiled, and finally evaporated nearly to dryness to expel the excess of acid. It is then diluted with cold water, and a saturated solution of sodium bicarbonate added in small excess, separating the last traces of alumina. After standing about three hours, the alumina is filtered and washed with moderately dilute solution of the bicarbonate. The filtrate is acidified, and the chromic acid reduced and precipitated by ammonium sulphide in a platinum dish, filtered, washed, re-dissolved to get rid of traces of alkali, re-precipitated, and finally weighed as chromic oxide.

This method, due to Baubigny, for the separation of aluminum from chromium, is very good and convenient if the solution be free from iron and contain but little alumina. Careful tests have shown that if iron be present some of it always remains in solution, while if there be much alumina it is almost impossible to wash out all of the chromate from the bulky precipitate with the cold solution of bicarbonate which must be used. It must also be noted in this connection that a solution of iron and chromium prepared by the Baubigny method was made ammoniacal; and it was proved that, while all of the iron was precipitated, this precipitate, even after the most careful washing with hot water, contained chromium.

Although the number of details in this process may seem very great, experience has shown that none of them can safely be neglected for the purpose of shortening the work; if the whole process be carefully followed out the results are very satisfactory, as shown by the following tests on a typical magnesian rock:—

Percentage	Cr_2O_3.	TiO_2.	BaO.	P_2O_5.
No. 1.	0·270	0·46	0·040	0·375
No. 2.	0·285	0·39	0·060	0·385
No. 3.	0·317	0·46	0·055	—
No. 4.	0·280	—	—	—
Average	0·288	0·44	0·052	0·380

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* *Proc. Am. Acad.*, xii., 435 seq. (*Bull.*, No. 27, U. S. G. S. p. 16 seq.).

The use of sodium nitrate for the fusions is not absolutely necessary, though one is more sure of complete oxidation if it be employed. In the analysis of chrome ores the best results have been obtained by fusing the finely-pulverised ore with sodium carbonate alone, but keeping it in clear fusion for an hour. The fused mass is treated like an ordinary silicate fusion, the silica after weighing being volatilised by hydrofluoric acid, and the residue, usually small, again fused with sodium carbonate, giving a clear solution in hydrochloric acid. — *American Chemical Journal*, vol. xiii., p. 106.

EXPERIMENTS ON THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF THE TARTRATE OF ANTIMONY AND POTASSIUM.*

By J. H. LONG and H. E. SAUER.

In an investigation by one of us on the polarisation of solutions of potasium antimony tartrate it was observed, incidentally, that several interesting features are presented in its precipitation by other salts, notably by carbonates, phosphates, and acetates. We have made this precipitation the subject of a series of tests, the main results of which are here given.

The tartrate used for the investigation was purified by several crystallisations from the purest obtainable commercial product. An amount sufficient for all tests was prepared, powdered, and preserved in uneffloresced condition in several stoppered bottles until used.

Precipitation by Sodium Carbonate.

When an alkaline carbonate is added to a solution of potassium antimony tartrate, a precipitate is not always formed immediately. In fact, by working at a low temperature, and mixing the solutions slowly more than the total amount of carbonate necessary for complete precipitation may be added without producing even an opalescence. The polarisation phenomena of such a mixture show that a chemical change of some kind has, however, taken place. When allowed to stand mixtures prepared in this way gradually become turbid, but without the escape of CO_2, and in time a precipitate settles out. The appearance of the precipitate may be very much delayed by mixing the solutions with the least possible agitation and by keeping the mixture in a cool place.

By boiling, of course, precipitation takes place immediately, and the amount of antimony thrown down stands in relation to the amount of carbonate used.

This precipitate is referred to in the American edition of Fresenius' Qualitative Analysis as antimonious hydroxide, but the composition is not given. A precipitate having the composition $Sb_2H_4O_5$ has been analysed by Schaffner. This corresponds to $Sb_2O_3{\cdot}2H_2O$, or—

$$2(SbOOH)+H_2O,$$

containing 74·08 per cent of antimony. In our investigations we find that the precipitate dried at 100° has practically the composition $Sb_2O_3{\cdot}H_2O$, containing 78·4 per cent of antimony. Slight variations in the amount of water were, however, observed, and these seemed to depend on the temperature and other conditions of precipitation rather than on the temperature of drying. The amount of antimony found was occasionally greater than called for by the formula with one molecule of water.

In the first series of experiments our tests were carried out in this general manner. 5 grms. of the tartrate was dissolved in 60—70 c.c. of water and cooled to 20° C. To this solution a weighed amount of sodium carbonate, dissolved in a small amount of water, was added, and the mixture diluted to exactly 100 c.c. at 20°. It was then allowed to stand 24 hours. Usually, in solutions containing only small amounts of carbonate, precipitation did not soon begin; in some solutions several hours elapsed, but in all cases as much precipitate as formed at all, settled out, leaving the supernatant liquid clear before the end of the 24 hours.

When abundant enough, a portion of the precipitate was taken for analysis, and the amount of antimony left in solution was also determined. This was done by conversion into sulphide, washing and drying with the usual precautions, and weighing in a Gooch filter. The analyses of the precipitates in this series gave, in the mean, 78·8 per cent of antimony. The general results of the experiments are given in this table.

100 *c.c. at* 20°.

No.	Amount of $KSbO\overline{T}$. Grms.	Amount of Na_2CO_3. Grm.	Sb_2S_3 from 50 c.c. Grm.	Per cent of $KSbO\overline{T}$ taken in solution.
1.	5	0·1	1·264	99·93
2.	5	0·3	1·078	85·22
3.	5	0·5	0·890	70·36
4.	5	0·7	0·718	56·76
5.	5	0·9	0·517	40·87
6.	5	1·2	0·369	29·17
7.	5	1·5	0·1763	13·94
8.	5	2·0	0·0493	3·88

It will be seen from a consideration of the numbers of the last column how incomplete is the precipitation even with an excess of the carbonate. For the precipitation of 5 grms. of tartrate, 0·7982 grm. of dry carbonate should be required on the assumption that 1 molecule of carbonate is sufficient for 2 of tartrate. But with these amounts, the table shows about one-half of the antimony is still in solution. We carried out numerous parallel tests, obtaining the same general results in all cases. Exactly the same values could not be expected of course, because the extent of precipitation seems to depend, not only on the amount of carbonate aad the temperature, but on the manner of mixing the solutions, and whether they are much shaken or little. As explained above, we avoided agitation as far as possible in this series of tests.

The precipitation of antimony takes place here without the liberation of CO_2, and possibly according to this equation—

$$2KSbOC_4H_4O_6+2Na_2CO_3+2H_2O= \\ =2KNaC_4H_4O_6+Sb_2O_3{\cdot}H_2O+2HNaCO_3.$$

This equation is suggested by the behaviour of the solutions prepared by adding the carbonate, dissolved in a definite amount of water, from a burette to solutions of the tartrate containing 5 grms. in 100 c.c. The carbonate solutions had a strength of exactly 2 per cent, and when run into the tartrate solution containing a little phenolphthalein, as indicator, nearly 80 c.c. was required to give colour instead of 40, which would be sufficient for this equation—

$$2KSbOC_4H_4O_6+Na_2CO_3+H_2O= \\ =2KNaC_4H_4O_6+Sb_2O_3{\cdot}H_2O+CO_2.$$

From the behaviour on polarisation it is evident that a reaction takes place immediately on mixing the solutions. The amount of rotation is very much decreased, even without precipitation, from which it follows, apparently, that the antimony must exist in soluble form other than tartrate, as suggested by one of us elsewhere (*American Journal of Science*, October, 1890). Something will be said below as to the form in which the antimony may be held here.

A study of the last column in the table above shows that the antimony in solution diminishes very regularly as the amount of added carbonate is increased. The extent of precipitation at this temperature is much below

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* From the *Journal of Analytical and Applied Chemistry*, v., No. 3.

what is called for by theory. The next tests were made with solutions mixed at the boiling heat.

The results are given in the following table:—

100 *c.c. Mixed at* 100° *C.*

No.	Amount of $KSbO\bar{T}$. Grm's	Amount of Na_2CO_3. Grm.	Sb_2S_3 from 50 cc. Grm.	Per cent of $KSbO\bar{T}$ taken in solution.
9.	5	0·1	1·135	89·73
10.	5	0·5	0·608	48·06
11.	5	0·8	0·2608	20·61
12.	5	1·0	0·1618	12·80

Here the precipitation is much more complete than before. Something similar is shown in another series of tests where the solutions were mixed hot, the mixture being diluted to 100 c.c., and kept in boiling water one hour. The supernatant liquid was filtered off, and after cooling was diluted to 100 c.c.

In three cases mixtures were made as before, but diluted to 250 c.c. before heating one hour in the water-bath. The results are given below:—

100 *c.c. Kept at* 100° 1 *Hour.*

No.	Amount of $KSbO\bar{T}$. Grms.	Amount of Na_2CO_3. Grm.	Sb_2S_3 in 50 c.c. Grm.	Per cent of $KSbO\bar{T}$ taken in solution.
13.	5	0·2	1·002	79·23
14.	5	0·5	0·5906	46·70
15.	5	0·8	0·2751	21·74
16.	5	1·1	0·1095	8·69
17.	5	1·5	0·0802	6·33
18.	5	2·0	0·0560	4·42
19.	5	3·5	0·0591	4·66
20.	5	5·0	0·0600	4·74

250 *c.c. Kept at* 100° 1 *Hour.*

21.	5	0·2	0·423	83·60
22.	5	0·8	0·1170	23·12
23.	5	2·0	0·0342	6·76

It will be seen that the results of experiments 11, 15, and 22 are nearly the same, and also that the amount of antimony precipitated reaches a maximum to decrease in the solutions containing the largest amounts of sodium carbonate. The excess of this salt appears, therefore, to have a marked solvent action, increased by heat, as shown on comparing the results of experiments 18, 19, 20, and 23 with experiment 8. Precipitation seems to be least perfect in the dilute solutions as indicated by the last tests. No escape of CO_2 was observed here, while in the stronger solutions made and kept hot the loss was much less than we expected. We found 0·3445 grm. CO_2 in 25 c.c. of the filtrate from No. 19, equivalent to 94·9 per cent of the amount originally present, while in the filtrate of No. 20 we found 97·4 per cent of the total CO_2. In the strong solutions the conditions are naturally favourable for the retention of the gas.

We tried to secure more perfect precipitation in hot solutions than that shown in No. 18, but without much success. From considerations above, theoretically, precipitation should be completed by addition of 1·5964 grms. of the carbonate to the solution of 5 grms. of the tartrate, but a test made with these amounts showed as much antimony in solution as was left in No. 17, when only 1·5 grms. of the carbonate was taken. It is evident from polarisation phenomena that the antimony here present does not exist as tartrate, and the increased amount with increase of added soda suggests the gradual formation of antimonite, even before a maximum in the oxide is reached.

Complete precipitation, if possible at all, must be looked for only at very low temperatures, and a study of the connection between temperature, amount of soda, and precipitation would undoubtedly be an interesting one.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

May 22nd, 1891.

Prof. W. E. Ayrton, F.R.S., President, in the chair.

Mr. F. H. Neville was elected a member of the Society.

Mr. C. J. Woodward exhibited *Dr. Schobben's Form of Lantern Stereoscope.*

This instrument consists of a double lantern, by which the two pictures of a stereoscopic slide are projected on a screen. The two pictures are coloured complementary tints by placing pieces pieces of red and green glass in front of the lenses, and each observer views the overlapping images through spectacles, the eyeglasses of which are also coloured red and green. The stereoscopic effect is very striking.

Mr. Boys stated he had tried to obtain a similar result with the aid of polarised light, by viewing two polarised images through Nicol's prisms. No effect was obtained, owing to elliptic polarisation produced by the screen, but he thought that if a dead gold screen had been used instead of an ordinary one the effect might have been obtained.

Prof. Perry, F.R.S., showed *A New Form of Steam Engine Indicator.*"

A galvanometer mirror is fixed excentrically to a steel disc forming one side of a chamber communicating with the cylinder. The pressure of the steam bulges out the disc and causes the mirror to deflect a ray of light thrown on it in the ordinary way. A rotation at right-angles to the former is imparted by the movement of the piston rod. The ray of light traces out the diagram on a screen suitably placed, and the complete figure is continuously visible owing to the persistence of impressions. This indicator possesses advantages over other forms, in being free from errors due to friction, or oscillations of the springs and the alteration of their elasticity due to temperature changes. The errors of ordinary indicators are considerable at high speeds owing to the ripples introduced into the indicator diagram. If the natural period of the spring is one-twentieth of the time of a revolution, the diagram is fairly free from ripples, but if it is as much as one-tenth no amount of friction in the indicator will prevent ripples forming. In the new indicator, the natural period of the disc can be made very short.

The steel discs are easily removable, and can be proportioned to suit different pressures and speeds.

For experimental and teaching purposes it is advantageous to see at once the alterations in the diagram caused by changes of load, pressure, &c. Several diagrams were exhibited to the meeting.

In reply to Prof. Carus Wilson, Prof. Perry stated that the deflection was proportional to the pressure in the cylinder within the limits any particular disc was intended for.

Mr. Addenbroke thought the instrument an important improvement on its predecessors, and considered it would prove of great service to electrical engineers.

Mr. Swinburne said a peculiar merit of the indicator was that it could be permanently attached to an engine, like an ordinary pressure gauge. He suggested the use of a small telescope instead of the ray method.

The President thought that the instrument could be modified so as to be useful for analysing the shape of the curves representing alternating currents.

"*On Blakesley's Method of Measuring Power in Transformers.*" By Prof. Perry, F.R.S.

This paper refers to the supposed error in Mr. Blakesley's formula, due to the fact that transformers show magnetic leakage. The proofs of the formula hitherto given have been obtained by treating the equations in the manner first adopted by Dr. Hopkinson. On this system the reactions of the primary and secondary currents are represented by the equations—

$$V = R_1C_1 + P\frac{dN}{dt} \qquad 0 = R_2C_2 + S\frac{dN}{dt};$$

where P and N are respectively the turns on the primary and secondary coils, and N is the magnetic flux between the coils. Here it is assumed that there is no magnetic leakage, and the author thinks that on this account the method is inferior to the original method of Maxwell, in which the induced electromotive forces are expressed in terms of coefficients of self and mutual induction. On the assumption that there are no eddy currents, Maxwell's equations are—

$$V = R_1C_1 + L_1\dot{C}_1 + M\dot{C}_2, \qquad 0 = R_2C_2 + M\dot{C}_1 + L_2\dot{C}_2;$$

in which, although L_1, M, and L_2 may not be constant, it may be assumed that they are respectively proportional to P, PS, and S if there is no magnetic leakage, and if the amount of magnetic leakage bears a constant proportion to the whole flux, the three quantities may still be assumed proportional to each other, although M^2 is less than L_1L_2. From these equations we obtain—

$$VC = R_1C_1^2 - R_2\frac{M}{L_2}C_1C_2 + \frac{L_1L_2 - M^2}{L_2}C_1\dot{C}_1.$$

Hopkinson puts down the last term as zero, but owing to the very rapid rate at which C_1 changes, the last term is very important, even though M may be but a small percentage less than $\sqrt{L_1L_2}$. On integrating this equation, the first two terms on the right-hand side yield Blakesley's formula, and the last term vanishes in the integral, because, however great, the magnetic leakage may be—

$$\int C_1\dot{C}_1 dt = 0$$

when taken over a period, because the functions are periodic.

Mr. Blakesley's formula thus appears to hold, whatever the magnetic leakage. The paper contains several tables of calculations showing the effect of magnetic leakage on the value of the terms in the equation.

Mr. Blakesley said he doubted the correctness of the assumption that the value of M was the same in the two equations, and thought that the result arrived at must be incorrect.

Dr. Sumpner did not doubt that if the coefficients could be considered constant, the formula was true whatever the leakage, but he did not consider that the action of transformers justified such an assumption. If the formula were true it would also hold if there were eddy currents, as these would merely produce the effect of additional secondary coils. He had analysed Blakesley's method by using a modification of the Hopkinson equations, and had shown that the power as estimated by Blakesley's formula had to be lessened by the fraction represented by the expression—

$$X = \frac{\int x\dot{A}_p\int A_s\, dt\, dt}{E + \int A_p A_s\, dt},$$

where A_p and A_s are the instantaneous values of the primary and secondary currents, and x is such that $N_p = N_s(1 + x)$, where N_p and N_s are the fluxes of magnetism through the primary and secondary coils at the same instant; E is a negligibly small quantity compared with the rest of the denominator. In obtaining this factor no assumption whatever had been made, and it was easy to see that if A_p and A_s could be assumed sine functions, and x a constant, the value of the factor X became x simply. In only one case did X reduce to zero, and that was when x was a sine function of the same period as A_p and A_s. He believed that in actual transformers x was approximately constant.

Mr. Swinburne pointed out that the split dynamometer was merely a wattmeter, and stated that he had transformers which, owing to magnetic leakage, would indicate an efficiency of over 100 per cent if tested by Blakesley's method. If this method gives an efficiency of 96 per cent, and leakage causes a drop of 2 per cent in E.M.F., the real efficiency is only about 94 per cent. He thought that the assumption that the currents followed a sine law was equivalent to supposing that there was no loss in hysteresis.

The President said that no one would be more glad than himself to find that Mr. Blakesley's method was accurate, but he could not agree with Prof. Perry that Dr. Hopkinson was wrong in abandoning the academical method of Maxwell.

Prof. Perry replied to the various points raised in the discussion.

A paper on "Current and Potential Difference Analogies in the Methods of Measuring Power," by Prof. W. E. Ayrton and Dr. Sumpner, was postponed.

NOTICES OF BOOKS.

The Romance of Science. Coal and What We Get from It. A Romance of Applied Science. Expounded from the Notes of a Lecture delivered in the Theatre of the London Institution, January 20th, 1890. By Raphael Meldola, F.R.S., F.C.S., &c, Professor of Chemistry in the Finsbury Technical College, City, and Guilds of London Institute. Published under the direction of the Committee of General Literature and Education appointed by the Society for Promoting Christian Knowledge. London: Society for Promoting Christian Knowledge, Northumberland Avenue, W.C.

Professor Meldola's undertaking to give an intelligible account of the successive stages in the development of the coal-tar industry without assuming any knowledge of chemical science on the part of the reader is undeniably bold. At the same time we must pronounce it at once meritorious and signally successful. An account both popular and scientific of one of the most interesting and complicated branches of industrial chemistry has been hitherto a desideratum. The subject is, indeed, a somewhat hackneyed one in semi-scientific lectures and after dinner speeches, but its treatment is ordinarily superficial and even inaccurate. Some speeches even congratulate us that we have "no longer to ransack the hemispheres for colouring materials, but find them at our very feet." This is, indeed, a misapprehension, for although coal-tar is produced in Britain in greater quantity than in any other country, yet its elaboration into dye-wares is carried on only to a comparatively small extent in this, the birthland of the industry in question. Hence the technology of coal-tar and its products is to every true Briton a "sore subject." We cannot help asking ourselves whether we shall ever succeed in wiping off this stigma and in assuming our legitimate place with respect to the colour manufacture. We must never forget that though pure science is absolutely cosmopolitan, yet applied science is more and more becoming a phase of war. Thus the invention of artificial alizarin has been a most disastrous event for certain districts in the south of France. Prof. Meldola justly says that the cultivation of the madder plant has had to be abandoned, and that the vast tracts of land devoted to this purpose have become available for other crops. But unfortunately there is no other crop suitable to the locality equally or more remunerative. Had such crops existed they would have been cultivated in preference to madder. But at present no little of the former madder-land is lying waste. Similar is the case with the cochineal, turmeric, safflower, &c., plantations. Should the attempts at the synthetic production of indigo prove commercially successful much British capital and much of the finest land in India will be thrown out of use. Hence the triumphs of organic synthesis have their shadow-side. What is gained by one country or one manufacture is taken from another. Hence we cannot afford to stand by and watch the transformation which industrial chemistry is effecting. In self-defence we must keep our place in the front line. Such establishments as the City and Guilds of London Institute are as essential to our safety as are our cruisers and torpedoes. The only misfortune is that in obedience with the dictates of examinationism we have to expend both more money-power and more brain-power in obtaining equal results than have our rivals. There are few thoughtful men who will not, if they open Professor Meldola's book, read it both with pleasure and profit. The way in which seemingly distinct departments of practical chemistry are shown to be correlated will prove, indeed, a chapter in the "Romance of Science."

Fifteenth Annual Report of Her Majesty's Inspectors of Explosives: Being their Annual Report for the Year 1890. Presented to both Houses of Parliament by Command of Her Majesty. London: Her Majesty's Stationery Office.

THIS report is from several points of view highly satisfactory. The number of deaths from manufacturing accidents is but eight, being slightly below the average (8·1) of the past ten years. These figures are the more important as the number of factories, their output, and the number of hands employed are increasing. The vigilance of the inspectors is fairly maintained, and the local authorities are becoming more alive to their duty in this respect. Steps are being taken to check the illegal practice of storing explosives in miners' houses, which has been too prevalent in Northumberland. It will scarcely be believed that it has been found necessary to warn traders against delivering explosives to young children. At Broxbourne a child of seven was actually sent alone to fetch explosives from a store.

The year has not been marked by any of those occurrences which would formally have been denominated treasonable outrages, but which are now euphemistically called "private warfare." Nor have there been in the United Kingdom any of those sweeping calamities which have occurred in former years. The only cases which called for special inquiry have been the explosion at Roslin Gunpowder Factory, January 22nd, 1890; the nitro-glycerin explosion at Colwill Quarry, Devonshire, February 18th, 1890; the explosion of gunpowder and gun-cotton near Buxton, March 1st, 1890; the explosion of a magazine at Pain's Firework Factory, July 6th, 1890; and the explosion of the glazing-house at Roslin Gunpowder Factory, October 22nd, 1890.

The number of persons employed in these arts appears to be 9820 persons in the regular factories, plus 206 persons *known* (the italics are the inspectors) to be employed in "small" and "toy" firework factories, or, in all, 10,026.

The first Roslin accident, which involved the loss of six lives, was traced to the bringing of matches into the factory.

The second Roslin accident was due to the use by one of the deceased of a steel implement, in deliberate violation of the rules. The inspectors very rightly contend for the establishment of "a rigorous, even a semi-military discipline in factories of explosives."

The new explosive "ballistite" will have to be watched, and its risks guarded against.

Of the fifteen accidents in the manufacture of nitroglycerin preparations, nine are referable to decompositions of the material.

Two more attempts have been made to render the chlorates practically available. Cycene No. 1 was condemned as becoming more sensitive to friction and percussion on keeping. Cycene No. 2 stood the tests more successfully, but it was diluted with a nitrate and a large percentage of combustible matter.

It is pointed out that nitro-compounds like dinitrobenzole are scarcely if at all affected by traces of acid, and under such circumstances show no tendency to spontaneous decomposition.

On the other hand, such nitro-compounds as gun-cotton and nitro-glycerin (which are, more strictly speaking, nitric ethers) are seriously affected by traces of acids.

Not a few serious accidents have been due simply to recklessness in playing with explosives, fuses, and detonators. But equal recklessness is shown by people who let such articles remain in unsafe and improper places.

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. cxii., No. 19, May 11, 1891.

On a New Oxide of Tungsten.—E. Péchard.—The author has previously announced (*Comptes Rendus*, vol. cxii., p. 720), that hydrogen peroxide converts alkaline paratungstates. It was interesting to examine if this reaction gave rise to the salts of a higher acid, *i.e.*, to pertungstates analogous to the permolybdates which the author has described. A solution of sodium paratungstate, mixed with hydrogen peroxide and boiled for a few minutes, quickly takes a yellow colour. No sodium paratungstate is then present. If the yellow liquid thus obtained is evaporated in a dry vacuum it deposits small, white, radiating crystals, which are distinguished from the paratungstate by their great solubility in water. These crystals ($NaO,2HO,W_2O_7$), contain a per-acid, W_2O_7Aq.

Thermic Study of Bibasic Organic Acids having Simple Functions.—G. Massol.—This paper and the accompanying remarks by M. Berthelot do not admit of useful abstraction.

On the Fourth Primary Amylic Alcohol.—L. Tissier.—The author has sought for the trimethylethyl-alcohol, $(CH_3)_3=C-CH_2OH$, and is engaged with the further study of this alcohol and its derivatives.

Vol. cxii., No. 20, May 19, 1891.

At the opening of the Session the Academie was informed of the death of the illustrious physicist Edmond Becquerel, which took place on the 11th inst.

On the Combustion- and Formation-Heat of Organic Chlorides.—MM. Berthelot and Matignon.—This memoir does not admit of useful abstraction.

Quantitative Studies on the Chemical Action of Light. Part 3: *Influence of Dilution.*—Georges Lemoine.—Setting aside the effects of absorption the author concludes that the chemical actions set up by light and by heat follow the same laws.

Calculation of the Temperatures of Fusion and Ebullition of the Normal Paraffins.—G. Hinrichs.—The results are given in the form of tables.

The Influence of the Alkaline Bases upon the Solubility of the Alkaline Salts.—M. Engel.—One mol. of anhydrous potassa or soda, (M_2O), precipitates approximately 1 mol. of the alkaline salt. The action of ammonia upon ammoniacal salts is different from that of potassa and soda upon potassium and sodium salts. The presence of ammonia scarcely diminishes at the outset the solubility of ammonium chloride and afterwards increases it decidedly.

The Determination of Silica in Presence of Iron.—M. Leclerc.—The presence of a large quantity of iron is generally considered capable of interfering with the determination of silica by evaporation to dryness. The decomposition of ferric chloride may be avoided by uniting it with potassium chloride so as to form a double salt, which is well known, and which has been long ago utilised by M. Schlœsing. For instance, in the determination of silicon in cast-iron, 1 grm. of the metal is treated with 20 c.c. of nitric acid and 10 c.c. of hydrochloric acid. After the reaction is over the chief part of the nitric acid is expelled at ebullition with two successive additions of hydrochloric acid—30 c.c. each; 3 grms. of ammonium chloride are added, and the liquid is concentrated to the state of a syrup. The evaporation is completed in the stove, so as to expel the last traces of the nitro compounds in the state of gas. The residue is taken up in hydrochloric acid; there are added 3 grms. pure potassium chloride and water enough to dissolve it, and the evaporation is then continued to dryness. The double iron and potassium salt crystallises at the same time as a certain quantity of double iron and ammonium chloride. These salts are soluble in cold water, but they are first dissolved in hydrochloric acid to remove accessory elements. The silica coagulates upon the residue of carbon; it filters and washes easily. After ignition at a high temperature it remains pulverulent, but dense and easy to weigh. Without the presence of ammonium chloride this silica would contain manganese; it would also be contaminated with potassa if all the nitric acid has not been previously expelled. Chrome is also redissolved completely by taking up the residue at first in concentrated acid. It is well to reduce a little of the chrome to chromous chloride by dissolving a little pure zinc or aluminium chloride in the liquid.

The Constitution and the Formation-Heat of the Bibasic Erythrates.—M. de Forcrand.—Not capable of useful abstraction.

On the Solution-Heat and the Solubility of some Organic Acids in Methylic, Ethylic, and Propylic Alcohols.—M. Timofeiew.—The author concludes that in the cases studied there is a correspondence between the molecular solubility and the heat of solution; the variation of the molecular solubility involving a variation of the heat of solution in the opposite direction.

Action of the Chlorides of the Bibasic Acids upon Sodic Cyanacetic Ether.—P. Th. Muller.—Not suitable for abridgment.

Formation of Nitrates in the Earth.—A. Müntz.—The rarity of nitrates in the soil, which seems to be in contradiction with the abundance of the nitrous ferments, depends on the rapid oxidation of the nitrates by the simultaneous action of carbonic acid and oxygen, which are always present in the atmosphere confined between the particles of the earth.

Archives Neerlandaises des Sciences Exactes et Naturelles.
Vol. xxiv., Parts 4 and 5.

On the Relations between Anhydrous Thorium Sulphate and its Hydrates, and on the Phenomena of Retardation in the Hydration and the Dehydration of this Salt.—H. W. Bakhuis Roozeboom.—The author's researches explain the apparent contradiction between the behaviour of anhydrous thorium sulphate and the general rules which he had given for the relations of the different hydrates of one and the same salt. In thorium sulphate hydration and dehydration are effected so slowly that there may result unstable conditions at great intervals of temperature.

On the Photogenic and Plastic Aliment of Luminous Bacteria.—W. Beyerinck.—This very interesting paper does not admit of useful abridgment.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. v., No. 6.

New Process for Oxidising Chrome Ores and Manufacturing Chromates.—J. Massignon and E. Vatel.—The yearly consumption of these salts in France alone averages two million kilos. yearly, representing a value of two million francs. There do not exist any chrome-works in France. The authors criticise the present method of manufacture, and examine the proposals made for its improvement, none of which they find satisfactory. They proceed as follows:—The ore, very finely ground, is mixed with calcium chloride and lime, or calcium carbonate, in such proportions that all the base derived from the caustic or carbonated lime introduced into the mixture may be a little in excess of what is required to convert all the chromium sesquioxide of the ore into calcium chromate, when this sesquioxide passes into the state of chromic acid. The calcium chloride is employed in the proportion of 1 equivalent to 3 of total lime. This mixture is obtained by working together the ground ore, and a paste is formed either with lime and calcium carbonate or calcium carbonate alone, slacked or stirred up in a strong solution of calcium chloride. If made with ground chalk it does not harden in the air; but if we use together lime and chalk the mixture sets like cement, and may be moulded into blocks or plates which become partially dry in the air. The air-dried blocks are placed in a furnace, where they are moderately heated to complete the desiccation, and then baked at a temperature sufficient to causticise the calcium carbonate. If the blocks are then left exposed to the air, at the common temperature, in about a month the oxidation is complete. The advantages of this process are economy of fuel and of labour; the waste of alkali is suppressed, and a larger proportion of the chromium oxide in the ore is utilised.

The Nitration of certain Aromatic Amines.—E. Noelting and L. Stocklin.—This memoir does not admit of useful abstraction.

Researches on the Colouring-matters derived from Triphenyl Methane.—E. Noelting.—The completion of a bulky memoir (Part 4) discussing the condensation-products of paranitrodimethylamidobenzhydrol with metatoluidin and its derivatives. Part 5 treats of the condensation-products of benzaldehyde and the nitrobenzaldehydes with the dialkylated derivatives of metatoluidin; and Part 6 deals with the condensation-products of orthoformic ether with dimethyl-metatoluidin and dimethyl-metaxylidin.

Vol. v., No. 7.

The Manufacture of Pure Yeast.—H. Elion.—This paper requires the two accompanying figures.

Action of Phosphorus Pentafluoride at a Red Heat upon Platinum Sponge.—Henri Moissan.—Platinum fluoride possesses the property of readily combining with the two gaseous phosphorus fluorides, producing a volatile crystalline compound, which is platinum fluorophosphide. It is also possible to form fluoroplatinum compounds by causing phosphorus pentafluoride to act upon very pure platinum sponge kept at a temperature a little above dark redness.

On the State of Bodies in Solution.—G. Wyrouboff.—The author concludes that salts may exist in solution in the state of hydrates.

On Homofluoresceine.—Edouard Grimaux.—On heating a mixture of orcine, chloroform, and soda, Herr Schwartz obtained a body, $C_{23}H_{18}O_5$, which he names trimethylfluoresceine or homofluoresceine. The author regards this body as identical with the orceine-aureine of Nencki, ($C_{22}H_{18}O_5$).

Formation of Coloured Lakes.—Léo Vignon.—The lakes obtained with stannic acid (safranine) were of a full red colour, whilst those obtained with metastannic acid were white, scarcely tinted with rose-colour.

MEETINGS FOR THE WEEK.

TUESDAY, 9th.—Royal Institution, 3. "The Kemble Period of Stage History," by William Archer.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8.
WEDNESDAY, 10th.—Geological, 8.
THURSDAY, 11th.—Royal, 4.30.
— Mathematical, 8.
— Royal Institution, 3. "The Orchestra considered in connection with the Development of the Overture," by A. C. Mackenzie, Mus. Doc.
FRIDAY, 12th.—Royal Institution, 9. "The Rate of Explosion in Gases," by Prof. Harold Dixon, F.R.S.
— Astronomical, 8.
— Physical, 5. "Alternate Current and Potential Difference Analogies in the Methods of Measuring Power," by Prof. W. E. Ayrton, F.R.S., and Dr. W. E. Sumpner. 'A Clock for Pointing out the Direction of the Earth's Orbital Motion in the Ether," by Prof. O. Lodge, F.R.S. "Some Experiments with Leyden Jars," by Prof. O. Lodge, F.R.S. "The Construction of Non-Inductive Resistances," by Prof. W. E. Ayrton, F.R.S., and Mr. Mather.
SATURDAY, 13th.—Royal Institution, 3. "The Scientific Study of Decorative Colour," by Prof. A. H. Church, M.A., F.R.S.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE, 22, Albemarle Street, London, W.

The NEXT ANNUAL GENERAL MEETING will be held at CARDIFF, commencing on Wednesday, August 19.

President Elect—
WILLIAM HUGGINS, Esq., D.C.L., LL.D., F.R.S., F.R.A.S.

NOTICE to CONTRIBUTORS of MEMOIRS.—Authors are reminded that, under an arrangement dating from 1871, the acceptance of Memoirs, and the days on which they are to be read, are now as far as possible determined by Organising Committees for the several Sections before the beginning of the Meeting. It has therefore become necessary, in order to give an opportunity to the Committees of doing justice to the several Communications, that each Author should prepare an Abstract of his Memoir, of a length suitable for insertion in the published transactions of the Association, and the Council request that he will send it, together with the Original Memoir, by book-post on or before August 1st, addressed thus:—"General Secretaries, British Association, 22, Albemarle Street, London, W. For Section ...." Authors who comply with this request, and whose papers are accepted, will be furnished before the Meeting with printed Copies of their Reports or Abstracts. If it should be inconvenient to the Author that his paper should be read on any particular days, he is requested to send information thereof to the Secretaries in a separate note.

Information about local arrangements may be obtained from the Local Secretaries, Cardiff.

G. GRIFFITH,
Assistant General Secretary.

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THE CHEMICAL NEWS.

Vol. LXIII., No. 1646.

NOTE ON CINNAMIC ACID.

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

A reaction by which cinnamic acid can be readily distinguished from benzoic acid and other compounds which resemble it more or less in appearance and properties, is the production of essence of almonds when dry cinnamic acid is treated with sulphuric acid and bichromate of potash. I find that when a small quantity of acid is kept for a few days in contact with sulphuric acid and bichromate of potash, without heating, the odour of hawthorn flowers thus produced gradually changes into an intense odour of honey. What produces the latter is yet unknown.

On various occasions, for some years past, I have endeavoured to produce cinnamic acid from the leaves of the bay (*Laurus nobilis*), but with only partial success. The long-continued frost of last winter killed the leaves and some of the branches of a fine bay tree in the garden of my villa at Putney, and these dead leaves contain a good deal of essence of cinnamon as compared with the fresh leaf.

It has been lately asserted that cinnamic acid is a more powerful antiseptic than salicylic acid; but this needs confirmation. It is said to destroy the virus (bacillus) of pulmonary tuberculosis.

Still more recently a spray of essence of cinnamon has been found more effective in the treatment of all forms of malarial fever than the usual treatment by quinine and arsenic. At Marguelane, in Turkestan, the spraying is performed several times daily in the hospital wards, and is stated to have proved more efficacious than essence of Eucalyptus used in the same manner.

DETERMINATION OF TURPENTINE IN PAINTS AND VARNISHES.

By H. JOSHUA PHILLIPS, F.I.C., F.C.S.

While much information has been published with regard to the composition and fabrication of various paints and varnishes, there appears to have been very little done in the way of detailing methods of their analysis. The cause of this may be put down to the complicated nature of these substances, together with the many little difficulties that attend the proximate estimation of their constituents. In a recent analysis of a sample of an enamel the writer found the distillation method here described to answer well for the determination of turpentine, leaving the residuum of linseed oil, gum, and pigment in a fit state for further examination.

When paints or varnishes are distilled in air, it is known that oxidation-products are formed giving a low result for turpentine, while the residue of linseed oil, &c., is rendered useless for further examination owing to the formation of the inert linoxyn, &c. In ordinary cases the distillation may be conveniently carried on in a gentle current of coal-gas.

Fig. 1 is a sketch of the apparatus used by the writer. B is a three-way tube fitted into tubulure of the retort, A, through a cork, the end of the tube being about half an inch from the surface of the sample; into the part B a thermometer, E, is fitted, supported by a rubber plug at C. D is connected with a supply of coal-gas. F is a tared receiver, which is to be kept in a basin containing cold water. G is a small tube for allowing the gas to escape. About 150 grms. of the sample are weighed into the retort, and connected to the tared receiver as in sketch. The retort is now suspended in a glass air-bath (a beaker with its bottom cut out is convenient), over wire-gauze on a tripod stand. Before proceeding with the distillation a gentle current of coal-gas is made to pass through the apparatus, and, when all the air has been driven out, the issuing gas is lighted at G, and the gas turned down until the flame is about the size of a pea. A rush of gas must be avoided, or there would be a loss of turps. A small flame is now placed under the retort, and the distillation proceeded with gently. The turpentine should drop into the receiver without affecting the gas issuing at G. The temperature necessary for the complete expulsion of turps may be about 220° C. When all the turpentine has come over detach F, and plug the end of the retort with a cork, leaving the gas still turned on until it be required to examine the residuum, which is thus kept free from oxidation.

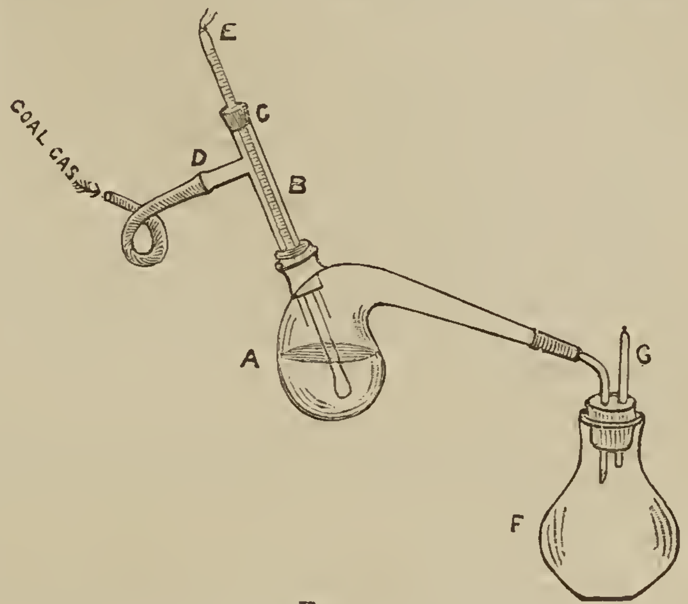

Fig. 1.

G. E. Railway Laboratory, Stratford, London, E.

A NEW METHOD OF MANUFACTURING SODA CRYSTALS, BASED ON PRACTICAL EXPERIENCE.

By THORVALD SCHMIDT.

In the year 1886 a small factory in Copenhagen commenced the manufacture of soda in small crystals, $Na_2CO_3 + 10H_2O$, *i.e.*, in the same combination as ordinary soda crystals. The object was to supply the consumers of perfectly pure soda with the article required, without compelling them to spend time and money on crystallising the soda in order to obtain a pure article from the soda as usually sold.

By degrees, as this pure article became better known, customers began to ask for it at their grocers, and the result was an extension of the factory's working. Then came the Scandinavian Industrial Exhibition of 1888, at which this process was awarded a prize and attracted public attention in a still greater degree. Steady development of the work and increased familiarity with it caused further observations to be made with regard to the cooling process, which were turned to good use. On Messrs. Sthyr and Kjaer, of Copenhagen, buying the inventor's process, and supplying the necessary capital, improvements followed rapidly, till—at the end of 1890—a considerable enlargement of the factory was made, and the most perfect apparatus supplied that many years' practical experience could suggest. The buildings, including alkali apparatus, weighing room, &c., occupy an area of about 160 square yards, and can produce about 20 tons daily, summer and winter, with a minimum result of 70 per cent $Na_2CO_3+10H_2O$ of the contents of the lye. The temperature of the water used for cooling is not, however, unimportant, as the following examples, taken from the actual workings, will show:—

On the 10th December, 1890, the water was turned on at 10.30 a.m., ad its temperature was 3 deg. Celsius (37·4 F.). At 2.30 p.m. the water was turned off, and the apparatus emptied. The crystallising process thus lasted four hours, and the result was 8 tons $Na_2CO_3+10H_2O$.

On the 16th January, 1891, the process lasted from 10.30 a.m. to 2.30 p.m. The temperature of the water was again 3 deg. Celsius (37·4 F.), and the result was exactly the same as on the previous occasion.

On the 22nd May, 1891, the process lasted from 6.30 a.m. till 3 p.m., or 8½ hours, but the temperature of the water at the commencement was 13 deg. Celsius (55·4 F.). The result was again the same. These figures show clearly how very important it is to lower the temperature sufficiently, no less than 4½ hours having been saved by so doing.

In this factory there are three apparatus, and when the lye has been filled into them no attention is required, except that a look-out must be kept when they are ready, as the soda then runs down of its own accord on the drying apparatus.

The lye made in the evening is clear by next morning, and, with sufficiently cold water, can be ready by 10.30 a.m. if the filling is done by 6 a.m. By 12 noon the apparatus is again ready to take in new lye, and can be emptied again at 6 p.m., so that the soda crystals can, under favourable circumstances, be set four times daily—that is, with three apparatus 32 tons are produced every 24 hours; but in unfavourable circumstances, with water of a temperature of 13 degrees Celsius (55·4 F.), only twice, producing 16 tons. The soda is ready for weighing and delivery ten hours after being put on the drying apparatus. The whole process, from the lye to the finished soda, consequently only takes 36 hours at the outside. One man can fill the lye into three apparatus in three hours, or into ten apparatus daily. The only labour required is for the weighing and transporting of the finished soda, otherwise the apparatus does all the work itself with 4½ to 5 horse-power. The soda is filled into bags, partly because these are cheaper and partly because the soda is easier to handle in this form. Compared with the ordinary soda crystals, these crystals are just as durable, and will not become disintegrated in the bags. As the public are gradually getting accustomed to this new form of soda, the sale is increasing more and more, whilst they are discarding the kind formerly used, viz., the large crystals. The soda in small crystals is more convenient for weighing at the shop, it is easier to use in the household, and it is more economical for the consumer.

The new soda has had a marked influence on the exports of soda crystals from England to Denmark, which has fallen off considerably during the last few years.

If soda prepared according to Leblanc's method is used, the mother-liquid, alkali, must be treated in the ordinary way; whilst if soda by the ammonia process is used, the work can be done without interruption, the mother-liquid being used afresh. This method has been introduced into Germany, and several manufactories based on it are in course of construction there. Although doubtless it is a simple matter to dissolve calcined soda, whether done in Leblanc's or the ammonia process, every attempt at imitation has hitherto failed on account of the result being too insignificant in proportion to the labour involved,—besides which, if the apparatus are not handled with extreme care and accuracy, they fail to work properly. In the factory belonging to Messrs. Sthyr and Kjaer the apparatus have been in constant use since last autumn, and not the slightest stoppage or accident has taken place. For this reason several German factories have had their apparatus made at Copenhagen of the best English steel, as they can thus be made under the inventor's personal supervision. An apparatus costs from £60 to £70, and always keeps clean.

Messrs. F. and A. Delcomyn have kindly undertaken to give all further information that may be required, and have also promised to carry out negotiations with intending buyers.

Copenhagen, May 23, 1891.

JUSTUS VON LIEBIG:

An Autobiographical Sketch.*

(Concluded from p. 267).

The lectures of Gay-Lussac, Thenard, Dulong, &c., in the Sorbonne, had for me an indescribable charm; the introduction of astronomical or mathematical method into chemistry, which changes every problem when possible into an equation, and assumes in every uniform sequence of two phenomena a quite certain connection of cause and effect, which, after it has been searched for and discovered, is called "explanation" or "theory," had led the French chemists and physicists to their great discoveries. This kind of "theory" or "explanation" was as good as unknown in Germany, for by these expressions was understood not something "experienced," but always something which man must add on and which he fabricates.

French exposition has, through the genius of the language, a logical clearness in the treatment of scientific subjects very difficult of attainment in other languages, whereby Thenard and Gay-Lussac acquired a mastery in experimental demonstration. The lecture consisted of a judiciously arranged succession of phenomena, that is to say, of experiments whose connection was completed by oral explanations. The experiments were a real delight to me, for they spoke to me in a language I understood, and they united with the lecture in giving definite connection to the mass of shapeless facts which lay mixed up in my head without order or arrangement. The Antiphlogistic or French chemistry had, it is true, brought the history of chemistry before Lavoisier to the guillotine; but one observed that the knife only fell on the shadow, and I was much more familiar with the phlogistic writings of Cavendish, Watt, Priestley, Kirwan, Black, Scheele, and Bergmann, than with the antiphlogistic; and what was represented in the Paris lectures as new and original facts appeared to me to be in the closest relation to previous facts, so much so, indeed, that when the latter were imagined away the others could not be.

I recognised, or more correctly perhaps the consciousness dawned upon me, that a connection in accordance with fixed laws exists not only between two or three, but between all chemical phenomena in the mineral, vegetable, and animal kingdoms; that no one stands alone, but each being always linked with another, and this again with another, and so on, all are connected with each other, and that the genesis and disappearance of things is an undulatory motion in an orbit.

What impressed me most in the French lectures was their intrinsic truth, and the careful avoidance of all pretence in the explanations; it was the most complete contrast to the German lectures, in which the whole scientific teaching had lost its solid construction through the preponderance of the deductive method.

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* Read at a joint Meeting of Societies in the Chemical Laboratories, University College, Liverpool, on Wednesday evening, March 18, 1891, by Prof. J. Campbell Brown, D.Sc.

An accidental occurrence drew A. von Humboldt's attention to me in Paris, and the interest which he took in me induced Gay-Lussac to complete in conjunction with me a piece of work which I had begun.

In this manner I had the good fortune to enjoy the closest intercourse with the great natural philosopher; he worked with me as he had formerly worked with Thenard; and I can well say that the foundation of all my later work and of my whole course was laid in his laboratory in the arsenal.

I returned to Germany, where through the school of Berzelius, H. Rose, Mitscherlich, Magnus, and Wöhler, a great revolution in inorganic chemistry had already commenced. Through the support of von Humboldt's warm recommendation, an extraordinary professorship of chemistry at Giessen was conferred upon me in my 21st year.

My career in Giessen commenced in May, 1824. I always recall with pleasure the twenty-eight years which I spent there; it was as if Providence had led me to the little university. At a larger university or in a larger place my energies would have been divided and dissipated, and it would have been much more difficult, and perhaps impossible, to reach the goal at which I aimed; but at Giessen everything was concentrated in work, and in this I took passionate pleasure.

The need for an institution in which the students could be instructed in the art of chemistry, by which I mean familiarity with chemical analytical operations, and skill in the use of apparatus, was then being felt; and hence it happened that on the opening of my laboratory for teaching analytical chemistry and the methods of chemical research, students by degrees streamed to it from all sides. As the numbers increased I had the greatest difficulty with the practical teaching itself. In order to teach a large number at one time it was necessary to have a systematic plan, or step by step method, which had first to be thought out and put to the proof.

The manuals which several of my pupils have published later (Fresenius and Will) contain essentially, with little deviation, the course which was followed at Giessen; it is now familiar in almost every laboratory.

The production of chemical preparations was an object to which I paid very particular attention; it is very much more important than is usually believ ed, and one can more frequently find men who can make very good analyses than such as are in a position to produce a pure preparation in the most judicious way. The formation of a preparation is an art, and at the same time a qualitative analysis, and there is no other way of making one's self acquainted with the various chemical properties of a body than by first producing it out of the raw material, and then converting it into its numerous compounds and so becoming acquainted with them.

By ordinary analysis one does not learn by experience what an important means of separation crystallisation is in skilful hands; and just as little the value of an acquaintance with the peculiarities of different solvents. Consider only an extract of a plant or of flesh which contains half a dozen crystalline bodies in very small quantities imbedded in extraneous matter, which almost entirely masks the properties of the others; and yet, in this magma, we can recognise by means of chemical reactions the peculiarities of every single body in the mixed mass, and learn to distinguish what is a product of decomposition and what is not, in order to be able to separate them afterwards by means which will exert no decomposing influence. An example of the great difficulty of finding the right way in such researches is afforded by the analysis of bile by Berzelius. Of all the numerous substances which he has described as its constituents no one is, properly speaking, contained in the natural bile.

An extremely short time had been sufficient for the famous pupils of the Swedish master to give a wonderful degree of perfection to mineral analysis which depends on an accurate knowledge of the properties of inorganic bodies; their compounds and their behaviour to each other were studied in all directions by the Swedish school with a keenness quite unusual previously and even now unsurpassed. Physical chemistry, which investigates the uniform relations between physical properties and chemical composition, had already gained a firm foundation by the discoveries of Gay-Lussac and von Humboldt on the combining proportions of bodies in the gaseous state, and those of Mitscherlich on the relations between crystalline form and chemical composition; and in chemical proportions the structure appeared to have received its coping-stones and to stand forth completed. All that foreign countries had acquired in bye-gone times in the way of discoveries now yielded rich fruit also in Germany.

Organic chemistry—or what is now called organic chemistry—had then no existence. It is true that Thenard and Gay-Lussac, Berzelius, Prout, and Döbereiner, had already laid the foundations of organic analysis, but even the great investigations of Chevreul upon the fatty bodies excited but little attention for many years. Inorganic chemistry demanded too much attention, and, in fact, monopolised the best energies.

The bent which I acquired in Paris was in a quite different direction. Through the work which Gay-Lussac had done with me upon fulminating silver I was familiar with organic analysis, and I very soon saw that all progress in organic chemistry depended essentially upon its simplification; for in this branch of chemistry one has to do not with different elements which can be recognised by their peculiar properties, but always with the same elements whose relative proportions and arrangement determine the properties of organic compounds.

In organic chemistry an analysis is necessary to do that for which a reaction suffices in inorganic chemistry.

The first years of my career in Giessen I devoted almost exclusively to the improvement of the methods of organic analysis, and the immediate result was that there began at this little university an activity which had never before been seen.

For the solution of innumerable questions connected with plants and animals, on their constituents, and on the reactions accompanying their transformation in the organism, a kindly fate brought together the most talented young men from all the countries of Europe, and anyone can imagine what an abundance of facts and experiences I gained from so many thousands of experiments and analyses, which were carried out every year, and for so many years, by twenty and more indefatigable and skilled young chemists.

Actual teaching in the laboratory, of which practised assistants took charge, was only for the beginners; the progress of my special students depended on themselves. I gave the task and supervised the carrying out of it; as the radii of a circle have all their common centre. There was no actual instruction; I received from each individual every morning a report upon what he had done on the previous day, as well as his views on what he was engaged upon. I approved or made my criticisms. Every one was obliged to follow his own course. In the association and constant intercourse with each other, and by each participating in the work of all, everyone learned from the others. Twice a week, in winter, I gave a sort of review of the most important questions of the day; it was mainly a report on my own and their work combined with the researches of other chemists.

We worked from break of day till nightfall. Dissipations and amusements were not to be had at Giessen. The only complaint, which was continually repeated, was that of the attendant (Aubel), who could not get the workers out of the laboratory in the evening, when he wanted to clean it.

The remembrance of this sojourn at Giessen awakened in most of my pupils, as I have frequently heard, an agreeable sense of satisfaction for well-spent time.

I had the great good fortune, from the commencement of my career at Giessen, to gain a friend of similar tastes and similar aims, with whom, after so many years, I am still knit in the bonds of warmest affection.

While in me the predominating inclination was to seek out the points of resemblance in the behaviour of bodies or their compounds, he possessed an unparalleled faculty of perceiving their differences. A keenness of observation was combined in him with an artistic dexterity, and an ngeniousness in discovering new means and methods of esearch or analysis such as few men possess.

The achievement of our joint work upon uric acid and oil of bitter almonds has frequently been praised; it was his work. I cannot sufficiently highly estimate the advantage which the association with Wöhler brought to me in the attainment of my own as well as our mutual aims, for by that association were united the peculiarities of two schools — the good that was in each became effective by co-operation. Without envy and without jealousy, hand in hand, we pursued our way; when the one needed help, the other was ready. Some idea of this relationship will be obtained if I mention that many of our smaller pieces of work which bear our joint names were done by one alone; they were charming little gifts which one presented to the other.

After sixteen years of the most laborious activity I collected the results gained, so far as they related to plants and animals, in my "Chemistry Applied to Agriculture and Physiology," two years later in my "Animal Chemistry," and the researches made in other directions in my "Chemical Letters." The last-mentioned was generally received as a popular work, which, to those who study it more closely, it really is not, or was not at the time when it appeared.

Mistakes were made, not in the facts, but in the deductions about organic reactions; we were the first pioneers in unknown regions, and the difficulties in the way of keeping on the right path were sometimes insuperable.

Now, when the paths of research are beaten roads, it is a much easier matter; but all the wonderful discoveries which recent times have brought forth were then our own dreams, whose realisation we surely and without doubt anticipated.

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Here the manuscript ends, and it is to be hoped that more of it will yet be found.

Liebig's reference to Wöhler is very touching, and shows a side of his character which all his pupils knew well; they tell many genial stories illustrating his unselfishness and kindness of heart. One could have wished that he had not considered the stories "bordering on the fabulous," or how he "found favour in the sight of Humboldt, Gay-Lussac, and Thenard, out of place here" They would have been far from out of place. Mr. Muspratt supplies one of these stories as he heard it from Liebig's own lips, in the Münich Laboratory, as follows:—

Liebig frequently spoke, in most grateful terms, of the kind manner in which he—a youth barely eighteen—was received by Gay-Lussac, Thenard, and other eminent chemists, in Paris.

In the summer of 1823 he gave an account of his analysis of fulminating silver before the Academy. Having finished his paper, as he was packing up his preparations, a gentleman came up to him and questioned him as to his studies and future plans, and, after a most exacting examination, ended by asking him to dinner on the following Sunday. Liebig accepted the invitation, but, through nervousness and confusion, forgot to ask the name and address of his interviewer. Sunday came, and poor Liebig was in despair at not being able to keep his engagement.

The next day a friend came to him, and said—"What on earth did you mean by not coming to dine with von Humboldt yesterday, who had invited Gay-Lussac and other chemists to meet you?" "I was thunderstruck," said Liebig, "and rushed off, as fast as I could run, to von Humboldt's lodgings, and made the best excuses I could." The great traveller, satisfied with the explanation, told him it was unfortunate, as he had several members of the Academy at his house to meet him, but thought he could make it all right if he would come to dinner next Sunday. He went, and there made the acquaintance of Gay-Lussac, who was so struck with the genius and enthusiasm of the youth that he took him into his private laboratory, and continued, in conjunction with him, the investigation of the fulminating compounds.

REACTIONS OF DIMETHYLMETA-PHENETIDINE.

By EDOUARD GRIMAUX.

If carbonyl chloride is allowed to react upon this base in presence of aluminium chloride there is formed a fine blue colouring-matter, whilst under the same conditions dimethylaniline yields a crystalline violet. If purified by ordinary methods this compound has a great tinctorial power; it dyes a very pure and fine blue on silk, wool, and on cotton mordanted with tannin.

If the blue is heated with sulphuric acid to 100° it is destroyed and converted into a red fluorescent matter of feeble lustre, resembling the colour obtained by heating dimethylmetamidophenol with dehydrating agents.

This blue must be regarded as a hexamethylated and trioxethylated derivative of rosaniline.

The meta-base yields a nitroso-derivative, which in most of its reactions behaves like nitroso-dimethylaniline. It yields oxazines with gallic acid, gallic ether, pyrogallol, resorcine, &c., eurrhodines with metadiamines, and an indophenol with α-naphthol.

Among the numerous colours thus obtained that furnished by resorcine is most remarkable for its beauty. If we heat a solution of resorcine and of the hydrochlorate of the meta-nitroso base, there is formed besides a non-fluorescent blue a colouring-matter which dyes silk of a fine violet, having a magnificent red fluorescence. Orcine and lutorcine behave like resorcine, but these fluorescent violets are not stable if exposed to light.

The nitroso-derivative of the meta-base differs from nitroso-dimethylaniline, as it does not yield with β-naphthol a blue analogous to Meldola's blue.

The meta-base has been submitted to various reagents with the following results:—

1. With phthalic anhydride alone no reaction; in presence of zinc chloride or sulphuric acid, formation of a red fluorescent colour, which appears identical with rhodamine.
2. With arsenic acid at 175°, a rose-colour, which does not appear to be an oxidation product, but results from the formation and condensation of dimethylamidophenol.
3. With phthalyl chlorides production of a green matter resembling the phthalic green derivative of dimethylaniline.
4. If heated with the chloride of dimethylmeta-amidobenzoic acid it gives a fine blue colouring-matter.
5. It turns rose-colour if heated with chloroform and soda.
6. If gently heated with phenylsulphonic chloride there is a violent reaction, with the transient formation of a blue matter quickly passing to a yellow.
7. With benzylic aldehyd and zinc chloride, with phenylchloroform, colouring-matters are also formed.

The ortho-base behaves quite differently from the meta base. It gives no colouring-matter with carbon oxychloride, phthalic anhydride, chloroform and soda, benzylic aldehyd or phenylchloroform.

The ortho-base with arsenic acid at 175°, or with phenylsulphurous chloride, gives a fine blue colour, which is also produced if the hydrochlorate is heated alone to 175—180°.

Neither the meta- nor the ortho-base gives colours with copper chloride, which so readily converts dimethylaniline into Paris violet.

The author, in concert with M. Lefevre, has begun the study of the nitro-derivatives of the ortho- and meta-bases.—*Bulletin de la Soc. Chimique de Paris* (Series 3, vol. v., p. 647).

HYDRATED LEAD OXIDE.

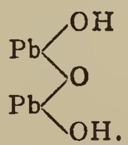
By C. LUEDEKING.

There seem to be at least two hydrated oxides of lead—$3PbO.H_2O$ obtained by Payen (*Ann. Chim. Phys.* [4], viii., 302), and $2PbO.H_2O$ prepared by Schaffner (*Ann. Chem.*, Liebig, li., 175). Payen obtained his hydrate in the form of strongly-refracting octahedra by allowing an ammoniacal solution of lead acetate to crystallise in a closed vessel. It is very questionable whether the crystals so obtained are entirely free from basic salt or ammonia. Calvert (*Compt. Rend.*, xxii., 480) observed that hydrated oxide of lead can combine with ammonia, and Winkelblech (*Ann. Chem.*, Liebig, xxi., 29) maintains that the hydrated oxide so obtained always contains small amounts of basic salt which cannot be removed by excess of alkali.

Schaffner claims to be able to obtain his hydrated oxide entirely free from basic salt by precipitating a solution of lead acetate with a slight excess of potassium hydrate.

It is possible to obtain the hydrated oxide of lead of Schaffner in excellent crystals in another way, which may form the basis for obtaining from other metals also hydrated oxides soluble in potassium hydrate. When litharge is boiled with a strong solution of potassium hydrate for some time, a considerable amount of it passes into solution. The potassium hydrate solution, when strong, deposits on cooling a large quantity of crystals of anhydrous protoxide of lead, as had been observed by several authors previously. The solution, after it has become perfectly cold, however, still contains a large amount of lead oxide. When now it is exposed in a small beaker to the air, carbon dioxide is slowly absorbed and potassium carbonate formed. Thus the lead is gradually and very slowly deprived of its solvent, and all conditions for crystallisation pertain. After several weeks the bottom of the vessel will be found covered with magnificently developed crystals, perfectly colourless and transparent, and having a high refractive power for light and brilliant lustre. These crystals, on examination, are found to be the hydrate, $2PbO.H_2O$, in a state of absolute purity. They belong to the tetragonal system, are simple in development and short and thick in habit, showing the prism $\infty P \infty$, and the pyramid P at either end. The angle between the opposite edges, over the solid angle of the pyramid, is 101°. The axial relations are 1 : 1 : 0·824. Their reaction is alkaline, and on exposure to the air they soon become opaque, absorbing carbon dioxide and forming lead carbonate. In this metamorphosis, however, they maintain sharply their original form. On heating they lose their water and become yellow litharge, but nevertheless maintain the original crystalline form.

The structure of this hydrate is probably the following—



We may consider that it is rather to be expected that the weaker the base the fewer OH radicals will it contain. Take, for example, calcium hydrate—a much stronger base—and we have all the affinities of calcium saturated with hydroxyl groups.

The less the basic powers of an element, when it can form hydrates, the greater the likelihood of its forming such hydrates as that we have examined, and even other such as $3PbO.H_2O$, which has, in fact, been actually obtained. Thus it will be easy to form from a strong base a hydrated oxide containing the normal number of hydroxyl groups, while for a weak base this will be difficult, and *vice versâ*. This will explain in a chemical way what appears at first anomalous and only mechanical admixture, viz., the small amount of water contained in many oxides of the heavier metals.—*American Chemical Journal*, vol. xiii., p. 120.

Chemical Laboratory, Washington University.

THE DISSOCIATION OF MAGNESIUM OXIDE BY MEANS OF METALLIC MAGNESIUM.

By H. N. MORSE and J. WHITE, Jun.

In former papers (*Amer. Chem. Journ.*, xi., 258 and 348) we have described the dissociation which takes place when the oxides or sulphides of zinc and cadmium are heated in a vacuum with their respective metals. Since then we have found that the oxide of magnesium undergoes an equally unmistakable dissociation when it is heated in the same way with metallic magnesium.

The apparatus which we employed was essentially the same as that used in the dissociation of the oxides and sulphides of zinc and cadmium, except that, owing to the energetic action of the vapours of magnesium on silicates, it was found advantageous to enclose the mixture of oxide and metal in a tube of sheet-iron. The iron tube was made by forming a thoroughly-cleansed strip of the metal, from 40 to 45 centimetres long, around an iron rod of proper thickness, and closing one end with the hammer. It was then prepared for use by inclosing it in a glass tube, exhausting with the Sprengel pump, and heating to redness until it ceased to give off volatile matter.

Owing to the presence of considerable quantities of occluded hydrogen in commercial magnesium, as observed by Dumas (*Compt. Rend.*, xc., 1027), the metal was distilled in a vacuum in the manner described by Burton and Vorce (*Amer. Chem. Journ.*. xii., 219). The oxide of magnesium, also, was heated to redness in a vacuum until it ceased to give off carbon dioxide. The metal and then the oxide were dropped into the iron tube. This was then placed in a larger tube of hard glass which had been closed at one end. The length of the glass tube was usually about 80 centimetres, or twice that of the iron tube. The outer tube was then drawn out at the open end, attached to the Sprengel pump, exhausted, and finally heated in a combustion furnace along that portion which was occupied by the iron tube, The quantities of magnesium employed in our experiments varied from 4·5 to 10 grms.; those of the oxide, from 1·5 to 3 grms.

In every case the phenomena which presented themselves when the tube had reached a bright red-heat were similar to those observed when the oxides of zinc and cadmium were heated with their metals. The oxide formed in the cool portion of the glass tube, and fell upon the bottom in a long line which extended even into the connecting tube of the pump itself. This transportation of the oxide continued until the greater portion of the metal had distilled to and condensed about the open end of the iron tube. At the same time gas was evolved and collected in the eudiometer placed over the outlet of the pump. This gas proved to be a mixture of carbon dioxide and free oxygen. The proportion of the oxide thus transported to the cooler portion of the glass tube was quite variable, and appeared to depend on the thoroughness with which the oxide and metal were mingled in the iron tube. It was always found to be greater when the mixture of oxide and metal which remained in the inner tube after one experiment was re-heated with an additional quantity of magnesium. It was not possible to determine the exact amount of oxide which was carried out of the iron tube, owing to the presence in it of some distilled metal; but on several occasions that portion of the oxide which was nearest the pump, and appeared to be free from metal, was collected and weighed. The quantity varied from 0·1 grm. to 1·5 grm. In some cases only a small fraction of the oxide remained in the iron tube.

As in the case of the oxides of zinc and cadmium, the evolution of oxygen was most rapid during early stages of the experiment, before the tube had become filled with the vapours of the metal. The carbon dioxide, which must have come from the carbon contained in the iron, was removed by caustic potash, and the oxygen determined by means of an alkaline solution of pyrogallic acid. The quantity of oxygen found varied from 1·5 to 3 c.c.—*American Chemical Journal*, vol. xiii., p. 128.

Chemical Laboratory, Johns Hopkins University.

DETERMINATION OF AVAILABLE OXYGEN IN PEROXIDES BY MEANS OF GASEOUS HYDROCHLORIC ACID.

By L. L. de KONINCK and AD. LECRENIER.

Among the procedures employed for the determination of the available oxygen of the manganese oxides, or for the determination of the peroxide in ores, the method of Bunsen is very often preferred. The sample is treated with strong hydrochloric acid, and the chlorine liberated is received in a solution of potassium iodide. The iodine set free is then determined by means of a standard solution of sodium thiosulphate.

The hydrochloric acid is necessarily employed in considerable excess, and the necessity of raising the liquid to ebullition for a few minutes so as to expel all the chlorine liberated, causes a notable quantity of the acid to pass into the solution of potassium iodide, which falsifies the results if the titration with thiosulphate is not effected rapidly. In fact, the hydriodic acid formed is decomposed in contact with the oxygen of the atmosphere.

The authors have obtained results very satisfactory in every respect by using hydrochloric gas in place of the liquid acid.

The oxide in question is placed at the bottom of a flask with a small quantity of water (two or three parts to one of oxide), and when the different parts of the apparatus are connected and found air-tight, a very slow current of carbonic anhydride is introduced, followed by hydrochloric acid gas. The latter gas is absorbed by the water, and the solution of the sample and the liberation of chlorine begin immediately, favoured by the rise of temperature due to the absorption of the gas.

The reaction is accelerated by heating the bottom of the flask by means of a very small flame. In a few moments the solution is complete, and its greenish colour, due to manganese chloride, disappears, giving place, in case of natural oxides of manganese, to the yellow colouration of ferric chloride, or to a decided green, if the ore contains cobalt at the same time.

At this moment the entrance of the hydrochloric acid gas is stopped, whilst the rapidity of the current of carbonic anhydride is increased, and the solution in the flask is still heated.

When the hydrochloric acid has thus been entirely expelled, the apparatus is dismounted and the iodine set free is titrated.

It is necessary to use in the analysis a quantity of water such that the chlorides formed may not be deposited until after the solution has become cold, and at the same time too large an excess must be avoided. If the water is deficient a part of the oxide may become coated with a protective layer of chloride, or which renders the ulterior attack of the oxide very difficult.

As regards the quantity of the acid it is found that when operating upon 0·3 to 0·4 grm. of oxide the quantity is 1·27 grm., corresponding to 5 c.c. of acid at 25 per cent. Of this quantity of acid about the half is utilised for the reaction, whilst the other half constitutes the excess which is absorbed by the solution.

The process is perfectly applicable to the determination of the available oxygen in samples of red lead. No modification is required in the process as just described. —*Revue Universelle des Mines*, Jan., 1891.

SEPARATION AND DETERMINATION OF NICKEL AND COBALT.

By CONSTANTIN KRAUSS.

(Continued from p. 264).

A further modification of the Liebig process consists in mixing the solution of both metallic salts with an excess of potassium cyanide, and boiling until no free hydrocyanic acid can be recognised. The nickel is then precipitated with bromine water, and the cobalt is determined in the filtrate.

Fr. Gauhe has carefully studied this modification, and has arrived at very satisfactory results.

According to a further modification of the Liebig process, H. Roser adds to a mixture of nickel and cobalt oxide first hydrocyanic acid and then ammonia, and heats to ebullition. He then boils with ammonium sulphide and sulphur until the deep black liquid becomes perfectly clear. All the nickel is thus precipitated as nickel sulphide, whilst all the cobalt remains in solution as ammonium cobalticyanide.

This process also gives satisfactory results, but it has no advantage as compared with those just described, as the precipitate of nickel sulphide must be re-dissolved and again precipitated.

13. C. Rœssler adds to the solution of a cobaltous salt a measured volume of a normal silver solution, and heats on the water-bath, adding sodium carbonate as long as a precipitate of Ag_4O,Co_2O_3 is produced. It is then digested with a little ammonia in order to dissolve any silver carbonate which has been carried down. The liquid is then filtered, and after acidulation with nitric acid the excess of silver is determined volumetrically by Volhard's process.

Krauss always obtained by this method deficient values. More favourable results appeared if caustic potassa, free from haloids, is used instead of sodium carbonate. In this case the method is applicable in presence of moderate quantities of nickel.

14. Clemens Winkler mixes a perfectly neutral solution of cobaltous chloride with elutriated mercuric oxide, and drops in the cold solution of permanganate, shaking the vessel continuously, until the liquid has a faint permanent rose colour. The cobalt separates out as hydroxide, $Co_2(OH)_6$.

He uses a decinormal solution of cobalt (5·86 grms. cobalt per litre) and a solution of permanganate containing 5·27 grms. permanganate per litre.

According to the author's experiments, this method yields good results, whether the proportion of cobalt is very large or very small, especially if there is added from time to time a little mercuric oxide and a few drops of ferric chloride free from the ferrous salt.

The results are less favourable in presence of nickel. The author verifies Winkler's statement that for the proportion Co : Ni = 1 : 4 the results are just admissible in practice. In presence of nickel, the quantity of cobalt to be determined must not be too small—not less than 0·03 grm. If there is very little cobalt present, it is advisable previous to titration to add a measured volume of a normal cobalt solution, and to take this addition into account in calculating the results. The use of large quantities of cobalt is not advantageous; the most favourable results were obtained when from 0·075 to 0·1 grm. cobalt has to be determined, and a solution of permanganate is taken only half as strong as that proposed by Winkler.

The objection raised against this method in various quarters, *i.e.*, that the mercuric oxide interferes with a recognition of the end of the reaction, is considered by Krauss as quite unfounded. The mercuric oxide, on the contrary, facilitates the reaction by carrying down the suspended cobalt oxychloride, and thus clearing the solution.

Gauhe's proposal, to add, when standardising the normal solution of cobalt, so much nickelous chloride that it may have the same shade of colour as the solution under examination, is regarded by Krauss as useless.

Good results, suitable for practical purposes, may be obtained in presence of a considerable proportion of nickel if during titration there are added from time to time a few c.c. of ferric chloride (free from ferrous chloride), shaking well and titrating, not up to a permanent red colouration, but merely to a rapid and complete clarification.

B.—*Methods Depending on the Different Behaviour of the Sulphides of Both Elements.*

1. H. Fleck (*Journ. Prakt. Chemie*) allows the solution of both metals, mixed with ammonium chloride and supersaturated with ammonium, to stand for twelve hours exposed to the air in a shallow capsule. He adds ammonium sulphide in excess, and evaporates on the water-bath until turmeric paper is no longer turned brown. When cold, he adds, at the lowest available temperature, a few c.c. of potassium cyanide, and allows the mixture to stand for some minutes. The precipitate formed is filtered and washed with alcohol at 80 per cent. By dissolving the ignited precipitate and re-precipitation with ammonia and ammonium sulphide, pure cobalt sulphide is obtained.

The nickel is precipitated from the filtrate as nickel cyanide by the addition of hydrochloric acid, and determined in the known manner.

This method, according to Krauss, gave no favourable results, as an appreciable quantity of cobalt sulphide passes into solution.

A. Guyard (*Bulletin de la Soc. Chimique*) recommends this method, but has not improved it in any manner.

2. C. Kunzel (*Journ. Prakt. Chemie*) proposes to titrate both metals with potassium sulphide in an ammoniacal solution.

Krauss standardised a solution of potassium sulphide (using sodium nitro-prusside as an indicator) by means of a known solution, both of nickel and cobalt. The results were very fluctuating, which was the more striking as more potassium sulphide was always used for cobalt than for an equal quantity of nickel. This fact renders it probable that the sulphides have no constant composition, a conjecture which the author supports by several experiments.

Definite quantities of cobalt and nickel were precipitated with potassium sulphide, avoiding any excess; the precipitates were filtered off, and washed with cold water. If the sulphides thus obtained were decomposed with ammoniacal solution of copper, or solution of silver, and the combined sulphur was determined, it was found that cobalt combines with a rather larger proportion of sulphur than does nickel. This unequal composition of the sulphides, joined to the fact that they are not absolutely insoluble in ammonia, renders the method of Künzel nearly worthless.

(To be continued).

Centenary of the Birth of Michael Faraday.—H.R.H. The Prince of Wales has fixed 4 o'clock on Wednesday, the 17th June, for the delivery by Lord Rayleigh of the first of the two Lectures at the Royal Institution in conection with this Centenary; and Friday evening, the 26th June, at 9 o'clock, has been appointed for the second of these Lectures, which will be given by Professor Dewar.

EXPERIMENTS ON THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF THE TARTRATE OF ANTIMONY AND POTASSIUM.*

By J. H. LONG and H. E. SAUER.

(Concluded from p. 270).

Precipitation by Sodium Acetate.

Some instructive results were obtained in a series of tests with sodium acetate. With cold, dilute solutions, the precipitation is very slow, but on application of heat it becomes quite marked. In the next table are given the results found by adding to a solution of the tartrate (5 grms.) solutions of different amounts of the acetate. The mixtures were carefully made and diluted to 100 c.c. at 20°, and were then allowed to stand 48 hours. In the first experiment (No. 24) only an opalescence appeared in that time, but in the other cases the mixture soon became cloudy, to precipitate and settle long before the end of the 48 hours. The clear supernatant liquids were then filtered off, the filtrate and washings in each case being diluted to 250 c.c. The antimony was determined in 50 c.c. and calculated as tartrate, the results being shown in the last column.

100 *c.c. at* 20°. *Filtrate Made to* 250 *c.c.*

No.	Amount of $KSbO\overline{T}$. Grms.	Amount of $NaC_2H_3O_2$. Grm.	Sb_2S_3 in 50 c.c. Grm.	Per cent of $KSbO\overline{T}$ taken in solution.
24.	5	2	trace	(100)
25.	5	5	0·439	86·77
26.	5	10	0·454	89·72
27.	5	15	0·460	90·90

These numbers show that in the cold precipitation by the acetate is far from complete. It also appears that while a small amount of the acetate does not produce actual precipitation, a large excess gives less precipitation than does a much smaller amount. It is possible that the excess of acetate exerts a solvent action on antimonious hydroxide, which we may look upon as precipitated in the first stage of the reaction, or it may be that a new soluble compound is formed by double decomposition in this manner:—

$$KSbOC_4H_4O_6+NaC_2H_3O_2=KNaC_4H_4O_6+SbOC_2H_3O_2.$$

Free acetic acid has the power of dissolving a small amount of the precipitate, $Sb_2O_3 \cdot H_2O$, as we found by a series of experiments. We also found that a well-washed precipitate of this composition was slightly dissolved by gently warming with a solution of sodium acetate.

Acetates of antimony are scarcely mentioned in the literature, yet these experiments and others speak for their existence.

The polarisation tests of the solutions of tartrate and acetate, mixed in the cold, show a steady decrease in the rotation with increase in the amount of added acetate, suggesting a progressive decomposition of the tartrate. With 2 grms. of acetate in solution only faint opalescence is produced, while with 5 grms. a marked precipitate is formed. As this precipitate decreases with further addition of acetate it is possible that for some amount between the 2 and 5 grms. it is a maximum.

With elevation of temperature, all this is changed, however. (See table below.)

100 *c.c. at* 100°. *Filtrate Made to* 250 *c.c.*

No.	Amount of $KSbO\overline{T}$. Grms.	Amount of $NaC_2H_3O_2$. Grm.	Sb_2S_3 from 50 c.c. Grm.	Per cent of $KSbO\overline{T}$ taken in solution.
28.	5	2	0·438	86·56
29.	5	5	0·381	75·30
30.	5	10	0·312	61·66
31.	5	15	0·291	57·50

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* From the *Journal of Analytical and Applied Chemistry*, v., No. 3.

Now 2 grms. of the acetate gives a good precipitate, and the amount of antimony thrown down from solution increases with added acetate. After heating a solution of 5 grms. of tartrate and 10 grms. of the acetate for an hour on the water-bath, the presence of free acetic acid was readily shown in the filtrate by titration with half normal KOH and phenol-phthalein. No turbidity was produced in the solution until nearly 12 c.c. of the alkali had been added, and the colour appeared, on addition of 30 c.c., as required by theory from the equation—

$$2KSbOC_4H_4O_6 + 2KOH = 2K_2C_4H_4O_6 + Sb_2O_3 \cdot H_2O.$$

When alkali is added to a mixture of acetate and tartrate, prepared in the cold, a *precipitate* forms immediately and grows heavier with increase of the precipitant. Alkali, in absence of the acetate, produces a *turbidity*, but no actual precipitate at the start.

These facts seem to lead to the conclusion that at low temperatures antimony forms a stable and soluble compound with acetic acid which is decomposed with precipitation of the antimony and liberation of the acid at a higher temperature.

The 12 c.c. of half normal KOH added to the filtrate from the boiled solution before an opalescence appeared, indicated that two-fifths of the tartrate had been decomposed, which corresponds closely to what is found by determination of the antimony in No. 30. The reaction at the higher temperature is probably this—

$$2KSbOC_4H_4O_6 + 2H_2O + 2NaC_2H_3O_2 = \\ = 2KNaC_4H_4O_6 + Sb_2O_3 \cdot H_2O + 2HC_2H_3O_2,$$

and the first alkali added simply combines with the free acetic acid. The amount subsequently added decomposes either the tartrate, $KSbOC_4H_4O_6$, in the manner indicated by an equation above, or an intermediate product, possibly $SbOC_2H_3O_2$.

The manner of precipitation strongly suggests the existence of such a product.

Precipitation by Sodium Phosphate.

Solutions of phosphates precipitate the potassium antimony tartrate in the same general manner, but the reaction appears to require a longer time for its completion. We made experiments with a number of solutions, the chief results of which are given below.

In these examples the solutions were made hot, mixed, and kept in the water-bath one hour. The filtrates obtained were strongly acid, and their behaviour on titration suggested presence of free phosphoric acid, which could be liberated in this manner—

$$2KSbOC_4H_4O_6 + 2H_2O + HNa_2PO_4 = \\ = 2KNaC_4H_4O_6 + Sb_2O_3 \cdot H_2O + H_3PO_4.$$

100 *c.c. at* 100°.

No.	Amount of $KSb\overline{OT}$. Grms.	Amount of HNa_2PO_4. Grm.	Sb_2S_3 from 50 c.c. Grm.	Per cent of $KSb\overline{OT}$ taken in solution.
32.	5	0·2	1·234	97·56
33.	5	0·5	1·1930	94·32
34.	5	0·8	1·1370	89·89
35.	5	2·0	0·9335	73·77
36.	5	5·0	0·6379	50·43
37.	5	10·0	0·3851	30·52
38.	5	15·0	0·3192	25·24

Cold solutions can be mixed without producing precipitation, even when 1 grm. of the phosphate is present. Solutions so made were examined with the polariscope, which showed that the large rotation characteristic of the tartrate was very much diminished, probably by some decomposition in the active molecule. This behaviour can be accounted for by assuming the existence of a preliminary reaction in which the antimony, in part at least, is held in an unstable form by the phosphoric acid.

It will be seen from the table that the precipitating power of the phosphate is much more marked than that of the acetate, while both fall short of the carbonate. A few tests were made with solutions of borax as a precipitant, but quantitative results were not obtained. We observed also that solutions of several other oxygen salts are unable to precipitate the antimony. This appears to be true of sulphates, nitrates, and oxalates—at all events with solutions of moderate concentration. Cold mixtures of the tartrate with sodium hypophosphite and sodium sulphite precipitate very slowly, but if heated, decomposition begins soon. Even with sodium thiosulphate, some time elapses before a precipitate forms, which finally, after heating, appears to consist wholly of sulphide.

The reasons for these differences in behaviour are not immediately apparent. The problem is complex, as we have at least four factors to deal with, viz., mass, concentration, time, and temperature. It was shown by one of us by polariscopic observations (*loc. cit.*) that long before a precipitate is visible in these solutions, a change has begun, and that this change is a progressive one. A solution of 5 grms. of the tartrate with 0·5 grm. of sodium carbonate, if carefully made and kept at a low temperature, remains perfectly clear during 24 hours or longer; so clear that it can be examined in a polarisation tube 400 m.m. in length. Observations made at intervals through the 24 hours show a gradual and marked decrease in the angular rotation of the solution. Finally, a precipitate forms and separates out, but the change in the rotation, for a given temperature, is probably completed independently of this. Actual precipitation must, therefore, be preceded by a stage of preparation, which, in some cases, may be prolonged almost indefinitely.

As a further contribution to the subjects of these precipitations, we have in mind the study of the behaviour of several other salts.

Chicago, March, 1891.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, June 1, 1891.

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:—R. W. Peregrine Birch; William Edmonds; Nicholas Eumorfopoulos; Mrs. Charles Hoare; Mrs. Edward Singleton; and Harold Swithinbank.

The special thanks of the Members were returned for the following donation to the Fund for the Promotion of Experimental Research:—

Mrs. Priestley .. .. .. £21.

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

NOTICES OF BOOKS.

The Romance of Science Series. Colour-Measurement and Mixture. By Captain W. de W. Abney, C.B., R.E., F.R.S. Published under the direction of the Committee of General Literature and Education appointed by the Society for Promoting Christian Knowledge. London: Society for Promoting Christian Knowledge, Northumberland Avenue, W.C.

Colours are undoubtedly a subject most interesting not merely to the man of science, but to the general outside public. It must further be at once recognised that there are very few authorities capable of expounding the laws of colour so ably as Captain Abney. It may perhaps, however, be questioned whether the author has not approached his subject too much from the point of view of the mathematico-physicist. That he should so do is, of course, in perfect accordance with the special title of the volume, "Colour Measurement and Mixture"; but many readers will think that a greater prominence given to the chemical and biological phase of the subject would have been more in keeping with the general title of the series.

Captain Abney recognises three "colour constants," viz., hue, luminosity, and purity. What is here called "hue" is generally spoken of in the tinctorial arts as "tone," *e.g.*, the modification in a blue solution or pigment according as it approaches to or receives from a red on the one hand or a green on the other.

As a standard light, the author for sound reasons dismisses the sunlight as a standard, as well as gaslight, the limelight, and the glow-lamp. He prefers the arc-light. Concerning the magnesium light he does not pronounce an opinion. He finds the prismatic spectrum more convenient than the diffraction spectrum which gives only about one-third of the light. A list of the principal colours in the spectrum, drawn up by Prof. Rood, gives ten gradations in place of the ordinary seven.

The demonstration of the existence of the ultra violet and infra-red rays invisible to the human eye will be found very interesting. In a succeeding chapter the spectral diagnosis of colours which appear identical to the eye is very clearly demonstrated. The origin of sunset colours and of the luminosities of sunlight at different altitudes is also made fully intelligible.

In chapter xi. we find it shown why and how red, yellow, and blue, were formerly recognised as the primary colours, and in what lay the error of the observers. The present three-colour theory (red, green, and violet), was, as most of our readers know, due to Thomas Young, and was revived by Clerk-Maxwell and Helmholtz. Some of us may have met with the plausible but fallacious essay in which Lord Brougham, Chancellor and Sciolist, sought to demolish this theory. In speaking of colour-blindness Captain Abney wisely points out that in the registration of cases of colour-blindness the eye of the observer ought first to be tested.

This book will amply repay a careful perusal.

Practical Work in Organic Chemistry. By Fredk. Wm. Streatfeild, F.I.C., &c., Demonstrator of Chemistry at the City and Guilds of London Institute's Technical College, Finsbury. With a Prefatory Notice by Prof. R. Meldola, F.R.S., Foreign Secretary of the Chemical Society. London and New York: E. and F. N. Spon.

This work forms a member of the series of "Finsbury Technical Manuals," issued by Messrs. Spon under the general editorship of Professor Silvanus Thompson. It is totally distinct from the elementary manuals of chemistry now so numerous. The laboratory work here proposed—after a general elementary foundation has been laid—has been divided into a series of programmes arranged to meet the demands of the various chemical industries, and which fairly cover the elementary principles involved in those arts in which organic chemistry is concerned. Prof. Meldola, however, very wisely recommends the student, if his time permits it, to work through all the programmes so as to acquire a wider range of practical knowledge.

A few remarks made by Prof. Meldola on the general working of the Finsbury Technical College are too important, and, we may add, too encouraging to be passed over. He tells us that during the six years of his connection with the Finsbury College there has been "a steady increase in the number of evening students." He is convinced by "the zeal with which men who are engaged all day, often in very arduous occupations, will carry on supplementary work in the evening hours that such instruction supplies a distinct want." The real value of the training obtained at the City and Guilds of London Institute is "amply shown by the numerous records of promotion or improved position which the evening students have been enabled to take. Another favourable sign is the fact that a considerable number of day-students who have completed their courses and have obtained appointments in the London district, re-enter the College as evening students."

Another and still more valuable symptom is "the fact that the competition produced by the spread of the Polytechnic movement has had no appreciable effect upon the evening attendance, and this *in spite of the fact that we cater for no examination.*"

This is doubly important: it shows that there are still young men who study to know and not to "pass," and that there are still employers who can and do recognise ability even when unaccompanied by the certificate of any board of examiners.

The work contains, first, instructions on the performance of the more general operations, and directions for organic analysis, in which, however, we find no mention of the Kjeldahl process for the determination of nitrogen; then follow the four programmes, the study of oxalic acid and its reactions, ethyl alcohol and its reactions, the preparation and decomposition of ethyl acetate and of the composition and reactions of some natural fats and oils, and, lastly, coal-tar and coal-tar products.

This book must be pronounced an excellent guide for the careful and conscientious student.

Elements of Crystallography for Students of Chemistry, Physics, and Mineralogy. By G. Huntingdon Williams, Ph.D., Associate Professor in the Johns Hopkins University. Second edition, revised. London: Macmillan and Co.

Crystallography is a subject which attracts but few students. Of course the mineralogist can make little progress without he is able to express the forms of the substances which come under his consideration. But mineralogy itself is not a very popular study,

Prof. Williams commences his work with a bibliography of the subject, in which we find not a single English name and only two American.

We learn that the scope of this book embraces only geometrical crystallography, leaving the physical and chemical consideration of crystals untouched. After general remarks on crystalline structure, and an account of the general principles of crystallography, he takes up in succession the isometric, the tetragonal, hexagonal, orthorhombic, monoclinic, and triclinic systems, and discusses aggregates and the imperfections of crystals.

An appendix treats of zones, projection, and the construction of crystal figures. In speaking of crystallographic notation the author mentions the symbols of Weiss, Naumann, and Miller (Whewell). Griffin's system is not referred to at all.

We may perhaps hope that the volume before us may extend the study of crystallography.

CORRESPONDENCE.

CONDY'S FLUID.

To the Editor of the Chemical News.

Sir,—We shall esteem it a favour if you will kindly inform your readers that we have just obtained a second injunction in the United States against a person who has used the designation Condy's Fluid for a fluid not manufactured by us.

Five injunctions have been granted in this country against persons selling colourable imitations of Condy's Fluid.

We beg to enclose particulars of some of these judgments.—We are, &c.,

H. J. Bollman Condy.

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. cxii., No. 21, May 25, 1891.

Researches on the Camphenic Series.—MM. Berthelot and Matignon. — A thermo-chemical study of a elass of carbides isomeric with oil of turpentine, and which generate camphor and borneol. The authors consider that their observations throw a new light on chemical combination, and on the fundamental truth that atomicity does not pre-exist in an absolute manner in the elements or components of a compound, but is manifested in the finished compound and in the type which it realises.

On the Tensions of Saturated Watery Vapour up to the Critical Point, and on the Determination of this Critical Point. — L. Cailletet and E. Colardeau.—The contents of a "sealed paper" deposited June 23, 1890. This memoir cannot be reproduced without the accompanying figure and diagram.

The Analysis of Light Diffused by the Sky.—A. Crowe.—The blue of the sky, as observed in England by Lord Rayleigh, is more saturated than that observed at Potsdam by Prof. Vogel. The blue of the sky observed by the author at Montpellier, in January, 1890, is deeper than those observed in England and Germany.

Relation between Atomic Weight and Liquid Density.—Al. Moulin.—The author's results are given in the form of tables.

On Argentous Chloride.—M. Guntz.—According to the temperature at which it is produced the argentous chloride (silver subchloride) varies in colour from deep violet-red to a black-violet. The action of light tends to produce the black modification without a loss of chlorine. By the action of heat the subchloride is decomposed, turning pale yellow, and leaving silver and silver chloride. The action of dilute nitric acid (1 eq. = 2 litres) is absolutely null; thus 50 c.c. of dilute nitric acid left for 24 hours in contact with 2 grms. Ag_2Cl gave no appreciable turbidity on the addition of a solution of sodium chloride. Strong nitric acid reacts upon argentous chloride, especially in heat, yielding silver chloride more or less mixed with subchloride and forming lakes of various colours (Carey Lea's photochlorides).

Action of the Presence of the Mineral Salts of Potassium on the Solubility of Potassium Chlorate.—Ch. Blarez.—Saturated solutions of potassium chlorate, mixed with caustic potassa or a soluble salt of potassium, cause a part of the chlorate which was dissolved to pass out of solution.

Electrolysis of the Salts of Boron and Silicon of Igneous Fusion.—Adolphe Minot.—The author refers to the experiments of H. Sainte-Claire Deville, who decomposed a double aluminium and sodium chloride containing a little silicon, and obtained a grey casting composed of an alloy of aluminium and silicon. He substitutes for the aluminium salt used by Deville a mixture of sodium chloride (60 parts) and double aluminium and sodium fluoride (30 parts). To the salts, at the instant of their fusion, he adds alumina and silica, 5 parts of each. The bath is contained in a cast-iron crucible lined with carbon, which serves as a cathode. The anodes consist of plates of carbon agglomerate. It is maintained at a temperature of 850°. The operation is divided into seven periods, the density of the current being gradually raised from 0·15 to 1 ampère, and the electromotive force from 0·54 to 2·50 volts. In this manner, by operating upon bauxites and natural aluminium silicates, it is practicable to produce the entire series of alloys of iron — silicon, aluminium, and, finally, chemically pure aluminium. Alloys containing 8·9 per cent of silicon are found superior to pure aluminium.

On Two New Crystalline Combinations of Platinum Chloride with Hydrochloric Acid.—Leon Pigeon. —The compound of platinic chloride with hydrochloric acid, previously known under the name chloroplatinic acid, is represented by the formula $PtCl_4.2HCl.6H_2O$. The two newly-discovered compounds are—

$$PtCl_4.2HCl.4H_2O \text{ and } PtCl_4.HCl.2H_2O.$$

The first is obtained by dissolving the red crystals of chloroplatinic acid in a small quantity of water and adding a large quantity of sulphuric acid, when a yellow precipitate is deposited. The second compound is obtained by heating chloroplatinic acid to 100° in a vacuum in presence of melted potassa.

On Bismuth Salicylate. — H. Causse. — This compound is a neutral salicylate with 4 mols. of crystalline water. It forms colourless microscopic prisms, very similar to dehydrated quinine sulphate. It is insoluble in water, and is readily decomposed by acids and alkalies.

On the Solution-Heat and the Solubility of certain Bodies in the Methylic, Ethylic, and Propylic Alcohols. — W. Timifiew. — A thermo-chemical paper, not adapted for useful abstraction.

Bulletin de la Société Chimique de Paris. Series 3, Vol. v., No. 7.

Preparation and Properties of Silver Fluoride.—Henri Moissan.—The author first prepares silver carbonate by precipitating pure silver nitrate in a dilute solution with solution of sodium bicarbonate. The precipitate is washed by decantation with abundance of distilled water. The thick deposit is placed in a platinum capsule, and hydrofluoric acid free from silver is added. The liquid is rapidly evaporated, at first over an open fire. When crystallisation has commenced the capsule is placed on a sand-bath, and the mass is stirred with a spatula until it is completely dry. The black pulverulent residue dissolves easily in water. It is filtered; the solution is placed in a platinum capsule, and evaporated in a vacuum with exclusion of light over sulphuric acid. There is thus obtained a light yellow mass, tough and elastic. Its fusion-point is 435. It reacts very energetically upon the non-metallic chlorides.

Action of Hydrofluoric Acid upon Phosphoric Anhydride. Preparation of Phosphorus Oxyfluoride. —Henri Moissan.—The author confirms the remark of Prof. Thorpe, that Mallet's reaction must produce phosphorus oxyfluoride, and not pentafluoride. When hydrofluoric acid, perfectly dry, and kept in the gaseous state at a temperature above 19·5°, is passed over phosphoric anhydride, the latter becomes hot and a gaseous body is given off, PF_3O_2. This gas is at once decomposed on contact with water. Its sp. gr. is 3·72, the theoretic density of phosphorus oxyfluoride being 3·63. Hence phosphoric acid must never be employed for drying hydrofluoric acid.

Transformation of Starch into Dextrine by the Butyric Ferment. —A. Villiers.—The author considers that further researches are needed to decide if the dextrines which he has obtained are identical with those produced by the action of acids or of diastase.

The Fermentation of Starch by the Action of the Butyric Ferment.—A. Villiers. — Not merely potato-starch, but other starches ferment under the same conditions under the action of the butyric ferment. The resulting products are not always identical.

On Cotton-Dyeing.—Leo Vignon.—The author has shown that if silk, wool, and cotton are immersed in acid, alkaline, or saline liquids of known compositions, and placed in the calorimeter, they give rise to definite, constant, and measurable thermic phenomena. He has tried to modify the molecule of cotton so as to confer on it given chemical functions, and has then sought in what extent its tinctorial properties were changed. Schutzenberger and Thenard have shown that a number of non-nitrogenous substances are capable of fixing nitrogen in forms other than the ammoniacal. The author's samples, after being nitrogenised, were found capable of taking up considerable proportions of acid colouring-matters.

Influence of Hydrofluoric Acid and Fluorides upon the Activity of Yeast.—Dr. J. Effront.—Fluorides increase the activity of yeast when it is in excess, and produce a maximum effect when insufficient quantities of yeast have been employed.

Use of Manganese Sulphide as a Pigment.—Ph. de Clermont and R. Guiot.—The authors render the colour of the green sulphide permanent by removing the water of hydration. This is done by heating it gently in a current of hydrogen sulphide, of carbon dioxide, or of ammonia.

The Formation of the Iso-purpurates.—Raoul Varet.—Silver, mercury, or copper cyanides do not react upon picric acid or the picrates so as to form an iso-purpurate. Zinc cyanide, on the contrary, does so react, but much more slowly than the alkaline cyanides.

Vol. v., No. 8.

The Column which Emerges in the Measurement of Temperatures with the Mercurial Thermometer.—Ch. Ed. Guillaume.—The author proposes the following correction for that part of the mercurial column which emerges from the bulb, and is generally at a lower temperature—$c = n\ \alpha(T - \tau)$; n signifies the number of degrees not exposed to the temperature of the bulb; α the coefficient of the relative expansion of the mercury in the glass, about 0·00016; T the temperature sought for; τ the mean temperature of the n degrees which emerge. If, *e.g.*, the temperature sought is 400°, the number of degrees emerging 350, and their mean temperature 20°, we have $c = 350 : 0{\cdot}00016\ (400 - 20) = 21{\cdot}3$. The difficulty lies in the determination of τ.

A Contribution to the Study of the Production of Urea.—Dr. Popoff.—The transformation of ammoniacal salt into urea in the animal economy cannot be ascribed to the action of a soluble ferment, but results from a function of the living cell.

Researches on Derivatives of Xylose.—G. Bertrand.—Xylite cannot be combined with ethylic aldehyd. Numerous attempts to obtain a benzoic or ethylic acetal with the product of the hydrogenation of arabinose have completely failed. This is a character which completely distinguishes arabinose and xylose.

The Theory of the Phenomena of Dyeing.—Leo Vignon.—The author has shown by the thermo-chemical method that animal textile fibres which can be dyed readily possess basic or acid functions, whilst vegetable fibres having little aptitude for dyeing manifest very feeble chemical functions, and especially no basic functions. Cotton, if submitted to the action of ammonia, fixes nitrogen, acquires basic functions, and becomes able to absorb acid colouring-matters in an acid bath. Stannic acid fixes basic colouring-matters such as saffranine, whilst metastannic acid—which is merely stannic acid polymerised, having undergone a great attenuation in its acid functions—exerts no absorbent power upon saffranin. All soluble colouring matters, artificial or natural, contain either a salifiable group, OH, or the basic groups, NR_2, or the acid radicles, NO_2. We know no colouring-matter consisting solely of a carbide, or possessing no other chemical functions than those of an alcohol, acetose, or aldehyd. All the phenomena of dyeing obtained with soluble colouring-matters necessitate two essential conditions:—(1) The presence of acid or basic functions in the absorbents; (2) The presence of the same functions in the colouring-matters. The sole provisional exception to this rule is that of the tetrazo-dyes.

The following papers, all by M. Berthelot, have appeared in the *Comptes Rendus*, and have been noticed in due course. We submit that if a paper is read before two societies, or sent for insertion to two journals, the fact should be distinctly mentioned.

On the Explosion Wave.

On the Relations between the Change of Volume, the Stability of Compounds, and the Heat liberated in Chemical Reactions.

On Photo-Chemical Actions.—Action of Heat upon Carbon Monoxide.

A Reaction of Carbon Monoxide.

The Determination of Mineral Matters contained in Vegetable Soil, and their Function in Agriculture

The Presence and the Function of Sulphur in Plants.

New Observations on the Volatile Nitrogenous Compounds emitted by Vegetable Soil.

On the Specific Odour of the Soil.

The Preparation of Pure Hydrogen.

History of Chemical Science in the Middle Ages.

Vol. v., No. 9.

Facts toward the History of the Nitrogenous Principles contained in Vegetable Mould.—MM. Berthelot and André.—The insoluble nitrogen contained in the humic compounds may be gradually rendered assimilable. The actions of plants are certainly not identical with those presented by acids and alkalies in our experiments. Nevertheless they are comparable as regards the chemical mechanisms brought into play by the earthy carbonates and carbonic acid, as well as by the acids formed in plants.

The Reactions of the Oxyalkoylic Derivatives of Dimethylaniline.—Edouard Grimaux.—The author seeks to establish the function of the oxyalcoholic groups, such as oxymethyl, OCH_3, oxyethel, OC_2H_5, substituted in the nucleus C_6H_5 of dimethylaniline; and to trace, at the same time, the difference of reaction of the bases according to the place which these groups occupy with respect to $N(CH_3)_2$. The author has studied the meta and ortho bases: the properties and reactions of these bases will be described *in extenso*.

Antiseptic Properties of Sulphonic Amethylcamphophenol.—P. Cazeneuve and M. Rodot.—The substance in question is but slightly antiseptic. Experiments on animals prove that it is not absolutely poisonous.

On the Pyrogenous Transformation of the Campho-sulphophenols into Homologues of Ordinary Phenols.—P. Cazeneuve.—Not adapted for useful abridgment.

The Falsifications of Bees' Wax and their Detection.—A. and P. Buisine.—This memoir will be inserted *in extenso*.

Revue Universelle des Mines et de la Metallurgie.

Vol. xiii., No. 1.

Determination of Available Oxygen in Peroxides by means of Gaseous Hydrochloric Acid.—Prof. L. L. de Koninck and Ad. Lecrenier.—(See p. 280).

Iodometric Determination of Nitrates and Chlorates. — L. L. de Koninck and Ed. Nihoul. — This paper will also be inserted *in extenso*.

February, 1891.

This issue does not contain any chemical matter.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vi., No. 61.

This issue does not contain any chemical matter.

Archives Neerlandaises des Sciences Exactes et Naturelles. Vol. xxv., Part 5.

This issue is entirely taken up with mathematical papers.

MEETINGS FOR THE WEEK.

Wednesday, 17th.—Royal Institution, 4. (Faraday Commemoration Lecture). The Rt. Hon. Lord Rayleigh, M.A., F.R.S.
— Microscopical, 8.
— Meteorological, 7.
Thursday, 18th.—Royal, 4.30.
— Chemical, 8. Ballot. "The Action of Sulphuric Acid on Dehydracetic Acid," by N. Collie. "The Refractive Power of certain Organic Compounds at Different Temperatures," by Dr. W. H. Perkin, F.R.S.
Friday, 19th.—Quekett, 8.

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THE CHEMICAL NEWS.

Vol. LXIII., No. 1647.

ON ELECTRICAL EVAPORATION.*

By WILLIAM CROOKES, F.R.S.

It is well known that when a vacuum tube is furnished with internal platinum electrodes, the adjacent glass, especially near the negative pole, speedily becomes blackened, owing to the deposition of metallic platinum. The passage of the induction current greatly stimulates the motion of the residual gaseous molecules; those condensed upon and in the immediate neighbourhood of the negative pole are shot away at an immense speed in almost straight lines, the speed varying with the degree of exhaustion and with the intensity of the induced current. Platinum being used for the negative pole, not only are the gaseous molecules shot away from the electrode, but the passage of the current so affects the normal molecular motions of the metal as to remove some of the molecules from the sphere of attraction of the mass, causing them to fly off with the stream of gaseous molecules proceeding from the negative pole, and to adhere to any object near it. This property was, I believe, first pointed out by Dr. Wright, of Yale College, and some interesting experiments are described by him in the *American Journal of Science and Arts*.† The process has been much used for the production of small mirrors for physical apparatus.

This electrical volatilisation or evaporation is very similar to ordinary evaporation by the agency of heat. Cohesion in solids varies according to physical and chemical constitution; thus every kind of solid matter requires to be raised to a certain temperature before the molecules lose their fixity of position and are rendered liquid, a result which is reached at widely different temperatures. If we consider a liquid at atmospheric pressure,—say, for instance, a basin of water in an open room,—at molecular distances the boundary surface between the liquid and the superincumbent gas will not be a plane, but turbulent like a stormy ocean. The molecules at the surface of the liquid dart to and fro, rebound from their neighbours, and fly off in every direction. Their initial velocity may be either accelerated or retarded, according to the direction of impact. The result of a collision may drive a molecule in such a direction that it remains part and parcel of the liquid; on the other hand, it may be sent upwards without any diminution of speed, and it will then be carried beyond the range of attraction of neighbouring molecules and fly off into and mingle with the superincumbent gas. If a molecule of the liquid has been driven at an angle with a velocity not sufficient to carry it beyond the range of molecular attraction of the liquid it may still escape, since, in its excursion upwards, a gaseous molecule may strike it in the right direction, and its temporary visit may be converted into permanent residence.

The intrinsic velocity of the molecules is intensified by heat and diminished by cold. If, therefore, we raise the temperature of the water without materially increasing that of the surrounding air, the excursions of the molecules of the liquid are rendered longer and the force of impact greater, and thus the escape of molecules into the upper region of gas is increased, and we say that evaporation is augmented.

If the initial velocities of the liquid molecules can be increased by any other means than by raising the temperature, so that their escape into the gas is rendered more rapid, the result may be called "evaporation" just as well as if heat had been applied.

Hitherto I have spoken of a liquid evaporating into a gas; but the same reasoning applies equally to a solid body. But whilst a solid body like platinum requires an intense heat to enable its upper stratum of molecules to pass beyond the sphere of attraction of the neighbouring molecules, experiment shows that a very moderate amount of negative electrification superadds sufficient energy to enable the upper stratum of metallic molecules to fly beyond the attractive power of the rest of the metal.

If a gaseous medium exists above the liquid or solid, it prevents to some degree the molecules from flying off. Thus both ordinary and electrical evaporation are more rapid in a vacuum than at the ordinary atmospheric pressure.

I have recently made some experiments upon the evaporation of different substances under the electric stress.

Evaporation of Water.—A delicate balance was taken, and two very shallow porcelain dishes were filled with acidulated water and balanced on the pans. Dipping into each dish—touching the liquid but not the dish—was a platinum wire, one connected with the induction coil and the other insulated. The balance was left free to move, but was not swinging, the pointer resting at the centre of the scale. The water in connection with the coil was first made positive. After $1\frac{3}{4}$ hours there was scarcely any difference between the weight of the insulated water and that which had been exposed to the positive current. Equilibrium being restored, the current was reversed, the negative current being kept on the dish for two hours. At the end of this time the electrified water was decidedly lighter. After having again restored equilibrium, the electrification of the dishes was reversed, *i.e.*, the one that had before been insulated was made negative and the other one was insulated. In an hour the electrified water had become decidedly lighter than the insulated water. The experiment was performed in a room of uniform temperature, and any draught was prevented by the glass case of the balance. In a subsequent experiment in which the quantities were weighed, it was found that negatively electrified water lost in $1\frac{1}{2}$ hours $\frac{1}{1000}$th part of its weight more than did insulated water.

This experiment shows that the disturbing influence which assists evaporation is peculiar to the negative pole even at atmospheric pressures.

The metal cadmium was next experimented upon.

A U-shaped tube was made, having a platinum pole sealed in each end. 6 grains of pure cadmium were put in each limb and fused round the platinum wire. The ends of the tube were then put into an air bath, and kept at a temperature of 200° C. during the continuance of the experiment.* The exhaustion remained at 0·00076 m.m., or 1 M. The induction current was kept going for thirty-five minutes. At the end of this time it was seen that most of the cadmium had disappeared from the negative pole, leaving the platinum wire clean, no metal being deposited near it, and the molecules appearing to have been shot off to a distance of about $\frac{3}{4}$ inch. The appearance of the positive pole was very different; scarcely any of the cadmium had been volatilised, and the condensed metal came almost close to the pole. The tube was opened, and the remaining wires and metal were weighed. The cadmium was then dissolved off the poles in dilute acid; the residue was washed, dried, and weighed.

	Positive pole.	Negative pole.
Original weight of cadmium ..	6·00 grs.	6·00 grs.
Cadmium remaining on the pole	3·65 ,,	0·25 ,,
Cadmium volatilised in 35 mins.	2·35 ,,	5·75 ,,

The difference between the amount of cadmium driven from the two poles having proved to be so decided,

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* A Paper read before the Royal Society, June 11, 1891.

† Third Series, vol. xii., p. 49, January, 1877; and vol. xiv., p. 169, September, 1877.

* Cadmium melts at 320° and boils at 860°.

another experiment was tried in a tube so arranged that the metal could be more easily weighed before and after the experiment. For this purpose a tube was blown U-shaped, having a bulb in each limb. The platinum poles were, as before, at the extremities of each limb, and in each bulb was suspended from a small platinum hook a small lump of cadmium, the metal having been cast on to the wire. The wires were each weighed with and without the cadmium. The tube was exhausted, and the lower half of the tube was enclosed in a metal pot containing paraffin wax, the temperature being kept at 230° C. during the continuance of the experiment. A deposit around the negative pole took place almost immediately, and in five minutes the bulb surrounding it was opaque with deposited metal. The positive pole with its surrounding luminosity could be easily seen the whole time. In thirty minutes the experiment was stopped, and after all was cold the tube was opened and the wires weighed again. The results were as follows:—

	Positive pole.	Negative pole.
Original weight of cadmium ..	9·34 grs.	9·38 grs.
Weight after experiment	9·25 ,,	1·86 ,,
Cadmium volatilised in 30 mins.	0·09 ,,	7·52 ,,

Finding that cadmium volatilised so readily under the action of the induction current, a large quantity, about 350 grs., of the pure metal was sealed up in a tube, and the end of the tube containing the metal was heated to a little above the melting-point; the molten metal being made the negative pole, in a few hours the whole quantity had volatilised and condensed in a thick layer on the far end of the tube, near, but not touching, the positive pole.

Volatilisation of Silver.—Silver was the next metal experimented upon. The apparatus was similar to that used for the cadmium experiments. Small lumps of pure silver were cast on the ends of platinum wires, and suspended to the inner ends of platinum terminals passing through the glass bulb. The platinum wires were protected by glass, so that only the silver balls were exposed. The whole apparatus was enclosed in a metal box lined with mica, and the temperature was kept as high as the glass would allow without softening. The apparatus was exhausted to a dark space of 3 m.m., and the current was kept on for 1½ hours. The weights of silver before and after the experiment, were as follows:—

	Positive pole.	Negative pole.
Original weight of silver ..	18·14 grs.	24·63 grs.
Weight after the experiment	18·13 ,,	24·44 ,,
Silver volatilised in 1½ hours	0·01 ,,	0·19 ,,

It having been found that silver volatilised readily from the negative pole in a good vacuum, experiments were instituted to ascertain whether the molecules of metal shot off from the pole were instrumental in producing phosphorescence. A glass apparatus was made as follows:—A pear-shaped bulb of German glass has, near the small end, an inner concave negative pole, of pure silver, so mounted that its inverted image is thrown upon the opposite end of the tube. In front of the pole is a screen of mica, having a small hole in the centre, so that only a narrow pencil of rays from the silver pole can pass through, forming a bright spot of phosphorescence at the far end of the bulb. The exhaustion was pushed to a high point, 0·00068 m.m., or 0·9 M. The current from an induction coil was allowed to pass continuously for some hours, the silver pole being kept negative, so as to drive off a certain portion of the silver electrode. On subsequent examination it was found that the silver had all been deposited in the immediate neighbourhood of the pole, whilst at the far end of the tube the spot that had been continuously glowing with phosphorescent light was practically free from silver.

An egg-shaped tube was next made, having two negative poles connected together, so placed as to project two luminous spots on the phosphorescent glass of the tube. One of the electrodes was of silver, a volatile metal; the other was of aluminium, practically non-volatile. On connecting the two negative poles with one terminal of the coil, and the positive pole with the other terminal, it was seen in the course of half an hour that a considerable quantity of metal had been projected from the silver negative pole, blackening the tube in its neighbourhood, while no projection of metallic particles took place from the aluminium positive pole. During the whole time of the experiment, however, the two patches of phosphorescent light opposite the two negative poles had been glowing with exactly the same intensity, showing that the active agent in effecting phosphorescence was not the molecules of the solid projected from the poles, but the residual gaseous particles, or "radiant matter."

In the tubes hitherto made containing silver, it had not been easy to observe the spectrum of the negative pole, owing to the rapid manner in which the deposit obscured the glass. A special tube was therefore devised, of the following character:—A silver rod was attached to the platinum pole at one end of the tube, and the aluminium positive pole was at the side. The end of the tube opposite the silver pole was rounded, and the spectroscope was arranged to observe the light of the volatilising silver "end on." In this way the deposit of silver offered no obstruction to the light, as none was deposited except on the sides of the tube surrounding the silver. At a vacuum giving a dark space of about 3 m.m. from the silver, a greenish-white glow was seen to surround the metal. This glow gave a very brilliant spectrum. The spark from silver poles in air was brought into the same field of view as the vacuum glow, by means of a right-angled prism attached to the spectroscope, and the two spectra were compared. The two strong green lines of silver were visible in each spectrum; the measurements taken of their wave-lengths were 3344 and 3675, numbers which are so close to Thalén's numbers as to leave no doubt that they are the silver lines. At a pressure giving a dark space of 2 m.m. the spectrum was very bright, and consisted chiefly of the two green lines and the red and green hydrogen lines. The intercalation of a Leyden jar into the circuit does not materially increase the brilliancy of the lines, but it brings out the well-known air lines. At this pressure not much silver flies off from the pole. At a higher vacuum the luminosity round the silver pole gets less and the green lines vanish. At an exhaustion of about one-millionth of an atmosphere the luminosity is feeble, the silver pole has exactly the appearance of being red hot, and the volatilisation of the metal proceeds rapidly.*

If, for the negative electrode, instead of a pure metal such as cadmium or silver, an alloy was used, the different components might be shot off to different distances, and in this way make an electrical separation—a sort of fractional distillation. A negative terminal was formed of clean brass, and submitted to the electrical discharge *in vacuo*; the deposit obtained was of the colour of brass throughout, and on treating the deposit chemically I

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* Like the action producing volatilisation, the "red heat" is confined to the superficial layers of molecules only. The metal instantly assumes, or loses, the appearance of red heat the moment the current is turned on or off, showing that, if the appearance is really due to a rise of temperature, it does not penetrate much below the surface. The extra activity of the metallic molecules necessary to volatilise them is, in these experiments, confined to the surface only, or the whole mass would evaporate at once, as when a metallic wire is deflagrated by the discharge of a powerful Leyden jar. When this extra activity is produced by artificial heat one of the effects is the emission of red light; so it is not unreasonable to imagine that when the extra activity is produced by electricity the emission of red light should also accompany the separation of molecules from the mass. In comparison with electricity, heat is a wasteful agent for promoting volatilisation, as the whole mass must be raised to the requisite temperature to produce a surface action merely; whereas the action of electrification does not appear to penetrate much below the surface.

could detect no separation of its component metals, copper and zinc.

A remarkable alloy of gold and aluminium, of a rich purple colour, has been kindly sent me by Prof. Roberts-Austen. Gold being very volatile in the vacuum tube, and aluminium almost fixed, this alloy was likely to give different results from those yielded by brass, where both constituents fly off with almost equal readiness. The Au-Al alloy had been cast in a clay tube, in the form of a rod 2 c.m. long and about 2 m.m. in diameter. It was sealed in a vacuum tube as the negative pole, an aluminium pole being at the other side. Part of the alloy, where it joined the platinum wire passing through the glass, was closely surrounded with a narrow glass tube. A clean glass plate was supported about 3 m.m. from the rod of alloy. After good exhaustion the induction current was passed, the alloy being kept negative. Volatilisation was very slight, but at the end of half an hour a faint purple deposit was seen both on the glass plate and on the walls of the tube. On removing the rod from the apparatus it was seen that the portion which had been covered by the small glass tube retained its original purple appearance, while the part that had been exposed to electrical action had changed to the dull white colour of aluminium. Examined under the microscope, the whitened surface of the Austen alloy was seen to be pitted irregularly, with no trace of crystalline appearance.

This experiment shows that, from an alloy of gold and aluminium, the gold is the first to volatilise under electrical influence, the aluminium being left behind. The purple colour of the deposit on glass is probably due to finely-divided metallic gold. The first deposit from a negative pole of pure gold is pink; this changes to purple as the thickness increases. The purple then turns to green, which gets darker and darker until the metallic lustre of polished gold appears.

Returning to the analogy of liquid evaporation, if we take several liquids of different boiling-points, put them under the same pressure, and apply the same amount of heat to each, the quantity passing from the liquid to the gaseous state will differ widely in each case.

It was interesting to try a parallel experiment with metals, to find their comparative volatility under the same conditions of temperature, pressure, and electrical influence. It was necessary to fix upon one metal as a standard of comparison, and for this purpose I selected gold, its electrical volatility being great, and it being easy to prepare in a pure state.

An apparatus was made that was practically a vacuum tube with four negative poles at one end and one positive pole at the other. By a revolving commutator I was able to make electrical connection with each of the four negative poles in succession for exactly the same length of time (about six seconds); by this means the variations in the strength of the current, the experiment lasting some hours, affected each metal alike.

The exposed surface of the various metals used as negative poles was kept uniform by taking them in the form of wires that had all been drawn through the same standard hole in the drawplate, and cutting them by gauge to a uniform length; the actual size used was 0·8 m.m. in diameter and 20 m.m. long.

The comparison metal gold had to be used in each experiment; the apparatus thus enabled me to compare three different metals each time. The length of time that the current was kept on the revolving commutator in each experiment was eight hours, making two hours of electrification for each of the four negative electrodes; the pressure was such as to give a dark space of 6 m.m.

The fusible metals, tin, cadmium, and lead, when put into the apparatus in the form of wires, very quickly melted. To avoid this difficulty a special form of pole was devised. Some small circular porcelain basins were made, 9 m.m. diameter; through a small hole in the bottom a short length of iron wire, 0·8 m.m. in diameter, was passed, projecting downwards about 5 m.m.; the basin was then filled to the brim with the metal to be tested, and was fitted into the apparatus exactly in the same way as the wires; the internal diameter of the basins at the brim was 7 m.m., and the negative metal filed flat was thus formed of a circular disc 7 m.m. diameter. The standard gold pole being treated in the same way, the numbers obtained for the fusible metals can be compared with gold, and take their place in the table.

The following table of the comparative volatilities was in this way obtained, taking gold as = 100:—

Palladium	108·00
Gold	100·00
Silver	82·68
Lead	75·04
Tin	56·96
Brass	51·58
Platinum	44·00
Copper	40·24
Cadmium	31·99
Nickel..	10·99
Iridium	10·49
Iron	5·50

In this experiment equal surfaces of each metal were exposed to the current. By dividing the numbers so obtained by the specific gravity of the metal, the following order is found:—

Palladium	9·00
Silver	7·88
Tin	7·76
Lead	6·61
Gold	5·18
Cadmium	3·72
Copper	2·52
Platinum	2·02
Nickel	1·29
Iron	0·71
Iridium	0·47

Aluminium and magnesium appear to be practically non-volatile under these circumstances.

The order of metals in the table shows at once that the electrical volatility in the solid state does not correspond with the order of melting-points, of atomic weights, or of any other well-known constant. The experiment with some of the typical metals was repeated, and the numbers obtained did not vary materially from those given above, showing that the order is not likely to be far wrong.

It is seen in the above table that the electrical volatility of silver is high, while that of cadmium is low. In the two earlier experiments, where cadmium and silver were taken, the cadmium negative electrode in 30 minutes lost 7·52 grs., whilst the silver negative electrode in 1½ hours only lost 0·19 gr. This apparent discrepancy is easily explained by the fact (already noted in the case of cadmium) that the maximum evaporation effect, due to electrical disturbance, takes place when the metal is at or near the point of liquefaction. If it were possible to form a negative pole *in vacuo* of molten silver, then the quantity volatilised in a given time would be probably much more than that of cadmium.

Gold having proved to be readily volatile under the electric current, an experiment was tried with a view to producing a larger quantity of the volatilised metal. A tube was made having at one end a negative pole composed of a weighed brush of fine wires of pure gold, and an aluminium pole at the other end.

The tube was exhausted and the current from the induction coil put on, making the gold brush negative; the resistance of the tube was found to increase considerably as the walls became coated with metal, so much so that, to enable the current to pass through, air had to be let in after a while, depressing the gauge ½ m.m.

The weight of the brush before experiment was

35·4940 grs. The induction current was kept on the tube for 14½ hours; at the end of this time the tube was opened and the brush removed. It now weighed 32·5613, showing a loss of 2·9327 grs. When heated below redness the deposited film of gold was easily removed from the walls of the tube in the form of very brilliant foil.

After having been subjected to electrical volatilisation, the appearance of the residual piece of gold under the microscope, using a ¼-inch object-glass, was very like that of electrolytically deposited metal, pitted all over with minute hollows.

This experiment on the volatilisation of gold having produced good coherent films of that metal, a similar experiment was tried, using a brush of platinum as a negative electrode. On referring to the table it will be seen that the electrical volatility of platinum is much lower than that of gold, but it was thought that by taking longer time a sufficient quantity might be volatilised to enable it to be removed from the tube.

The vacuum tube was exhausted to such a point as to give a dark space of 6 m.m., and it was found, as in the case of gold, that as a coating of metal was deposited upon the glass the resistance rapidly increased, but in a much more marked degree, the residual gas in the tube apparently becoming absorbed as the deposition proceeded. It was necessary to let a little air into the tube about every 30 minutes, to reduce the vacuum. This appears to show that the platinum was being deposited in a porous spongy form, with great power of occluding the residual gas.

Heating the tube when it had become this way non-conducting liberated sufficient gas to depress the gauge of the pump 1 m.m., and to reduce the vacuum so as to give a dark space of about 3 m.m. This gas was not re-absorbed on cooling, but on passing the current for ten minutes the tube again refused to conduct, owing to absorption. The tube was again heated, with another liberation of gas, but much less than before, and this time the whole was re-absorbed on cooling.

The current was kept on this tube for 25 hours; it was then opened, but I could not remove the deposited metal except in small pieces, as it was brittle and porous. Weighing the brush that had formed the negative pole gave the following results:—

	Grains.
Weight of platinum before experiment ..	10·1940
,, ,, after experiment ..	8·1570
Loss by volatilisation in 25 hours	2·0370

Another experiment was made similar to that with gold and platinum, but using silver as the negative pole, the pure metal being formed into a brush of fine wires. Less gas was occluded during the progress of this experiment than in the case of platinum. The silver behaved the same as gold, the metal deposited freely, and the vacuum was easily kept at a dark space of 6 m.m. by the very occasional admission of a trace of air. In 20 hours nearly 3 grs. of silver were volatilised. The deposit of silver was detached without difficulty from the glass in the form of brilliant foil.

A NOVEL METHOD FOR THE PRODUCTION OF SODIUM AND POTASSIUM NITRITE.

By H. N. WARREN, Research Analyst.

The surface, or catalytic action, which platinum exerts upon ammonia when in the presence of oxygen, with the production of the white cloud of ammonium nitrite, is, when carefully peformed, more than striking as regards the quantity of nitrite thus formed, but by employing a more energetic form of platinum the effects may be considerably enhanced.

The most powerful surface action that I have been successful in producing was obtained as follows:—Platinum was dissolved by the aid of aqua regia, evaporated to dryness, and the resulting platinic chloride thus formed maintained at a temperature of 400° F. as long as any chlorine continued to be evolved; the residue was now boiled with a slight excess of sodium carbonate, and the platinic hydrate thus produced dissolved by means of oxalic acid, the solution concentrated, and a sufficiency of asbestos yarn added to absorb the solution; the yarn, which now measured about a yard in length, when dried and ignited contained about 12 per cent of platinum, presenting a grey colour characteristic of that metal when in the spongy form, the asbestos meanwhile retaining its original ropy properties without becoming brittle, as is the case when platinic chloride is used in place of the oxalate. The so-prepared asbestos was next introduced into a combustion-tube somewhat longer than the same, and connected to an apparatus evolving ammonia gas: a current of air being at the same time injected into the apparatus, in order to furnish a mixture of oxygen and ammonia, the action of the platinised asbestos was now started by applying the flame of a Bunsen burner to the more remote end of the tube. Directly the mixed gases are allowed to impinge upon the platinised surface, dense clouds of ammonium nitrite are evolved, and in several instances the whole length of the asbestos became intensely heated, the ammonium nitrite thus formed being conveyed into a solution of caustic soda, and, by so doing, producing an equivalent of sodium nitrite; the ammonia thus evolved being retained for a further supply of ammonium nitrite.

Some idea as to the delicacy of this so-prepared asbestos can be obtained when I mention that for several minutes, while the apparatus was in complete working order, scarcely any excess of ammonia could be detected at the further end of the tube, the whole of it being converted into that of nitrite.

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

ASSOCIATION *VERSUS* DISSOCIATION IN SOLUTIONS.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

The view that electrolytes in aqueous solutions are partially dissociated into their ions is chiefly based on the correctness of the evidence as to the number of molecules or acting units present afforded by the depression of the freezing-point of the solvent. If this method is reliable, it will afford consistent evidence in whatever way it may be applied.

When $5H_2SO_4$, for instance, are dissolved in $15H_2O$, some of the acid molecules become dissociated according to the modern physical theory of solution, so that the solution consists of *more than* twenty acting units; according to the hydrate theory, on the other hand, the acid and water combine together to a certain extent, so that the solution consists of *less than* twenty acting units. By adding this solution to some other crystallisable liquid, such as acetic acid, we can, according to the physical theory, determine the number of acting units of which it is composed; and the result shows that, instead of consisting of more twenty acting units, it consists of only 6·5 units. Thus the very phenomenon on which the physical theory is based gives most emphatic evidence against that theory.

The sulphuric acid and water together produce a smaller depression of the freezing-point of acetic acid than the water alone does, so that on adding sulphuric acid to dilute acetic acid, the freezing-point of the latter is actually raised. A series of determinations was made

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* Abstract of a Paper read before the German Chemical Society.

in which different amounts of sulphuric acid were added to weak acetic acid, and the results gave the data requisite for the construction of the following table, in which the depression actually produced by the water and sulphuric acid is compared with that which would be produced if these two acted independently.* In the extreme case the observed depression amounts to only one-third of the calculated value.

Molecules to 100 $C_2H_4O_2 = x$.		Depression for 14·4 $H_2O+(x-14·4)H_2SO_4$.	
	Calculated.	Found.	Difference.
14·4	—	—	—
15·0	6·76°	5·65°	− 1·11° = 16 p.c.
17·5	8·00	3·77	− 4·23 = 53 ,,
20	9·08	2·95	− 6·13 = 68 ,,
25	12·53	3·45	− 9·08 = 72 ,,
30	17·09	6·00	− 11·09 = 65 ,,
35	24·70	9 65	− 15·05 = 61 ,,
40	∞	14·00	∞
45	∞	19·15	∞
50	∞	26·00	∞
55	∞	39·50	∞

In these determinations the minimum proportion of sulphuric acid to water corresponded to that of a 40 per cent solution, and such a solution is held to behave anomalously, owing to its strength being too great for the correct application of Van t' Hoff's theory of the lowering of the freezing-point. On plotting out all the results, however, it was evident that the phenomenon which they exhibited would also be exhibited by solutions containing a far smaller proportion of sulphuric acid; but to remove all doubt that this was the case, the following determinations were made:—

Water	+	Molecules of Sulphuric acid To 100 ($C_2H_4O_2$).	=	Total	Depression.
16·8	+	0	=	16·8	7·32°
16·8	+	0·017	=	16·827	7·23
16·8	+	0·035	=	16·835	7·18
16·8	+	0·054	=	16·854	7·16
16·8	+	0·097	=	16·897	7·03

In the second and third of these determinations the sulphuric acid and water form solutions containing only 0·1 and 0·6 per cent of the former respectively, and such solutions, Arrhenius maintains (Chem. News, lxiii., 148), behave in strict accordance with the dissociation and osmotic pressure theories. Each molecule of acid becomes, according to him, dissociated into 2·14 ions (on the average), forming, that is, 1·14 more acting units than were present before the dissolution. Yet the present determinations show that this is not the case; the number of acting units is *diminished* by 0·21 and 0·32 in the two cases, instead of being *increased* by 1·14.

Other substances which possess a strong affinity for water behave like sulphuric acid, and actually raise the freezing-point of weak acetic acid. This was found to be the case with hydrochloric acid to a very marked extent, and in a smaller degree with calcium chloride. With phosphoric acid there was no raising of the freezing-point of weak acetic acid of the strength which was taken, but the additional lowering produced was almost nil—that is, the water and phosphoric acid caused a depression scarcely in excess of that caused by the water only. With nitric acid the additional depression was considerable, but yet it was notably smaller than that which would be produced if no combination between the water and acid had occurred.

It must be remarked that, according to the hydrate theory, the present results will not afford any indication of the actual hydrates present. When sulphuric acid, for instance, is dissolved in water, the present hydrate theory represents the *whole liquid* (unless excessively dilute) to consist of one or more hydrates. When this liquid is cooled, the water molecules which coalesce to form solid water are derived from these hydrates, the latter becoming decomposed into other hydrates containing less water and the only portion of the liquid which acts as the "foreign substance" is that from which none of the solvent can be separated by cooling, that is, the sulphuric acid, and not the hydrate. It is the mechanical or physical effect of these "foreign" molecules to which the lowering of the freezing-point of the solvent must be mainly attributed in the case of dilute solutions, for the chemical union of the acid and water can have but a small effect on the result, since the heat absorbed by the decomposition of a high hydrate into that next below it is very small in comparison with the heat evolved by the crystallisation of the water which it gives up (see *Proc. Chem. Soc.*, 1889, p. 149). When there are two dissolved substances present, the results will be very complicated; the acetic acid and the sulphuric acid, for instance, will each combine with some water in proportions dependent on their relative affinities for water and on the masses of each present, and the molecules acting as "foreign" molecules and causing the depression will be those water molecules which are combined by the acetic acid (the solvent) and the molecules of the hydrate of sulphuric acid. The case is evidently too complicated for any deductions to be drawn as to the composition of the latter.

In a case where the substance added to the acetic acid and water has a much smaller affinity for the water than the acetic acid has, this latter will appropriate nearly the whole of the water, and the other substance will remain almost anhydrous, or will itself combine with the acetic acid to form compounds analogous to hydrates. In such a case the whole of the water (being combined with the solvent itself), as well as the other substance, will act as the "foreign substance."

This was found to be the case with alcohol when added to acetic acid containing water, the depression of the freezing-point observed being practically identical with that which is produced by the alcohol and water when acting separately. The same was also the case when water and acetic acid were added to sulphuric acid as a solvent, the latter, as might have been expected, taking practically the whole of the water, and the acetic acid none.

Other results were obtained with calcium chloride and alcohol, and also with calcium nitrate and alcohol, dissolved in water. These two salts, which both possess a considerable affinity for alcohol, appear to combine with it, and depress the freezing-point of water to a smaller extent than that calculated on the assumption that they and the alcohol act independently; but the diminution of the depression was not large unless the proportion of salt added was considerable.

The only conclusion which can be drawn from these results is that when two substances possessing a strong affinity for each other are mixed, there are fewer acting units present than when they are separate, and that, therefore, these two substances do not interact so as to produce dissociation, but combination.

ON THE
USE OF AMMONIUM SELENITE FOR THE DIAGNOSIS OF THE ALKALOIDS.

By A. J. FERREIRA DA SILVA.

In a note presented to the Academy in June, 1885, Lafon pointed out a new reagent for morphine and codeine. It is ammonium sulphoselenite, which he prepared by dissolving 1 grm. ammonium selenite in 20 c.c. of undiluted sulphuric acid. This reaction gives a green colour with

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* For the exact method of calculation the present number of the *Berichts* must be consulted.

the two alkaloids mentioned, but others behave in a different manner. It is a precious reagent in the toxicological study of poisoning cases by the alkaloids of opium.

The author finds that its use may be advantageously extended for the detection of some other alkaloids.

He has operated upon the following alkaloids: atropine, aconitine, berberine, brucine, caffeine, cinchonine, cinchonidine, cocaine, curarine, delphine, digitaline, eserine, morphine, narcotine, narceine, papaverine, pilocarpine, solanine, saponine, senegine, and veratrine. The following results were obtained :—

Atropine.—No colouration.

Aconitine.—No immediate colouration; after twenty minutes a very slight rose-colour.

Berberine.—Greenish yellow colour, becoming successively very brown, rose at the margins, and violet in the middle; half-an-hour afterwards entirely vinous red, which lasts for three hours.

Brucine.—Reddish or rose-colour, becoming pale orange. Half-an-hour after an amber colour, and no deposit.

Caffeine.—No distinct colouration. At the end of three hours the liquid was reddish, and there appeared a very slight deposit, which was not red.

Cinchonine.—Nothing.

Cinchonidine.—Nothing.

Cocaine.—After half-an-hour no decided colouration nor precipitate. After the lapse of three hours the same reaction as caffeine.

Curarine.—Slight violet colouration, after some time reddish. No red deposit at the end of three hours.

Delphine.—Slightly reddish colouration passing into a violet red. No precipitate at the end of three hours.

Digitaline.—No immediate colour. Half-an-hour after the liquid was yellowish. After three hours a reddish deposit.

Eserine.—Lemon-yellow colour, turning to orange. Three hours afterwards the colour paler.

Morphine.—Bright greenish blue; half-an-hour after maroon-yellow and no deposit. After three hours the liquid maroon-brown; no red deposit.

Narcotine.—Bluish colour, becoming violet and then reddish. After half-an-hour a fine reddish colour and no precipitate. After three hours a small red deposit.

Narceine.—Yellow-green colour, becoming brownish, and after half-an-hour reddish. Afterwards a red deposit at the bottom of the capsule, which is very distinct in two or three hours.

Papaverine.—Bluish colour; the liquid becomes bottle-green, dirty yellowish green, violet-blue, and then red. A small bluish deposit at the bottom of the capsule.

Pilocarpine.—Nothing.

Solanine.—Canary-yellow, and then brownish. After half-an-hour a rose-coloured ring. After three hours the liquid violet-red.

Saponine.—Yellowish, becoming slightly reddish. (Reaction not distinct).

Senegine.—Light dirty yellow. After three hours liquid reddish.

Veratrine.—Indistinct yellowish colour, sometimes with a green tone, after half-an-hour yellow. After three hours' deposit red and liquid yellowish. (Reaction indistinct).

Lafon's reagent thus enables us to distinguish not only morpheine and codeine, but also berberine, eserine, narcotine, papaverine, solanine, and narceine; the former by colour reactions; narceine not only by the immediate production of a yellowish green colour passing into brown and after half-an-hour to reddish, but also by the formation of a red deposit, which is seen more distinctly after the lapse of two or three hours adhering to the sides, and the bottom of the capsule.

The author in producing these reactions places small portions of the alkaloids upon watch-glasses set upon white paper, or in small porcelain capsules (3 c.m. in diameter and 4 c.c. in capacity).—*Comptes Rendus*, vol. cxii., p. 1266.

DETECTION AND SEPARATION OF THE PLATINUM METALS, AND IN PARTICULAR OF PALLADIUM AND RHODIUM, IN PRESENCE OF THE COMMON METALS.

By A. JOLY and E. LEIDIÉ.

When the platinum metals are united with large quantities of common metals, such as copper, iron, lead, bismuth, and tin, great difficulty is experienced in the detection of their presence and in their accurate separation. The studies which the authors have undertaken during the last two years on the combination formed by some of the metals of native platinum with nitrous acid, and the alkaline nitrites taken together, with facts previously observed by Fischer and Lang (palladio-nitrites, platino-nitrites), by Claus and W. Gibbs, enable this separation to be effected in most cases.

We first exclude osmium, ruthenium, and iridium. We admit, for instance, that the platinum ores have first been treated by the method of Deville and Debray, that the osmium and ruthenium have been eliminated in the state of volatile compounds, and that the iridium has been separated by means of lead. The residues from these operations will have left in a solution which we will suppose to be hydrochloric small quantities of platinum, palladium, and rhodium, with common metals such as lead, iron, copper, bismuth, tin, &c., which pre-existed in the ore, or which may have been introduced as impurities in the considerable quantities of lead which have to be used.

The reactions exerted by potassium nitrite upon the hydrochloric solutions of the metals just mentioned are perfectly definite.

The progressive addition of potassium nitrite to a solution of palladium chloride kept luke-warm, occasions the progressive decolouration of the liquid, and when this becomes neutral it takes a characteristic gold-colour, and after concentration it deposits crystals of palladio-nitrite, which are sparingly soluble in the cold, especially in presence of an excess of alkaline chlorides.

Platinum is transformed under the same conditions as palladium into a colourless platino-nitrite. It is here necessary that the potassium chloroplatinate which is necesssarily formed at first shall not be deposited, and this requires that the chief part of the platinum must be previously eliminated, or that the liquid is sufficiently diluted.

In a hot and dilute solution of rhodium chloride potassium nitrite determines the formation of a white, crystalline precipitate of double nitrite, insoluble in a solution of potassium chloride. It is to be remarked that the precipitation of the double salt takes place when the liquid is still acid.

If the hydrochloric solution contains lead this is precipitated in a slightly acid liquid along with the bismuth and the tin. The precipitation of the copper begins in an acid liquid, and is completed not until the moment when the liquid becomes distinctly alkaline. The presence of copper is shown on the first additions of nitrite by an intense green colouration. A bluish-white flocculent precipitate is then formed, which is gradually changed into a granular precipitate of a light blue. As for the iron it is only eliminated in the last place in the alkaline liquid in the form of a gelatinous brown precipitate, very soluble in dilute hydrochloric acid.

Suppose a hydrochloric solution of the above metals. To this solution suitably diluted (as may be found by trial on a small portion), and kept at 60°, potassium nitrite is progressively added. If the liquid is rich in platinum there is gradually formed a crystalline precipitate of the chloro-salt, perfectly free from the other metals. After cooling and separation of the chloro-salt it is heated again, and the additions of nitrite are continued. There is suddenly formed, especially on rubbing with a glass rod, the crystalline double rhodium precipitate, which carries down with it lead, bismuth, and tin.

This double salt is analogous in its composition to the double potassium and cobalt nitrite, and seems to behave like the latter. That is it which forms triple combinations containing lead and bismuth. The precipitate of rhodium is slightly cupriferous. At this point the liquid is still acid; it is allowed to cool to separate the rhodium salt, the precipitation of which is in general complete if the liquid contains a sufficiency of potassium chloride. If the mixture contains copper and iron more nitrite is added to render the liquid alkaline, and it is heated to ebullition. Iron and copper are filtered off, whilst the platinum and palladium are entirely present in the solution, which is of a gold colour. If the platinum and palladium are in considerable quantities the double nitrites are crystallised out. Otherwise the salts are transformed into chlorides by dilute hydrochloric acid and eliminated by known methods.—*Comptes Rendus*, vol. cxii., p. 1259.

SEPARATION AND DETERMINATION OF NICKEL AND COBALT.

By CONSTANTIN KRAUSS.

(Concluded from p. 281).

C.—*Methods depending on the Different Behaviour of the Phosphates of Both Metals.*

1. Ph. Dirvell separates cobalt and nickel (from accompanying metals) in the known manner, and determines the sum of both by weighing the metals reduced in a current of hydrogen. For further separation he re-dissolves the metals in nitric acid, evaporates down the solution, and re-dissolves in 50 c.c. water.

So much of a phosphatic solution (mixed with an equal volume of a solution of ammonium carbonate), that thirty times as much phosphate is present as the joint weight of the cobalt and nickel. The mixture is now slowly heated, boiled for a few seconds, and mixed with 2—3 c.c. ammonia, when the chief part of the precipitate formed is re-dissolved. If it is now cautiously heated to 100° we obtain a purple-violet precipitate, which when filtered, washed, and ignited, corresponds to the formula $CO_2P_2O_7$. The nickel is thrown down from the filtrate by means of sulphuretted hydrogen and determined in the known manner.

According to Krauss this method, after some experience, yields satisfactory results. The liquid must be frequently agitated, especially after the addition of the ammonia, and the ebullition must not be continued too long. The cobalt obtained generally contains nickel. The clear solution is then decanted off, the precipitate dissolved in a little phosphoric acid, and re-precipitated as before.

The separation of the nickel in the filtrate and its determination as nickel sulphide cannot be recommended, as it has no constant composition and is not insoluble in the ammoniacal solution. According to Krauss it is preferable to treat the ammoniacal solution of nickel with potassa-lye in excess, to boil until all the ammonia has escaped, and to precipitate with bromine water.

Pisani's proposed modification—the use of ammonium acetate in place of ammonium carbonate—cannot be regarded as an improvement.

J. Clark's modification of the Dirvell process (Chemical News, vol. xlviii., p. 262), is not considered by Krauss as in any manner an improvement.

D.—*Methods of Separation and Determination on Various Principles.*

1. N. W. Fischer's proposed separation of cobalt and nickel in an acetic solution by means of potassium nitrite has been already carefully studied by Fr. Gauhe and others and recommended as excellent (*Poggendorff's Annalen*, vol. lxxii., p. 474, and *Zeit. Anal. Chemie*, vol. v., p. 74).

2. Demarçay proposes to use for the separation of the two metals the behaviour of the ammoniacal solution of their salts with metallic zinc.

The experiments undertaken by Krauss show that nickel is first precipitated by metallic zinc, but that we have no certain indication when all the nickel is precipitated and the cobalt begins to fall. Demarçay, in his original communication, states that the *cobalt* is deposited first (*Bull. de la Soc. Chimique de Paris*, vol. xxxii, p. 610).

3. W. Skey proposes a method in the Chemical News, vol. xvi., p. 201, which Krauss finds unsatisfactory.

4. F. W. Clarke (Chemical News, vol. xx., p. 154), utilises the ready solubility of nickel ferricyanide in ammonia. The separation is approximately quantitative, but the quantity of nickel is generally found deficient. Further, after the destruction of the ferricyanides, it is necessary to separate these metals from iron.

5. W. Gibbs proposes to precipitate the nickel or cobalt salts with oxalic acid, to filter off the precipitate, and to titrate the excess of oxalic acid in the filtrate. This method was found especially inaccurate, as the metallic oxalates are somewhat soluble. Better results are obtained if, according to A. Classen, we precipitate the nickel as oxalate by adding acetic acid to a solution of potassium nickel oxalate, dissolve the precipitate in hydrochloric acid, heat to 50°, and titrate with permanganate. In this case it is certainly simpler to ignite the nickel oxalate and to weigh the resulting nickelous oxide.

6. M. Ilinski and G. von Knorre (*Berichte Deutsch. Chem. Gesell.*, vol. xviii., p. 699), mixed the solution of the two metals with a few c.c. of hydrochloric acid, and added to the hot liquid a hot solution of a sufficiency of nitroso-β-naphthol in acetic acid of 50 per cent. After some hours the precipitate of cobaltinitroso-β-naphthol is filtered off, washed with 12 per cent hydrochloric acid, first cold and then hot, and lastly with hot water. The dried precipitate, along with the burnt filter and a few knife-points full of pure oxalic acid, are placed in a Rose's crucible, and after incineration the metal is determined by ignition in a current of hydrogen. The nickel is found by determining the joint weight of nickel and cobalt in an aliquot part of the original substance or calculating the nickel from the difference; or the filtrate obtained on separating the cobalt is evaporated to dryness, ignited, dissolved in hydrochloric acid and a few drops of nitric acid, and the nickel is determined by precipitation with potassa lye.

According to the experiments of Krauss very good results are obtained by this process. The quantity of cobalt operated upon must not be too large, and care must be taken that it is entirely precipitated. A relatively very large proportion of nitroso-β-naphthol solution is required for this purpose, and the precipitate formed is very bulky.

The reaction with cobalt and nitroso-β-naphthol is so sensitive that a visible turbidity is occasioned by traces which cannot be distinguished by the nitrite reaction. An ignition of the precipitate with oxalic acid, or preferably in a feeble current of oxygen, is necessary, especially for large quantities of cobalt. If this precaution is omitted the results are always too high. The cobalt seems to form a compound with carbon which is not destroyed even by ignition ever the blast. If a considerable quantity of cobaltinitroso-β naphthol is ignited first over an open flame and then over the blast until there is no more emission of light from burning organic matter, and the mass glows with a uniform dark red, there is obtained a heavy black powder. If this is covered with cold hydrochloric acid there are formed a black residue and a solution of cobalt chloride of an intense violet colour, which, on evaporation, leaves a gelatinous mass. This can be destroyed by renewed ignition, whilst the black residue is incombustible. If the latter is treated with *aqua regia* at a boiling heat there is obtained a reddish brown or dark brown liquid, which becomes of an intense green on evaporation. From this solution cobalt carbonate is precipitated by sodium carbonate. If this is filtered off and the alkaline filtrate mixed with bromine water there is a further precipitation of cobalt oxide, and even in the filtrate from this precipitate cobalt can still be demonstrated after concentration and ignition.

The author refers, in conclusion, to the new element which Krüss and F. W. Schmidt have found accompanying cobalt and nickel. He expresses the conjecture that a variety of phenomena which he encountered during his researches may be explained by the presence of this element, such as the difficulty of obtaining sulphides of uniform composition, and above all, the fluctuating composition of the oxides, which render their iodometric determination almost impossible.—*Zeit. Anal. Chemie*, vol. xxx., p. 227—242.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

Method and Reactions of the Various Elements.

This condensed communication of micro-chemical manipulations and reactions is intended, as far as possible, to transplant the microscope from the workroom of the petrographist to the laboratory of the analytical chemist. The previous reluctance of chemists to take up these methods seems to me to have a twofold ground—on the one hand, in the belief that a tedious training in the use of the microscope is an indispensable preliminary, and, on the other, in the incompleteness and the unsuitable selection of the micro-chemical reactions which have hitherto been made known. To the former part I will return in the sequel. As regards the second I will state the points of view which I have considered decisive in the choice of reactions, and which must be decisive in future if the microscope is to become naturalised in chemical laboratories.

1. *Minimum Expenditure of Material.*—In order to be able to work with hundredths of a milligramme, in certain cases (*e.g.*, Cl, Pt, Tl, Mg) with millionths of a milligramme the reactions must be exceedingly sensitive. This depends not merely on the sparing solubility of the compounds to be produced, but on their molecular volumes, and quite as much on their ability to form larger crystals. For instance, under the microscope the reaction for silver by the formation of the chromate is quite as sensitive as that by formation of the much less soluble chloride, simply from the reason that the crystals of the chromate are about 100 times as large as those of the chloride. Intense colouration plays a subordinate part. If we have to do with powdery precipitates or coloured liquids, the colouration can scarcely be recognised under high magnifying power.

2. *Minimum Expenditure of Time.*—I felt tempted to give this condition the first place, since the extension of the micro-chemical method depends on it more than all others. That it is practicable, by means of micro-chemical reactions, to submit granules of 0·1 m.m. in diameter to a qualitative examination, is very important for the petrographer, and the chief weight has been laid upon it. Hence micro-chemical analysis, from its origin down to the present day, has remained almost exclusively in the hands of the petrographers. Chemists will feel much more interest in learning that, by the aid of chemical reactions, many investigations may be considerably abridged, and that even greater economy of time is probable on a further development of the method. The detection of the metals in a solution containing calcium, magnesium, zinc, manganese, cobalt, and nickel (about ½ m.grm. of each), was completed in 40 minutes. In another case, where silver, mercury, lead, bismuth, tin, antimony, and arsenic were present, the complete detection was effected within an hour. It is practicable to carry out the investigation on a single object slip of the ordinary long form, so that all the final products were disposed within this small space, which under some circumstances may be very convenient.

In order to economise time and room, reactions which require circumstantial preparation must be excluded, as also such as are tedious in execution. Thus Haushofer's proposed test for glucinum as a chloroplatinate must be rejected, because the crystallisation can be produced only with the aid of the exsiccator. The precipitation of zirconium oxide with potassium sulphate is excluded, since it often does not commence before the lapse of half an hour. The separation of cobalt and nickel by means of oxalic acid and ammonia, which has again been proposed for micro-chemical use by Haushofer, must be decidedly rejected, as it may take longer than half a day. Filtration is admissible only in cases where there is no other expedient. This cuts off many reactions otherwise suitable, as they can be carried out only in a clear liquid. Sparingly soluble compounds which crystallise well and readily best meet this condition, and are most suitable for micro-chemical reactions.

3. *Trustworthiness of the Reactions.*—The reactions must take place with certainty; they must be perceived without difficulty, and they must be characteristic. A reaction which is affected by a slight change in temperature, or in the composition of the solvent, must be at once renounced. It is not possible to work under such conditions when we have to deal at the outside with centigrammes. The number of reactions of general applicability is unpleasantly limited by changes in the form of the characteristic compounds which occur in presence of a third or fourth element. Such reactions may be characteristic in simple solutions, whilst in mixed solutions they may be useless. Cadmium and zinc, when each occurs alone, may be distinguished by means of their oxalates. If they occur together in the same solution the zinc may be recognised by means of oxalic acid, but not the cadmium. Calcium tartrate and calcium carbonate crystallise easily from solutions which contain no barium. If the latter is present neither of the metals can be recognised in the pulverulent or sphærolitic precipitates.

In order that the reactions may be distinct, which is desirable not alone for the sake of accuracy but for the speedy completion of a research, the characteristic crystals must not be so minute that it is necessary to use a magnifying power of 400 or 600 diameters. Especially in this most unfavourable case there should not be formed large masses of pulverulent or flocky by-products, among which the crystals may lie hid, as, for instance, the tiny crystals of zirconium oxide obtained by fusion with sodium carbonate (Lévy and Bourgeois) along with a large excess of pulverulent and granular matter.

(To be continued).

Apparatus for the Reduction of Gaseous Volumes to Normal Temperature and Pressure..—Prof. Lunge.—The author's apparatus, which should have been figured, gives the volume of a gas reduced to 0° and to a pressure of 760 m.m. (*Zeit. Angewandte Chemie*).—*Moniteur Scientifique Quesneville*, Vol. iv., Part 2.

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* *Zeit. Anal. Chemie*

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

May 21st, 1891.

Prof. A. Crum Brown, F.R.S., President, in the Chair.

Messrs. J. A. Foster, William MacDonald, and F. H. Moore were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick R. Holloman, Sugar Refinery, Rawcliffe Bridge, Selby; Arthur Michael, Torwood, Bonchurch, Isle of Wight; F. M. Perkin, Heriot Watt College, Edinburgh; Edmund Charles Rossiter, 39, Brook Green Road, Hammersmith; John Shields, The Byers, Bathgate, N.B.

The President announced that Dr. William Wegg had presented to the Society, through Mr. Warington, a daguerreotype containing the portraits of Messrs. Brande, Cooper, and Phillips.

The following papers were read:—

20. "*Bromo-derivatives of Betanaphthol.*" By Henry E. Armstrong and E. C. Rossiter.

The authors have completed the study of the compounds formed on brominating betanaphthol, to which they have referred in two previous notices (*Proc. Chem. Soc.*, 1889, 71; 1890, 32). They give the following directions for the preparation of tri- and tetrabromobetanaphthol.

Tribromo-β-naphthol is prepared by adding somewhat more than three molecular proportions of bromine to betanaphthol dissolved in thrice its weight of acetic acid; the solution becomes hot, but must *not* be cooled. When all the bromine is added, the mixture is allowed to stand during one hour, and is then heated on the water-bath, at first gently, afterwards at 100°, as long as hydrogen bromide is evolved. The white solid product is recrystallised once or twice from acetic acid, and then treated with twice the theoretical quantity of acetic chloride. The acetate is purified by crystallisation from acetic acid and benzene. When treated with alcoholic potash, it is easily converted into tribromonaphthol.

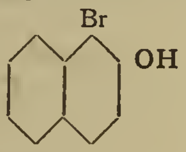
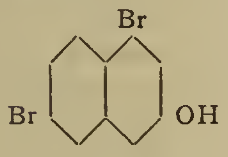
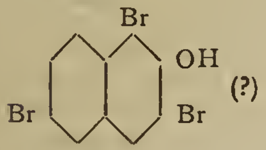
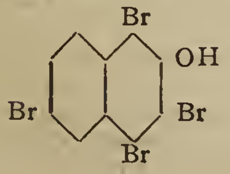
Tetrabromo-β-naphthol is prepared by adding somewhat more than four molecular proportions of bromine to betanaphthol mixed with an equal weight of acetic acid. The solution becomes very hot on adding the bromine, but must not be cooled. When all the bromine is added, the mixture is heated on the water-bath until it becomes quite solid. The product is purified by crystallising once or twice from acetic acid. It is then converted into the *acetate*, and this is crystallised from a mixture of benzene and acetic acid.

The properties of the bromobetanaphthols are summarised in the Table. The preparation of the bromobetanaphthaquinones and of the α-nitrobromonaphthols, included in the fourth column of this table, is described in the next note.

The entire product of the action of bromine in excess on betanaphthol has been carefully examined without any substance having been discovered which affords 1 : 2 : 3-bromophthalic acid on oxidation; the explanation of the discrepancy between the author's observations and the earlier experiments of Smith and Meldola, therefore, yet remain to be discovered.

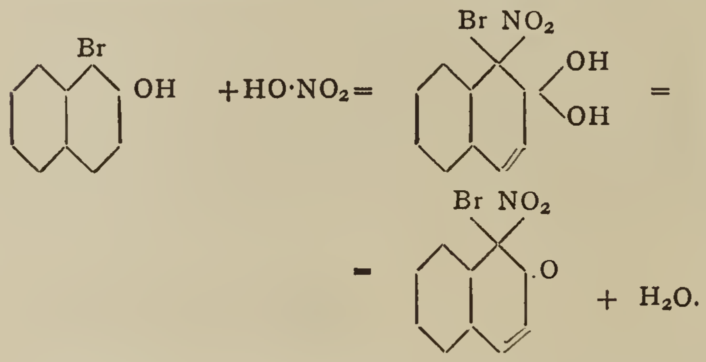
21. "*The Action of Nitric Acid on Naphthol Derivatives as Indicative of the Manner in which Nitration is Effected in the case of Benzenoid Compounds Generally. The Formation of Nitroketo-Compounds.*" By Henry E. Armstrong and E. C. Rossiter.

When warmed with nitric acid, the chloro- and bromo-derivatives of betanaphthol are converted into derivatives of betanaphthaquinone, but, as the authors have pointed out in their previous notice, the formation of these products is preceded by that of an unstable intermediate compound. When these intermediate compounds are carefully heated, they are converted into bromo-derivatives of betanaphthaquinone, and in preparing these latter it is

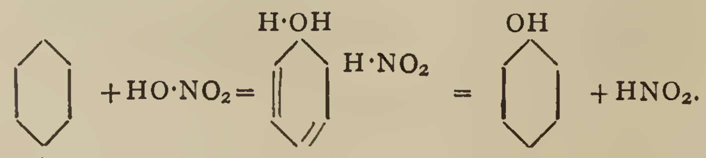
Bromo-derivative.	Description.	Acetate.	Convertible by HNO_3 into
Monobromo-β-naphthol— 	Slender needles very soluble in acetic acid. M. p., 84°.	—	α_1-nitro-β-naphthol. M. p., 103°.
Dibromo-β-naphthol— 	Long shining needles moderately soluble in acetic acid. Crystallised with 1 molecular proportion of acetic acid, m. p., 84°. M. p., 106°.	Elongated lustrous plates. M. p., 125°.	{ $C_{10}H_5BrO_2$. M. p., 145°. { $C_{10}H_4Br_2O_2$. M. p., 171°. α_1-nitrobom-β-naphthol. M. p., 122°.
Tribromo-β-naphthol— 	Lustrous needles less soluble than the dibromo-compound. M. p., 155°.	Soft interlacing needles. M. p., 184°.	$C_{10}H_4Br_2O_2$. M. p., 150°. α_1-nitrodibrom-β-naphthol. M. p., 163°.
Tetrabromo-β-naphthol— 	Very slender silky needles sparingly soluble in acetic acid. M. p., 172°.	Short colourless prismatic needles. M. p., 189 to 190°.	$C_{10}H_3Br_3O_2$. M. p., 190°. α_1-nitrotribrom-β-naphthol darkens at 135°; melts at 136° with decomposition.

desirable to separate the intermediate compound from the excess of nitric acid, and to decompose it by carefully heating it with acetic acid, except in the case of tetrabromobetanaphthol; tribromobetanaphthaquinone is so readily formed from this compound, and is so difficultly soluble and well characterised, that small quantities of tetrabromobetanaphthol may be detected in presence of the di- and tri-bromo-derivatives by simply heating the mixture with acetic acid and nitric acid. Thus, if nitric acid be added to dibromobetanaphthol, suspended in acetic acid, a clear solution is obtained, which, after a short time, deposits a crystalline substance; if quickly separated by filtration, this product is almost colourless, but it decomposes when kept, becoming yellow. It was conceivable, judging from the manner in which it was produced, that the compound was a nitrate, formed by the simple displacement of the hydroxylic hydrogen by NO_2, and the results of analysis were in accord with this view; but such a nitrate should be reconvertible into the parent substance by treatment with alkali, whereas actually it affords, as chief product, *bromonitronaphthol.* Bromobetanaphthol, in like manner, eventually yields α_1-nitrobetanaphthol, and the tri- and tetrabromo-derivatives afford di- and tri-bromonitrobetanaphthol; the bromine atom displaced by NO_2 by this method of treatment, there can be little doubt, is invariably that in the α_1-position.

The authors are of opinion that the intermediate compounds in question are nitrobromoketo-derivatives corresponding to the dichloroketo-compounds of Zincke, and that their formation affords evidence that the elements of nitric acid first become added to the bromonaphthol, thus—



The theory that the formation of such addition compounds precedes that of nitro-compounds generally appears to afford a satisfactory explanation of a large number of well-known facts which hitherto have remained unexplained. The non-production of nitro-compounds from paraffins and their derivatives, except in a certain very limited number of special cases, appears as the natural consequence of the inability of paraffins to form addition compounds. The theory affords a simple explanation of the formation of nitro-derivatives of *phenols* on nitrating hydrocarbons, to which Nölting has drawn special attention in the case of toluene and orthoxylene (*Berichte*, 1885, 2670; 1888, 3158), for if the addition compound lose HNO_2 instead of H·OH a phenol would result, thus—



An agent that would favour the separation of the elements of water from the addition compound would increase the production of the nitro-compound and diminish that of the phenol; and, as a matter of fact, it is known that when a mixture of nitric and sulphuric acid is used there is less of the phenol derivative produced than when nitric acid alone is employed. A compound such as the addition compound of benzene with nitric acid above represented, would obviously be unstable and prone to undergo oxidation; hence it is not difficult to understand that so large an amount of nitrous fume should be produced even on nitrating benzene. The reduction in the amount of such fume, and the improvement of the yield of nitro-derivative effected by adding sulphuric acid, is doubtless attributable to the action already referred to of the acid in promoting the separation of the elements of water; sulphuric acid must be supposed, in fact, in such cases to act not merely as a dehydrating agent in maintaining the nitric acid concentrated, but to exert a specific influence on the course of change. Lastly, the resinous matters often formed in large amount on nitrating many phenols are, doubtless, products of the interaction of several molecules of the addition compounds, or of the keto-compounds formed from them in the first instance.

The non-production of resinous matters when sulpho-acids are treated with nitric acid so as to form the corresponding nitro-compounds by displacement of the SO_3H group by NO_2, a modification which often makes it possible to prepare nitro-compounds not obtainable by the direct action of nitric acid, is also elucidated by the author's theory; the addition compound formed in such a case would very readily break up into sulphuric acid and the nitro-derivative, thus—

$$:C(OH)\cdot C(SO_3H): + HO\cdot NO_2 = \cdot C(OH)_2\cdot C(NO_2)(SO_3H)\cdot$$
$$= : C(OH)\cdot C(NO_2) : + HO\cdot SO_3H.$$

DISCUSSION.

Mr. GROVES said that he had been much struck, when preparing dinitrobenzene from benzene which had been most carefully purified, on observing that a very appreciable quantity of trinitrophenol was produced; the theory of nitration put forward by the authors would fully account for this.

22. "*A New Method of Preparing Nitro-Derivatives and the Use of Nitrogen Dioxide as a Nitrating Agent.*" By HENRY E. ARMSTRONG and E. C. ROSSITER.

Reference has been made in the foregoing note to the production from the compounds formed by the addition of the elements of nitric acid to the bromo-derivative of betanaphthol of nitro-derivatives of the naphthol *on treatment with alkali*, a bromine atom becoming displaced by NO_2. As in this interaction a bromine atom is removed and an atom of hydrogen is added to the CO group, such a method of treatment obviously is scarcely that best calculated to effect the formation of the nitro-derivative, and, as a matter of fact, the nitro-derivative is not the only product. On treating the addition compound, however, with sulphurous acid, a practically theoretical yield of the nitro-naphthol is obtained; this method appears to be of general application.

The authors have been naturally led to study the action of nitrogen dioxide, NO_2, on unsaturated compounds of various kinds, in the expectation of obtaining addition compounds which by loss of HNO_2 would pass over into nitro-derivatives of the substances treated. They find that such addition compounds are actually obtainable, and that, on treatment with alkali and reducing agents, they yield nitro-derivatives. Thus betanaphthol affords as much as 75 per cent of its weight of nitro-betanaphthol; alphanaphthol behaves similarly. In some cases, the addition compound is so unstable that it spontaneously decomposes; thus phenol at once yields a mixture of ortho- and para-nitrophenol. The authors propose to study the behaviour of unsaturated compounds generally towards nitric acid and nitrogen dioxide from the point of view indicated in this and the previous note.

23. "*Nitrification.* Part IV." By R. WARINGTON.

The first section of the paper describes early experiments, made in 1878—84, showing the existence of an agent producing only nitrites, and the means of separating it from soil. It was at first thought that the age of the culture was the factor which determined the loss of the power of producing nitrates, but this idea was negatived by subsequent experiments. Successive cultivation in ammoniacal solutions, made permanently alkaline with disodium carbonate, was found to be a certain method of obtaining a purely nitrous agent. Pasture soil yielded the nitrous agent more readily than arable soil.

The isolation and properties of the nitrous organism are next described. The gelatinous matter which appear under certain conditions at the bottom of old cultures was in 1883 examined microscopically, and found to consist of circular corpuscles imbedded in a zooglœa. In 1886 this jelly was spread on gelatin, but it yielded no nitrifying organism. In 1889 a systematic attempt at the isolation of the organism commenced. Successive cultivations were made in an ammonium carbonate solution, supplied with phosphates, &c., but containing no organic matter. A series of transparent cultures was obtained, containing only nitrites. These cultures were spread on gelatin and agar-agar, the composition of the jelly being made to correspond, as far as possible, with that of a nitrifiable solution. The later cultures yielded on gelatin one organism only, a short bacillus. This and all the other organisms obtained by cultivation on gelatin from nitrified solutions were seeded into both liquid and solid media suceptible of nitrification, but without result. Microscopical examination of the nitrified solutions showed that cocci were abundantly present, but these never appeared on the gelatin cultures.

The first attempts to separate the nitrous organism by the dilution method failed. By substituting an ammonium chloride solution with calcium carbonate for the ammonium carbonate, success was obtained in October, 1890, three nitrified cultures seeded with dilutions of 1/10,000, 1/100,000, and 1/1,000,000, giving no growth on gelatin.

The nitrous organism thus obtained oxidises ammonia to nitrous acid, and has no effect on nitrites. It produces nitrous acid in solutions of asparagine, milk, urine, and urea. Grown in broth containing calcium nitrate, it does not reduce the nitrate to nitrite. It produces no turbidity or visible change when grown in broth or in any of the other solutions named.

The nitrous organism requires no organic matter for its nutrition; it is apparently capable of assimilating carbon from acid carbonates. The presence of either calcium or sodium acid carbonate distinctly favours nitrification; neutral sodium carbonate greatly hinders nitrification. The proof that carbon is assimilated from carbonates has been furnished by Winogradsky. The energy that is required for the decomposition of a carbonate is apparently furnished by the oxidation of ammonia on nitrogenous organic matter. Calcium acetate (0·25 grm. per litre) favours nitrification when only the nitrous organism is present.

The nitrous organism occurs as nearly circular corpuscles, varying from minute points up to nearly 1·0 μ in diameter; these circular organisms stain deeply. It also occurs as oval cocci, the length frequently exceeding 1·0 μ, the ends occasionally more or less truncated.

The remainder of the paper deals with the nitric organism. Results obtained in 1880—81 revealed the existence of an organism which energetically converted nitrites into nitrates, but was apparently unable to oxidise ammonia. In 1886 and 1890 attempts were made to separate the active organism from the 1881 cultures by growths on gelatin and potato; none of the organisms thus separated had any power of oxidising either ammonia or nitrites. Recent results show that the nitric organism develops freely in inorganic solutions containing potassium nitrite, phosphates, &c., especially if supercarbonates are present. Monosodium carbonate, 1—4 grms. per litre, exerted a very favourable influence, 6 grms. a retarding influence. Disodium carbonate greatly hinders its action.

The nitric organism produces neither nitrites nor nitrates in ammoniacal solutions, even when carbonic acid, or monosodium carbonate, or calcium acetate is supplied. In the absence of ammonia it energetically converts nitrites into nitrates; the presence of ammonia is apparently a great hindrance to its action.

An attempt to isolate the nitric organism by the dilution method failed, but apparently only one other organism (a stout bacillus growing on gelatin) was present in some of the cultures obtained. The stained preparations from these cultures contained an abundance of the minute circular organisms observed in pure cultures of the nitrous organism; the form of the two organisms is thus apparently similar.

The nitrification performed by soil thus appears to be the work of two organisms, one of which oxidises ammonia to nitrite, while the other oxidises nitrite to nitrate. The first organism is easily separated from the second by successive cultivations in solution of ammonium carbonate. The second is (probably) separated as easily from the first by successive cultivations in solution of potassium nitrite containing monosodium carbonate.

The paper was illustrated by micro-photographs, showing the nitrous organism as developed in ammoniacal solutions, milk, and broth; and the nitric organism grown in a solution of nitrite. The photographs were executed by A. Pringle, Esq., and Dr. Bousfield.

Discussion.

Prof. **Thomson**, referring to the method of cultivation on gelatinised silica described by Mr. Warington, said that the account given of the method reminded him of an observation made so far back as 1875; a solution of silica which he had prepared by dialysis had solidified, and he noticed, after a time, that a growth of what he thought was an ordinary mould had appeared on the surface; there could have been nothing present besides the silica, except traces of mineral salts.

Dr. **Munro** said that he was glad to see that his contention that organic matter was actually prejudicial to the growth of the nitrifying organism was now proved. Referring to the conclusion that two organisms were concerned, one of which converted the ammonia into nitrite, the other extending the oxidation to nitrate, he asked how those cases in which only nitrates were found were to be explained; it very rarely happened, for instance, that in well-waters the ammonia was converted into nitrate with intervention of nitrite. Perhaps two organisms were present, which did their work simultaneously.

Mr. **Warington**, in reply, said that the two organisms would have no difficulty in acting together in very weak solutions of ammonia.

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. cxii., No. 22, June 1, 1891.

Calorimetric Researches on Humic Acid derived from Sugar.—MM. Berthelot and André.—The result of these researches is that humic acid is a polybasic acid capable of losing one part of its water of hydration by mere desiccation, and even in the midst of water at ordinary temperatures in virtue of true dissociation. In this state it combines with three equivalents of potassa, forming insoluble salts; the first is monobasic, very stable, formed with the liberation of +18 cal., *i.e.*, comparable to that of the solid alkaline salts formed by the most powerful mineral acids. The two equivalents of base which then unite to the first salt form a tribasic salt equally insoluble, but liberate much less heat. These humic matters, comparable to those of the soil, undergo thus, under the influence of a base, phenomena of hydration; then, by the inverse action of acids, effects of spontaneous hydration by dissociation—a series of effects in virtue of which external energies should be continually introduced in the chemical reactions accomplished during the course of natural vegetation. Humic acid is formed from sugars with the liberation of heat, but this liberation expends only a portion of the thermic excess of these carbohydrates over carbon and water capable of being formed by total destruction. Hence it results that humic acid would be equally formed from carbon and water with absorption of heat, *i.e.*, that it contains an excess of energy capable of being expended in the course of the consecutive transformations which are effected either by purely chemical actions or with the concourse of microbian agents.

Determination of the Molecular Weight at the Critical Point.—P. A. Guye.—A purely mathematical paper not susceptible of useful abridgment.

Detection and Separation of the Platinum Metals, and in Particular of Palladium and Rhodium, in Presence of the Common Metals.—A. Joly and E. Leidié.—(See p. 292).

On the Specific Heats of Some Solutions.—W. Timofeiew.—The author gives his results in the form of a table.

On the Oxidation-Products of Uric Acids.—C. Matignon. — A thermo-chemical study of allantoine, alloxane, and alloxanthine.

On the Use of Ammonium Selenite for the Diagnosis of the Alkaloids.—A. J. Ferreira da Silva.—(See p. 291).

MEETINGS FOR THE WEEK.

Wednesday, 24th.—Geological, 8.
—— Society of Arts, 4. (Anniversary).
Thursday, 25th.—Chemical, 8. Extraordinary General Meeting.
—— Royal Society Club, 6.30. (Anniversary).
Friday, 26th.—Royal Institution, 9. (Faraday Commemoration Lecture). Prof. Dewar, F.R.S.
—— Physical, 5. "The Construction of Non-Inductive Resistances," by Prof. W. E. Ayrton, F.R.S., and Mr. T. Mather. "The Influence of Surface-Loading on the Flexure of Beams," by Mr. C. A. Carus-Wilson. "On Pocket Electrometers," by Mr. C. V. Boys, F.R.S. "On Electrification due to the Contact of Gases with Liquids," by Mr. J. Enright, B.Sc.

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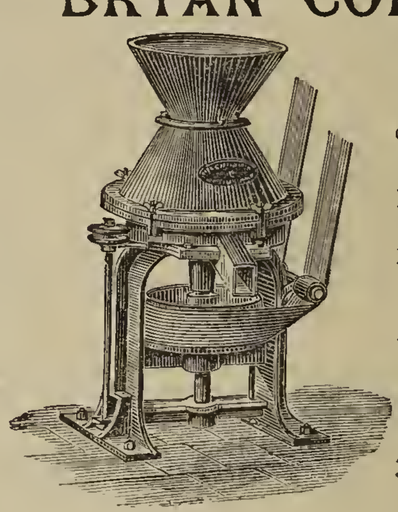

THE CHEMICAL NEWS.

Vol. LXIII., No. 1648.

ON A

NEW DEPARTURE IN MATTE SMELTING FOR COPPER AND SILVER IN REVERBERATORY FURNACES.

By W. BETTEL, Metallurgist and Chemist.

In October last, owing to the smelting arrangements at the Willows Mine being unsatisfactory, I was asked by the managing director of the Company to take this department under my supervision, a handsome bonus being promised if I were successful. This, in the directors' opinion, I have now earned.

The absence of sulphur in our ores and fluxes (except in trifling amounts), and the presence of antimony exceeding the percentage of copper in the ores to be smelted, the copper existing as azurite and malachite—average 4 per cent copper wet, and 40 ozs. silver per ton (2240 lbs.)—the bulk of the ore being hydrated oxide of iron and antimonious compounds—made the problem of matte production one of difficulty at first sight.

Other difficulties I had to contend with. Bad coal, containing from 18 to 40 per cent ash, gave little heat in the furnace and much trouble (with the clinker) in the grate; huge accretions forming in that part of the grate level with the bridge. I found that it was the practice of the furnacemen, once every twelve hours, to pour water into the grate through holes in the roof, to cool the clinker, which was then removed by steel bars and sledge hammers; the furnace in this manner being cooled to such an extent that fully four hours were lost every day.

This led me to devise a method of burning this poor coal to advantage, at the same time preventing the formation of the huge masses of clinker which retarded operations. This accomplished, as will be seen from the context, there still remained one more difficulty.

When I took charge, although the furnace had been running five months, only about 4000 lbs. matte was obtained: opinion being divided as to whether the copper and silver went into the slags, or were, in some way, volatilised. My opinion, that the matte would be found in and beneath the furnace bottom, received no credence, and it was with the greatest difficulty that I persuaded the management to let me "flow out" the furnace and alter another one (not then started) in order to carry out my arrangements with forced draught, then to excavate the bottom, &c., from the cooled furnace (there being no vault), and rebuild on an improved plan.

It was then found that the matte had penetrated four feet six inches below the furnace bottom, into every conceivable crack and crevice, lumps of matte three or four inches in diameter, *with cores of charcoal*, being formed here and there. For a time these appearances puzzled us, until in the soil, or "veldt," outside were found large roots, similar in shape to the lumps of matte. The roots had been carbonised and matte had flowed round the carbonised residue, assuming the shape of the original roots. Further, about four inches of each "bottom" was loose sand, proving that the temperature obtained in "smelting in" the bottoms and during the subsequent five months' smelting had been insufficient for ordinary operations.

About 60 tons of material, containing about 18 tons matte, was obtained in the excavation—every joint of the brickwork below the slag-line being a conduit for the conveyance of matte to the foundation. I had, therefore, to arrange a process for cooling the lower part of furnace bottom, sides, and bridge by vaults and brick tubes, working under a forced draught *with moist air*. When the furnace was ready, I decided to melt the sand bottom in successive layers with a material that would cause its cohesion and impart a slight fusibility under intense heat to produce a bottom almost impervious to molten matte. Then, for the protection of the sides I found a substance to replace the "daagga"—a "mending" composed of mud and sand in some quartz, from abandoned workings, which I had crushed and mixed with yellow clay. This stood fairly well.

Drawing upon my experience in furnace-work at (1) Middlesborough-on-Tees, where I was in practice as a metallurgical chemist and public analyst for six years; at (2) The Sheffield Smelting Company's Establishment (Gold, Silver, Platinum Metals, Lead, and Copper-Smelting, &c., Refining Works), and a similar establishment I had charge of in Birmingham, where, between the two, I had seven years' experience in silver, &c., smelting, and the advantage of an intimate acquaintance with the reduction of all classes of ores of gold, silver, copper, &c.; and (3) as smelting works manager at the New Morfa Copper and Silver Works, Swansea (Messrs. Williams, Foster, and Co., Ltd.), where I had charge of 30 smelting and refining furnaces, &c.,—I decided to adopt the following arrangements:—

1. To construct vaults as a foundation; over these a number of brick channels (suitably arranged along the whole width of the furnace), covered with bricks, rubbed joints and grouted, communicating to steam-blast arrangement at one corner (flue end) of furnace, to ashpit at outlets, and after cooling bridge, to "blowpipe jets" in bridge and roof.
2. To work the furnace under pressure with closed ashpit, using an injector arrangement similar to, but simpler than, the Körting's injector.

These gave me the following advantages:—(*a*) I could reduce the heat in the grate, *making the ash loose and friable*, and (*b*) transfer such heat as well as heat from furnace bottom abstracted by passage of air and steam through the brick tubes, in the form of hydrogen and carbonic oxide, to the laboratory—the hearth—of the furnace, where these gases are burnt with the hot blast from roof and bridge, producing an intense heat similar to that obtained in a Siemens regenerative gas furnace.

Having, by the brickwork tubes or channels, considerably reduced the usual depth between skimming plate and bottom, I smelted the bottom in three thin layers, the first two with sifted sand to which 1½ per cent lime was added and intimately mixed, and on these a seasoning charge of sharp slags smelted. The upper layer consisted of sifted river sand only, which, after smelting, was seasoned as before. During the smelting the heat had to be checked, as the bricks, although nearly as infusible as those of the Abernant (Dinas) Co., could not withstand the intense heat produced.

The next problem was to smelt refractory antimonial oxide and carbonate ores (70 per cent of which was delivered to furnaces in pieces from 2½—3 cubic inches), *without sulphides*, except in traces, *and still produce clean slags*, collecting 90 per cent at least copper and silver at one operation in the species of matte, or speiss, produced at a profit, coal being 50s. per 2000 lbs., stores generally about 500 per cent over English prices, and white labour £27 per month (furnacemen).

This I solved in the following manner. I selected as a type of slag, which would be as economical as any, Mr. Malvern W. Iles's type "C," containing about 27 per cent silica. This I produced by means of a flux. I found from one of our waste heaps out of the mine a silicious, ferrous, calcic, magnesic carbonate, containing 5 per cent and upwards of anthracitic carbon.

This, together with coal and "cobbing," and rich "sharp" slags composed the fluxing part of ou rcharges. Owing to absence of suitable crushing appliances, the coarse ore we are compelled to put in the furnace takes a considerable time to smelt, the heat of slag formation being proportionately high; otherwise, judging from the fluid slag produced and its comparatively low melting-point, were we able to more thoroughly mix our charges the capacity of our furnaces would be doubled. However, three charges are smelted in 24 hours in each furnace, *clean slags are produced*, the copper and silver are converted into a "matte"—*antimony being the collecting agent in place of sulphur*—and 90 per cent of copper and silver is recovered.

My explanation of the changes involved is as follows:—Oxide of antimony fluxed with lime and magnesia will dissolve in a bath of basic ferrous silicate, and be reduced by carbon conjointly and simultaneously with copper and silver, forming a fusible and brittle antimonide of copper and silver, with a formula of Sb_2Cu_5—provided that the slag does not contain more than 5 per cent magnetic oxide of iron; otherwise the slag is rich, copper and antimony are lost, and some silver volatilised. Excess of carbon is avoided as tending to throw down metallic iron, making the matte coarse and difficult to break.

After satisfying myself that the bottom of No. 1 furnace was in working order I commenced to smelt, and found *after three charges* that I had *saturated the bottom of a 3-ton furnace with* 500 *lbs. of matte*, instead of 36,000 lbs. which was lost in the old furnace. The bottom, at the time of writing, is an excellent order, and the furnace is delivering over 90 per cent copper and silver in form of "matte."

We concentrate for 35 ozs. ores 16·4 tons of ore, or 27½ tons of charge, into 1 ton matte = 91·3 per cent of silver recovered; about 7·5 to 8 per cent going into slags, and the remainder volatilised. We should consider on 35 ozs. ore 80 per cent recovery fairly good, and this was the percentage of extraction I had agreed to accomplish. The average composition of slags and "matte" is seen from the following analyses I have made from No. 1 furnace:—

Slag.

Silica	=27·05	per cent.
Ferrous oxide..	=53·30	,,
Ferric oxide	= 2·55	,,
Alumina	= 4·50	,,
Manganous oxide	= 3·00	,,
Phosphoric acid	= 0·21	,,
Arsenious acid	= 0·055	,,
Antimonious acid	= 0·130	,,
Cuprous oxide	= 0·45	,,
Silver	= 0·005	,,
Sulphur	= 0·05	,,
Bismuth oxide	= 0·10	,,
Lead oxide	= 0·45	,,
Lime	= 5·32	,,
Magnesia	= 2·80	,,
Total ..	=99·97	,,

"Matte."

Copper	=52·50	per cent.
Antimony . ..	=38·00	,,
Arsenic	= 2·00	,,
Sulphur	= 2·06	,,
Iron	= 3·60	,,
Lead..	= 0·25	,,
*Silver	= 1·59	,,
Total ..	=100·00	,,

* =520 ozs. silver per ton of 2240 lbs.

The silicious iron magnesian limestone is fairly represented by the following analysis, although the material is far from uniform in composition:—

Insoluble matter—principally silica	=37·40	per cent.
Alumina, with trace of manganese oxide ..	= 2·94	,,
Ferrous carbonate	= 9·57	,,
Calcic carbonate	=30·40	,,
Magnesic carbonate	= 8·92	,,
Water and volatile matter..	= 5·77	,,
Carbon (anthracitic)	= 5·00	,,
Total	=100·00	,,

The antimonial copper matte we produce, by an oxidising treatment in a special form of hot blast reverberatory furnace, yielded a crude copper (in shot) for silver extraction, assaying:—

Copper from "Matte."

Copper	=93·55	per cent.
Antimony	= 1·31	,,
Arsenic	= 0·60	,,
†Silver	– 3·26	,,
Oxygen and other substances not estimated	= 1·28	,,
Total ..	=100·00	,,

† =1064·9 ozs. per ton of 2240 lbs.

—containing practically all the silver—the slag containing about 15 ozs. per ton silver, and also 12 per cent of the copper and 10 per cent antimony in original matte. The remainder of antimony volatilised.

Although at the Willows Copper (Arg.) Syndicate's Works it was inconvenient to interfere with the arrangement of flues, still the steam for steam blast may be raised by means of heat from waste furnace gases (as is done in iron and steel works). Here we use an 8 horse-power locomotive boiler to supply steam-blast to two furnaces. This boiler consumes 800 lbs. coal for twenty-four hours, delivering steam at 20 lbs. pressure through four jets $\frac{4}{16}$ inch (bare) diameter—two to each furnace. The influence of steam in preventing the formation of all except "rotten" clinker is most marked, and with my arrangement the commonest coal can be made to yield good results, whilst with good coal the increased duty obtained (especially with the arrangement for heating the moist air) is very striking. Another peculiarity is, that the coal is burnt to a clean ash, and the only coal or coke which falls through the bars is during grating, and that is small in amount.

By adapting this furnace to copper-smelting, any grade of matte within reasonable limits may be obtained according to the character of flame produced, which may be altered at will from reducing to oxidising or neutral by suitable valves in the air passages, while for metal or regulus-roasting and copper-refining it could not be surpassed for ease (and cheapness) in working.

There is a modification of this hot-blast reverberatory furnace—for civilised places where decent iron castings and wrought iron fittings are procurable at reasonable rates—which I propose to work elsewhere if opportunity occurs. This plan embraces water-jacketting portions of the furnace most exposed to wear, and does not need more than a few inches of foundation (concrete)—no vault needed. From results already obtained I expect this furnace to be more economical than a gas furnace with regenerator, and, with certain modifications, would be found applicable to any operation requiring an intense, heat, which may be made oxidising, neutral, or reducing at will.

The Willows Copper (Arg.) Mine,
near Pretoria, Transvaal, South Africa,
March 27, 1891.

The Metallurgy of Steel.—The Société d'Encouragement pour l'Industrie Nationale, of Paris, France, has awarded a prize of 2500 francs to H. M. Howe for his work on "The Metallurgy of Steel," lately reviewed in these columns.

NOTE ON A VOLATILE COMPOUND OF IRON AND CARBONIC OXIDE.*

By LUDWIG MOND, F.R.S., and FRIEDR. QUINCKE, Ph.D.

In a paper on the action of carbonic oxide on nickel, communicated to the Chemical Society (*Journal*, lvii., 749, 1890) by us in conjunction with Dr. Carl Langer, and which dealt with the preparation and properties of nickel-carbon oxide, it was stated (p. 752) that all experiments to obtain a similar compound with other metals had been unsuccessful. Considering it very improbable that nickel should be the only metal forming such a compound, we have continued these experiments, more particularly with iron, under very varied conditions, and have at last succeeded in volatilising notable, although very small, quantities of iron in a current of carbonic oxide.

If very finely divided iron, obtained by reducing iron oxalate in a current of hydrogen at the lowest possible temperature, exceeding but little 400° C., is allowed to cool in hydrogen gas to 80° C., and then treated with carbonic oxide, the issuing gas imparts a yellow colour to the flame of a Bunsen burner into which it is introduced, which continues, even at ordinary temperature, for several hours; and by passing it through a heated glass tube a metallic mirror is formed at between 200° C. and 350° C., while at higher temperatures black flakes are formed.

On dissolving these mirrors the solutions gave all the known reactions of iron in remarkably brilliant colours. The oxide obtained by dissolving the mirror in nitric acid, precipitating with ammonia, and heating to constant weight, was reduced by hydrogen. We obtained from 0·4342 gr. of oxide 0·3037 Fe = 69·93 per cent. Fe=56, O=16 require 70·00 per cent. There can thus be no doubt of these mirrors consisting of iron. The black flakes obtained at higher temperature consist of iron and carbon. By the combustion of the substance and absorption of the carbonic acid formed in caustic potash, we found 79·30 per cent of carbon.

However, even under the most favourable circumstances, the quantity of iron obtained in this way has been very small. Treating 12 grms. of finely divided iron with carbonic oxide during six weeks, we volatilised only about 2 grms. of iron. As the action of the carbonic oxide became less energetic, after a time we had to interrupt the operation and heat the iron to 400° C. in a current of hydrogen for about twenty minutes every five or six hours. By passing 2½ litres of carbonic oxide per hour over the iron, the issuing gas contained at its best not more than 0·01 gr. of iron, which corresponds (if we assume the volatile iron compound to have the same composition as nickel-carbon oxide) to less than 2 c.c. of the compound in a litre of gas.

This great dilution makes the study of the properties and composition of the compound very difficult.

In passing the gases containing it through sulphuric acid the compound is completely absorbed, but the solution decomposes very rapidly.

In passing the gases through benzol or heavy mineral or tar oils the compound is partially absorbed, but all the substances we have tried only take up a small quantity of it. The solutions obtained are of a tawny colour, and decompose on exposure to the air, with separation of iron hydroxide.

The solutions in mineral oils boiling between 250° C. and 300° C. seemed to us the most suitable for studying the composition of the compound; but we found it impossible to exhaust it from these solutions by means of the vacuum pump.

On raising the temperature of the solution to 100° C., the solution remained clear, and under a vacuum of 500 m.m. mercury we obtained only a small quantity of a mixture of air and carbonic oxide (from 30 c.c. of oil about 5 c.c. of gas).

On raising the temperature to 180° C. the solution turned black from separated metallic iron, which was found free from carbon, and carbonic oxide was slowly evolved, which sometimes contained a very small quantity of carbonic acid, but was always quite free from hydrogen.

We have determined the quantity of iron and carbonic oxide obtained by heating about 30 c.c. of heavy mineral oil, through which the gas containing our compound had been passed from 8—16 hours in a glass vessel very nearly filled with the oil and connected by a capillary tube to a Hempel burette filled with mercury.

The tube was heated to 100° C. under a vacuum of 500 m.m. mercury, until the volume in the burette remained constant. The tube was cooled down to measure the exact volume of this gas, and was then heated up to 180° C. until no more gas was evolved, which took from 1—2½ hours. The increase in the volume of the gas by the latter operation gave us the carbonic oxide in the compound.

The iron contained in the oil was, if necessary after dilution with ether, collected on a filter and converted into oxide. The filtrate was distilled off, and the small residuum treated with hydrochloric acid and precipitated with ammonia, and the resulting small quantity of oxide of iron added to the first. In this way we obtained the following results :—

		Found.		Corresponding to.		Calculated.		
No.	Solvent.	Increase of volume. C.c./760 m.m.	Fe_2O_3. Grm.	CO. Grm.	Fe. Grm.	1 atom Fe to 4 atoms CO. Grm.	Proportion of atoms CO to 1 Fe.	Quantity absorbed of $Fe(CO)_4 = \frac{1}{4}$ CO.
1.	Paraffin oil.	31·32	0·0270	0·03917	0·01890	0·01958	4·144	7·83
2.	Petroleum oil.	34·29	0·0304	0·04288	0·02128	0·02144	4·030	3·57
3.	,,	20·2	0·0174	0·02527	0·01218	0·01263	4·150	5·05
4.	Kerosine.	38·18	0·0320	0·04775	0·02240	0·02387	4·264	9·54
5.	,,	50·45	0·0446	0·06310	0·03122	0·03155	4·042	12·61

These figures, although only approximate on account of the very small quantities of substance and the imperfect method we had to use for their determination, make it very probable that the volatile iron compound is iron tetracarbonyl [$Fe(CO)_4$], analogous to nickel tetracarbonyl [$Ni(CO)_4$].

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* A Paper read before the Chemical Society, June 15, 1891.

METHOD OF DETERMINING INDIGOTINE FOR COMMERCIAL PURPOSES.

By F. A. OWEN.

Under the above heading the author published a paper in the *Journ. Amer. Chem. Soc.*, in November, 1888. The process as there described has been materially modified, and as now practised in the mills of the Burlington Woollen Company, at Winooski, Victoria, is as follows :—

From the sample shave off and coarsely powder 2 or 3 grms., from which weigh with exactness two portions of 1 grm. each. In the first determine the moisture by drying in a watch-glass at 100° C., and afterwards ignite this portion and determine the ash. The second portion is brushed from the scale-pan directly into a glass mortar, ground for a time dry, then water is added and the grinding is continued for some time; the pestle is rinsed into mortar, and the whole allowed to settle for a minute or so, and all that will freely pour off is decanted into a glass-stoppered 200 c.c. flask. The sediment is re-ground with water, and decanted as before until the whole has been transferred. Three grms. of zinc dust and 60 c.c. of commercial strong ammonia are now added; then the flask is filled to ½ c.c. above the mark and shaken. Reduction takes place in from half an hour to two hours, during which time it should be shaken occasionally. When the reduction is complete the froth will subside and the solution become pale yellow, or, with some samples which contain chlorophyll or some non-reducible green colouring matter, greenish yellow. Then remove with a pipette 50 c.c. to a beaker or porcelain dish, add 5 or 6 drops of ether, and agitate by blowing air through with the pipette until most of the indigotine is precipitated. Acidify in moderate excess with HCl, heat to boiling, and pass through a tared filter; dry at 100° C., and weigh. It is not necessary to take any special care to prevent absorption of moisture while weighing, only the filter paper must be, as nearly as possible, in the same condition as when tared. The results are accurate. The lots when bought and re-tested should show no variation from the sample except in the percentage of moisture, which will be higher than in the sample. Indigo often loses 20 per cent in drying, and not unfrequently yields 80 per cent of indigotine, after drying. — *Jour. Amer. Chem. Soc.*, Jan., 1891.

SOME CHEMICAL PRODUCTS OF BACTERIAL GROWTH, AND THEIR PHYSIOLOGICAL EFFECT.

By E. A. von SCHWEINITZ,
Chemical Laboratory, Bureau of Animal Industry, Washington, D.C.

For a short time I have been engaged in studying the chemical products formed by the hog cholera and swine plague germs by their growth in artificial culture media, and have succeeded in isolating an albumose and ptomaine from each.

To distinguish the products the names *sucholotoxin* and *sucholoalbumin* have been given to the substances from the hog cholera cultures, and *suplagatoxin* and *suplagoalbumin*, respectively, from the swine plague cultures.

The albumoses are white, pulverulent substances, soluble with difficulty in water, and precipitated from this solution by absolute alcohol. They can be obtained in crystalline plates by drying over sulphuric acid, *in vacuo*.

The ptomaines are best obtained in the form of the double platinum salts, as the hydrochlorides are difficultly crystallisable. These double salts are very light yellow in colour, readily soluble in water, difficultly so in alcohol, and appear under the microscope as needle-like crystals. (Specimens of the albumoses and platinum salts were exhibited).

A subcutaneous injection of a small quantity of these substances is sufficient to produce death in guinea pigs in from 24—48 hours.

If, however, a much smaller quantity is injected, and the injection repeated a number of times, the animals are protected from the corresponding disease when communicated by direct inoculation with the germ. In quite a long series of experiments the check animals invariably died, while the treated ones recovered after inoculation with the germ.

More recently, Dr. W. H. Gray, of Washington, and myself have conducted some experiments upon guinea-pigs, and succeeded in producing great resistance, and subsequently immunity from diphtheria, by first treating the animals with the chemical products obtained from cultures of the germ.

There is every reason to hope that these results can be turned to practical application in the diseases of both animals and men.—*Jour. Amer. Chem. Soc.*, Jan., 1891.

NOTES ON THE ESTIMATION OF NITROGEN IN NITRATES BY KJELDAHL'S METHOD.

By LYMAN F. KEBLER.

In the history of analytical chemistry no method has been so universally adopted, in so short a time, as the "Kjeldahl Method" for the estimation of nitrogen. The fundamental reactions in the method, according to Dafert (*Ztschr. Anal. Chem.*, 1888, 27, 222), are as follows:—First, the sulphuric acid abstracts from the nitrogenous organic material the elements of water and ammonia gas, forming ammonium hydrate, and subsequently ammonium sulphate; second, the sulphurous annydride which is evolved reduces the nitrogenous compounds, but this is insignificant as compared with the first reaction.

The original method is not applicable for the estimation of nitrogen in all inorganic and organic combinations; but the method has been modified to such an extent that the nitrogen in almost all inorganic and organic combinations can be estimated by it.

The method, as followed by the writer, is given in detail in Bulletins Nos. 19 and 24 of the U.S. Agricultural Department.

The instructions which were followed did not indicate how the distillate should be received in the receptacle.

After making a series of experiments, the writer found it necessary to connect the end of the condenser with the receptacle by a glass tube dipping below the liquid contained in the receiving flask.

While working with this method, the writer observed that whenever the sulphuric acid was added to some material containing nitrates, nitric acid was evolved, and could be detected by its odour at the mouth of the flask. It was plainly evident that this must be overcome in some way. It was observed that when the sulphuric acid was added quickly and the flask shaken moderately, none, or very little, of the nitric acid escaped from the sulphuric acid; none escaped from the flask.

After this observation, a series of experiments were made, with the following results:—

1st. The sulphuric acid was added slowly in *eight** different experiments, when the maximum amount of nitrogen obtained was 16·03 per cent; minimum, 15·91 per cent; average, 15·97 per cent.

2nd. The sulphuric acid was added quickly in *twenty-six* different experiments, when the maximum amount of nitrogen obtained was 16·33 per cent; minimum, 16·03 per cent; average, 16·18 per cent.

The smaller the quantity of material employed, the greater the percentage obtained. In the above experiments as uniform a quantity of material as possible was employed.

If the sulphuric acid converts the nitrogen into ammonia, why add the potassium permanganate? From a large series of experiments, the writer concludes with Lenz (*Ztschr. Anal. Chem.*, 1887, 26, 590), that the potassium permanganate when added to a hot mixture destroys the organic compounds still remaining, and if the digestion is carried far enough all of the nitrogen is then converted into ammonia.

Of what value is the addition of metallic oxides or metals? The time consumed for complete oxidation when a metal or metallic oxide was added varied from *two to four hours*, while without the addition of these

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* The work was all done on sodium nitrate

rom *ten to thirty hours* were required for complete oxidation. In order that a method be practicable, its execution must require as little time as possible.

During the first part of the work, to prevent bumping, metallic zinc was used, but was soon found to be entirely unnecessary, especially when a Fletcher's circular burner was employed.

The results obtained by Kjeldahl's method were found by the writer to be a trifle lower than those obtained by the absolute method, agreeing very closely with those of Ruffle's method. The absolute method yielded, from *twelve* combustions, an average of 16·28 per cent, while the Ruffle's method yielded, from *ten* combustions, an average of 16·16 per cent. By comparing the above results, it was concluded:—

1. The Kjeldahl method is not as accurate as the absolute method for estimating nitrogen in nitrates, but is executed in much less time, since many estimations can be made at the same time, and is applicable for all practical purposes.
2. It is necessary to add the sulphuric acid quickly, that there may be no loss of nitric acid.
3. The end of the condenser must dip into the liquid contained in the receiver.
4. In order to economise time, a metal or metallic oxide must be added.
5. The potassium permanganate must be added to complete oxidation.
6. It is entirely unnecessary to add metallic zinc to the contents of the distillation flasks, to prevent bumping, especially when a Fletcher's circular burner is at hand.—*Journal of Analytical and Applied Chemistry*, Vol. v., No. 5.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1891.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

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

London, June 10th, 1891.

SIR,—We submit herewith 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 May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

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

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

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

The condition of the water supply to the Metropolis during the month of May was throughout entirely satisfactory, and was characterised more especially by the marked degree of freedom from brownish tint of the water, and by the great uniformity of composition and character among the different samples examined. Thus the mean amount of organic carbon present in the Thames-derived supply being 0·136 part, the maximum amount in any single sample examined was found to be only 0·150 part in 100,000 parts of the water.

The following Table shows the comparable results furnished by the examinations of the Thames-derived water made during the past three months respectively:—

Thames-derived Supplies.

	Ratio of brown to blue tint.	Oxygen required for oxidation.	Organic carbon per 100,000.	Organic carbon per 100,000.
	Means.	Means.	Means.	Maxima.
March..	14·1 : 20	0·049	0·146	0·209
April ..	13·9 : 20	0·055	0·155	0·190
May ..	9·6 : 20	0·042	0·136	0·150

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 294).

Apparatus.

ANY microscope, the magnifying power of which can be modified from 50 to 200 diameters, is suitable for microchemical work. Nicol prisms are a desirable appendage, as also a microgoniometer. On the contrary, the chemist can easily dispense with lenses which serve for observations in convergent polarised light. Complicated appliances for illumination are as useless in the applications of the micoscope to chemical research as are slides and fine screws on the work-table.

A microspectroscope may do good service, but can be but rarely used, as its arrangement takes much time. More useful is a microscope lamp for illuminating objects from above, which is otherwise difficult and imperfect. An essential condition is the largest possible distance of the objects. This makes work easy, and contributes to preserve the instrument from injury. I work generally at a distance of 3 c.m. when the magnifying power, according to the eye-piece, varies from 35 to 50 diameters, and when objects of 3 c.m. in length and breadth can still be seen at once. With so great a distance of the object a protection for the lowest object-glass is required only in particular cases. Frequently rinsing and cautiously wiping the lens with filter-paper free from dust or pure soft linen is sufficient to keep it in good condition for years. Certainly I wish hydrogen sulphide to be entirely banished from the room in which micro-chemical work is performed, and ammonium sulphide to be used there only exceptionally and immediately removed again. Hydrochloric and nitric acids at the degree of dilution and the small quantity in which they are used require special precautions only when working with high magnifying powers. Hydrofluoric acid and ammonium fluoride in acid solutions require precautions even at great distances. To cover the trial-drops with flat watch-glasses or microscopic covering-glasses is tedious and sometimes inadmissible. The lowest objective glass may be easily covered under all circumstances. A drop of water or glycerin is first placed on the lens, and then a round covering-glass of the smallest sort, or instead a round disc of mica which has been cut with a sharp cork-borer out of a thin, perfectly transparent leaf. Fragments of covering-glasses may also be used, though they are liable to be displaced or pushed off. As a matter of course, object-glasses which have been covered in this manner

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* *Zeit. Anal. Chemie.*

must be washed and wiped before the instrument is put away. Powers which exceed 300 diameters involve so much inconvenience, and for inexperienced operators so much uncertainty, that I should like to see them as far as possible dispensed with in micro-chemical work.

As a test-object for the lowest object-glass there may be used a precipitate of potassium or ammonium chloroplatinate (dilution of the platinum solution 1 : 100); for the highest objective, a precipitate of ammonium magnesium phosphate (from solution containing 0·05 per cent of magnesium), or a crystallisation of silver chloride from an ammoniacal solution containing 0·05 per cent silver.

Along with the microscope we must mention the slides, which serve, not merely as a support in microscopic examination, but have to serve also as a test-tube or an evaporating capsule in preparing the object. The stages which the author has obtained are thin enough and well annealed. If carefully handled they may be heated up to 300° over a naked flame. Now and then one will fly, whence it is prudent to have a small stock in reserve, and to work over a porcelain tray or plate to prevent loss. Besides the glasses of the customary form (76 by 26 m.m.) shorter ones are needed, which are obtained by cutting the full size in half. They serve for covering preparations, and are useful in sublimations. For both purposes the corners are rounded off in the blast flame, and pressed so that they are turned down for about 1 m.m. A small stock of microscopic covering-glasses is also needful. They serve chiefly for heating and concentrating very small quantities of liquid in cases where a strong heat is desirable without complete desiccation. Square glasses of 18 m.m. length in each side are suitable.

For reactions with hydrofluoric acid, hydrofluosilic acid, and soluble fluorides, the stage-glass must be covered with a thin film of hard Canada balsam. The simplest and most expeditious method is to evaporate down the Canada balsam upon the glasses themselves. But in this manner it is not easy to obtain an even surface without wrinkles and scars. A faultless film is obtained if the balsam is heated until it becomes thinly fluid, and after it has been spread out evenly it is left to evaporate at the ordinary temperature of a dwelling room. Several weeks are required for complete hardening. The end is reached more quickly with a solution of balsam in ether or carbon disulphide. For this purpose Canada balsam is evaporated in a flat capsule at about 120° until it scarcely froths, and a portion when allowed to cool scarcely takes an impression from the finger-nail. The mass after being coarsely powdered is dissolved to the consistence of olive oil. The glasses are then gently heated, covered with the liquid, which is quickly drained and shaken, and are then allowed to harden at the temperature of the room. Ethereal solutions readily become stratified and grow dull by including watery vapour. In moist air this may also happen with carbon disulphide. Subsequent heating on the water-bath does not always remove the evil. The layer is sufficiently hardened in ten minutes, so as to bear washing and gentle wiping. It resists dilute acids for a considerable time, but it is quickly softened and rendered dull by dilute potassa-lye, and even by ammonia.

(To be continued).

The Telethermometer.—Prof. Puluj (*Chem. Zeitung*).—By means of this instrument it is said to be possible to measure the temperature of distant or inaccessible objects.

A Physician on Educational Cram.—Says Dr. B. W. Richardson, in the *Asclepiad*, "In our money-grubbing, fee-gulping, pedantic days, with their hide-bound educational formulæ, John Hunter would have been nowhere. The very college where he is worshipped would have plucked him. Happy for him and for us that working in freedom from the tyranny of cramming his mind was permitted to run without impediment its immortal course."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

June 4th, 1891.

William Crookes, F.R.S., Vice-President, in the Chair.

Messrs. F. Stanley Kipping and Mr. Ernest F. Hooper were formally admitted Members of the Society.

Certificates were read for the first time in favour of Messrs. William A. S. Calver, 45, Barrington Road, Brixton, S.W.; John William Heap, 33, Upper Gloucester Place; Robert Lennox, 3, Inverness Terrace, Putney, S.W.; Rudolf Laurentz Leffler, 21, Havelock Street, Sheffield; Charles K. Scott, 26, Pigott Street, Limehouse, E.; Thomas Stephenson, Bellasis Road, Byculla, Bombay; Henry White, 8, Brown Street, Masboro', Rotherham.

The following papers were read:—

24. "*The Molecular Refraction and Dispersion of Various Substances in Solution.*" By Dr. J. H. Gladstone, F.R.S.

The paper is a continuation of that laid before the Society in March last, and deals entirely with solid and gaseous substances that have been dissolved in water or other liquids for examination.

The results are given in several tables. It cannot be expected that there should be anything like the same accordance between the experimental and calculated numbers as is usually found in the case of pure liquids, as in weak solutions the experimental error is greatly multiplied. Nevertheless, in the case of organic compounds, the agreement is frequently very close. Terpene hydrate and terpilene dihydrochloride appear as saturated compounds, and so do camphor and its derivatives; but benzyl camphor, $C_{17}H_{22}O$, and benzal camphor, $C_{17}H_{20}O$, substances recently prepared by M. Haller, give results, especially in dispersion, which are far in excess of what might have been anticipated. The sugar group presents some peculiarities. Cane sugar seems to show a refraction, and especially a dispersion, rather smaller than theory. Milk sugar, dextrose, and glucose are fairly accordant with theory; while mannitol, on the other hand, seems a little high in refraction.

Hydrogen chloride, bromide, and iodide give figures for the molecular refraction and dispersion much higher than the sum of the hydrogen and the halogen as determined from the paraffin compounds, and the values rise as the dilution becomes greater. Peculiarities analogous to this had previously been discovered by Perkin in regard to their magnetic rotation. Selenious and selenic acids, like the analogous sulphur compounds, afford optical values vastly less than what would be expected from the known values of their constituents. Metaphosphoric acid does the same.

The data relating to solutions of salts and alkalies, including compounds of aluminium, ammonium, barium, calcium, cerium, chromium, didymium, iron, iridium, lead, lithium, lanthanum, magnesium, potassium, silver, sodium, and tin. It will afford material for a revision of the refraction equivalents of the different metals, and of the electro-negative elements with which they are combined. They will also furnish additional means for determining the dispersion equivalents. Among the points noted are the following:—Ammonia, in strong contrast with the hydrides of chlorine, bromine, and iodine, appears to be uniform in its optical properties, whatever the strength of the solution; it agrees with what would be expected from theory. The refraction equivalents of cerium, didymium, and lanthanum are deduced from their salts at about 12·4, 16·4, and 15·5 respectively. The chlorates, bromates, and iodates are sufficiently represented to give an idea of their optical characters. At first sight it would appear that the addition of 3O to the haloid salts causes an inadequate increase of the molecular refraction, and a slight actual decrease in the molecular dispersion. But this probably arises from the fact that the haloid salts themselves, when dissolved in water, give a somewhat excessive value. The molecular refraction for ClO_3 in its salts dissolved in water comes out at about 18·3, that for BrO_3 at 24·9, and for IO_3 at 33·8.

DISCUSSION.

Dr. **PERKIN** remarked that there was a close agreement between Dr. Gladstone's conclusions and those which he had arrived at from the study of magnetic rotatory power. The very high values afforded by the elements sulphur and phosphorus, in comparison with the values deduced for these elements from sulphuric and phosphoric acids, were very striking. The magnetic rotatory power of caustic soda was also very high.

Dr. **GLADSTONE**, in the course of remarks on Dr. Perkin's comments, said that it was particularly noteworthy that sulphur retained its high value in carbon bisulphide.

25. "*The Nature of Solutions as Elucidated by a Study of the Densities, Heat of Dissolution, and Freezing-points of Solutions of Calcium Chloride.*" By S. U. PICKERING.

The curves representing these properties were examined in the same way as those representing various properties of sulphuric acid, and similar conclusions are drawn in the two cases, namely, that definite changes of curvature occurs at certain points which are the same, whatever property is examined, and which coincide, in all cases where such a coincidence can be ascertained with certainty, with simple molecular proportions of the salt and water; and consequently, that these changes represent the existence of hydrates in solution. The simplest hydrates indicated in the present case consist of $CaCl_2$ with 6, 7, and $8H_2O$; more complex hydrates exist also, as in the case of sulphuric acid.

26. "*Note on a Recent Criticism by Mr. Sydney Lupton of the Conclusions Drawn from a Study of Various Properties of Sulphuric Acid Solutions.*" By S. U. PICKERING.

Mr. Lupton (*Phil. Mag.*, xxxi., 418) applies a single parabolic equation to a portion of one of the author's sulphuric acid density curves, where a change of curvature was supposed to exist, and shows that it represents the results accurately if the experimental error is of a certain magnitude. This magnitude, however, is between 1000 and 10,000 per cent greater than the ascertained magnitude, and the equation, moreover, represents all the errors of like signs as being grouped together. Such a representation cannot disprove the existence of the particular change of curvature under investigation, still less that of the 101 others shown in the various curves examined by the author. The hydrate on which Mr. Lupton considers that his investigation throws "very grave suspicion" happens to be the one which the author has isolated in the crystalline condition.

DISCUSSION.

Professor **RAMSAY** doubted the validity of Mr. Pickering's methods of differentiating his curves. His own experience was that it was impossible to obtain results nearer than 2 or 3 per cent to the truth, with a curve drawn as carefully as possible, and a straight steel-edge laid along it to obtain tangents, Mr. Pickering, on the other hand, pursued a much more crude method, viz., he directly connected his experimental points by straight lines, and took the slopes of such lines as the tangents to his curves. This obviously did not eliminate any experimental error, but rendered it more marked.

Dr. **ARMSTRONG** said that he had no desire to intervene in the discussion which had arisen as to the validity of Mr. Pickering's method. It appeared to him, however, that Mr. Pickering's conclusions were in many respects open to question from a chemist's point of view; he thought, in fact, that Mr. Pickering both proved too much and was illogical. Prepared as the speaker was to believe in the existence of hydrates in solution, he could not imagine that so large a number as was suggested would arise, or that the 102 breaks in the sulphuric acid curves, for example, could possibly be interpreted as evidence of as many distinct hydrates. There was no independent evidence to support such a conclusion.

Then he thought Mr. Pickering was illogical, because he interpreted all the breaks as indicative of hydrates, notwithstanding that he asserted—doubtless with justice—that both water and sulphuric acid in the pure state consisted of complex molecules: surely in this case, as change would set in at either end of the curve, it must be impossible to say which of the breaks are to be regarded as indicative of change in the composition of the complex molecules of acid and water respectively, which are due to the formation of hydrates consisting of simple water and acid molecules, and which are due to the formation of hydrates, say, of simple water and complex acid molecules.

With regard to Mr. Pickering's contention that Mr. Lupton must be wrong, because the latter had dealt with the part of the curve which included that hydrate which of all others was the best characterised hydrate of sulphuric acid,—a hydrate that he had prepared before them in the room,—Dr. Armstrong said that, from experiments which were being carried on in his laboratory, he was inclined to believe that the said hydrate probably did not begin to form in solution until the temperature sank to within a few degrees of its point of fusion: it might well be, therefore, that it was not present in the solution to which Mr Lupton's conclusions related.

The more the speaker studied these questions experimentally, the more inclined he became to think that changes of composition, whenever they occurred, were indicated on curves drawn directly to represent the experimental results.

Dr. **MORLEY** said that it appeared to him that, even if Mr. Pickering was correct as to the number and position of breaks in the curves, it by no means followed that he had proved the existence of the particular hydrates suggested. A break in the curve should indicate that some new hydrate had just begun to form, but need not show what that hydrate was. Thus it was probable the hydrate $CaCl_28H_2O$ would begin to form before the entire liquid contained a percentage of calcium chloride corresponding to that formula; and when the liquid had attained that composition, it might be expected to contain, besides the hydrate $CaCl_28H_2O$, also higher and lower hydrates, such as $CaCl_29H_2O$ and $CaCl_27H_2O$.

Professor **RÜCKER**, while fully admitting that the concordance of the numbers obtained by Mr. Pickering from observations on different physical properties of the solutions might fairly be urged in his favour, thought it important that the agreement between results all of which depended on the application of the same method should not be regarded as conclusive evidence in its favour if it were otherwise open to grave doubt.

In reality, Mr. Pickering's results were obtained, not by calculation, but by a method of observation and experiment applied to curves, which themselves represented the results of other experiments. The instrument used was a flexible ruler. It was admitted that the curves had to be specially drawn and the scale of the co-ordinates carefully chosen, if the results were to be satisfactory, and it was difficult to believe that the conclusions arrived at did not in large measure depend on the details of this preliminary adjustment.

At all events, as in the case of all other experimental methods, the final test of validity is whether concordant results are obtained by different observers, and it was therefore important that those who had personally tested it should give the results of their experience.

The speaker had himself gone over Mr. Pickering's work in the case of one of the sets of observations on the densities of dilute sulphuric acid of different strengths, and he could bear witness to the care with which the curves were drawn. Nevertheless, the conclusion he arrived at was precisely similar to that which Professor Armstrong had expressed,

In the case of the more striking changes in direction and curvature which were clearly visible in the original curve, the various differential curves did not add much to the information it supplied. On the other hand, he thought that the evidence afforded by these secondary curves of changes of curvature, which could not otherwise be detected, was of the most untrustworthy character.

The assumption seemed often to be made that, because the results of experiments were more closely represented by two curves than by one, there must be a discontinuity, which was evidence of some physical change. That this conclusion might be fallacious is evident from the fact that, if a sufficient number of discontinuities were admitted, the results of experiment might be represented graphically with absolute fidelity.

His experience of the method would lead him to doubt any conclusions based upon it alone and not supported by independent evidence. It became untrustworthy just when it professed to become useful, by supplying information which could not otherwise be attained.

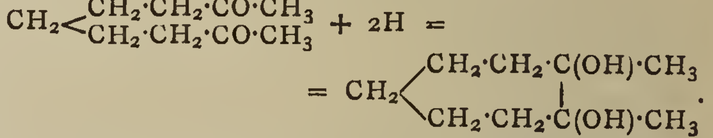
Mr. Pickering said that Mr. Lupton's equation represented the rate of change of the densities as a straight line, while the figure which the actually observed rate of change formed was as different from a straight line as could well be imagined (*C. S. Trans.*, 1890, 80). The straight line might be regarded as fitting a greater or smaller portion of this experimental figure, according to the latitude allowed to experimental error. In order that it should fit that portion of the figure which Mr. Lupton said it did, the latitude to be allowed would have to be 10 to 100 times greater than that for which there was any warrant. This, he considered, was not allowable. The figures here referred to (and exhibited at the meeting) were the first differential figures (rate of change) deduced *directly* from the determinations themselves; the question, therefore, of the accuracy attainable in differentiating a graph, raised by Professor Ramsay, did not apply to them.

It seemed somewhat rash of Professor Armstrong to hold that a particular hydrate ($H_2SO_4 4H_2O$) did not exist in solution at moderately high temperatures, because from a study of one property he had recognised it at low temperatures only, especially as it was from his own results at high temperatures that the speaker had been led to search for it, and finally to isolate it, at low temperatures. The multiplicity and complexity of the hydrates indicated must, no doubt, endanger the acceptance of his conclusions amongst chemists; but without reason, he thought, for we are at present in the dark as to the nature of liquid molecules (see *loc. cit.*, pp. 124, 129). He would be perfectly ready to accept any other explanation of the changes with weak solutions than that of their being due to hydrates, but he considered that we have at present no evidence in favour of any other view, or of their being due to changes in the aggregation of the solvent molecules, while the fact that they are precisely similar to the changes with strong solutions which occur at simple molecular proportions forces us to attribute them to the same cause as the latter, until some evidence to the contrary be forthcoming. He had already alluded to the question raised by Dr. Morley, as to why the existence of a hydrate should cause a change of curvature at exactly the strength of the solution corresponding to it (*loc. cit.*, p. 138), but he had left that question to those who had sufficient mathematical abilities to deal with it. Mendeléeff, however, appeared to consider that no exception could be taken on that score (*C. S. Trans.*, 1887, p. 779).

The fact mentioned by Prof. Rücker, that a flexible spring could be made to fit any complicated curvilinear figure by fixing it in position by a sufficient number of pins, did not appear to disprove the existence of definite changes of curvature in the figure; for the forces acting on the spring between any two given pins would be different from those acting on it between any other two; and, consequently, the form of the different portions of the spring would be represented by different equations, that is, there would be changes of curvature. He did not see how the position of these changes of curvature could be said, on either theoretical or practical grounds, to depend on the flexibility of the spring used; for he believed he was correct in saying that all springs, when acted on by forces of a similar nature, assumed similar forms, and any difference in the degree of curvature due to a difference in flexibility might be counteracted by a difference in the magnitude of the forces applied. In practice, he had used numerous springs of very different degrees of flexibility, without finding any difference in the position of the changes of curvature indicated. It seemed scarcely correct to say that the application of a flexible lath to a curvilinear figure led to different results in different hands, because Mendeléeff's conclusions respecting the densities of sulphuric acid differed from the speaker's; for Mendeléeff had an altogether insufficient number of experimental points at his disposal, and, as far as could be judged, did not use a flexible lath at all in examining them. The question as to whether a lath could or could not be used in locating changes of curvature which were not apparent to unassisted inspection might be most easily settled by submitting a fictitious series of determinations, calculated from sundry different equations, to examination with a lath, and ascertaining whether the position of the changes of curvature found coincided with those at which the equations had been changed. He was quite ready to submit his process to this crucial test.

27. "*Ethylic αα'-Dimethyl-αα'-Diacetylpimelate and its Decomposition Products.*" By F. Stanley Kipping, Ph.D., D.Sc., and J. E. Mackenzie, B.Sc.

When diacetylpentane is reduced with sodium and moist ether it is converted into dimethyldihydroxyheptamethylene (*cf.* Kipping and Perkin, *Chem. Soc. Trans.*, lix., 214), according to the equation—



$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CO\cdot CH_3\\ CH_2\cdot CH_2\cdot CO\cdot CH_3\end{matrix} + 2H = CH_2<\begin{matrix}CH_2\cdot CH_2\cdot C(OH)\cdot CH_3\\ |\\ CH_2\cdot CH_2\cdot C(OH)\cdot CH_3\end{matrix}.$$

As it seemed probable that other 1 : 7-diketones would behave in a similar manner, the authors have prepared αα'-dimethyl-αα'-diacetylpentane by the method described below. The action of reducing agents on this diketone is now being investigated by one of them, but, as a considerable amount of work has yet to be done on the subject, they describe in the present paper the preparation and properties of dimethyldiacetylpentane and of various other compounds obtained in the course of the research.

Ethylic αα'-dimethyl-αα'-diacetylpimelate,

$$CO_2Et\cdot CMeAc\cdot[CH_2]_3\cdot CMeAc\cdot CO_2Et,$$

is formed in considerable quantities when ethylic sodiomethylaceto-acetate (2 mols.) is treated with trimethylene bromide (1 mol.) in absolute alcoholic solution; it is a colourless oil boiling at 233—235° under a pressure of 50 m.m., and it combines readily with phenylhydrazine (2 mols.), yielding a reddish-yellow *dihydrazone*, which has the composition $C_{29}H_{40}N_4O_4$. On boiling with alcoholic potash the ethereal salt is readily decomposed, the principal products being αα'-dimethyl-αα'-diacetylpentane, αα'-dimethyl-α-acetylcaproic acid, and αα'-dimethylpimelic acid.

αα'-Dimethyl-αα-diacetylpentane,

$$CH_3\cdot CO\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot CO\cdot CH_3,$$

is a colourless liquid boiling at 202—204° under a pressure of 150 m.m.; when treated with hydroxylamine it is converted into a crystalline *dioxime*, $C_{11}H_{22}N_2O_2$, which melts at 93—94°.

aa'-Dimethyl-a-acetylcaproic acid,

$CH_3 \cdot CO \cdot CHMe \cdot [CH_2]_3 \cdot CHMe \cdot COOH$,

is a colourless oil boiling at 226—228° under a pressure of 70 m.m., seemingly with slight decomposition. The *silver* salt, $C_{10}H_{17}O_3Ag$, *ethylic* salt, $C_{12}H_{22}O_3$, *methylic* salt, $C_{11}H_{20}O_4$, and the *hydroxime*, $C_{10}H_{19}NO_3$, are described.

aa'-Dimethylpimelic acid,

$CO_2H \cdot CHMe \cdot [CH_2]_3 \cdot CHMe \cdot CO_2H$,

separates from light petroleum in well-defined crystals, melts at 80—81°, and is readily soluble in most ordinary solvents. The *silver* salt, $C_9H_{14}O_4Ag_2$, and the *barium* salt, $C_2H_{14}O_4Ba$, were prepared.

Ethylic-aa'-dimethylpimelate,

$COOEt \cdot CHMe \cdot [CH_2]_3 \cdot CHMe \cdot COOEt$,

is formed in the place of ethyl dimethyldiacetylpimelate when trimethylene bromide is treated with ethyl sodiomethylacetoacetate in alcoholic solution, the alcohol employed being not quite anhydrous; it is a colourless oil boiling at 190—191°, under a pressure of 80 m.m.

28. "*Volatile Platinum Compounds.*" By W. PULLINGER.

At Prof. Lothar Meyer's suggestion, the author has further studied the volatile compounds of platinum with chlorine and carbon monoxide described by Schützenberger, with the object, if possible, of determining their vapour density. He describes their behaviour when heated in various gases, as they do not completely volatilise, even in carbonic oxide, he was unsuccessful in accomplishing his object.

In preparing the compounds, he has obtained a novel compound of the formula $PtCl_6C_2O_2$, as a non-volatile, yellow, crystalline solid, easily soluble in water, and recoverable apparently unchanged from the solution. Liquid carbonyl chloride at 100° is found to act as a solvent of Schützenberger's compounds, depositing them on cooling in large crystals.

The author has prepared the compound $PtBr_2CO$ by heating platinous bromide in an atmosphere of carbonic oxide; apparently it is the only product even when excess of the gas is used. It crystallises in well-defined needles melting at 177°, and volatilising with extreme difficulty even in an atmosphere of carbonic oxide.

Directions are given for the preparation of platinic bromide and iodide, from which it appears that platinum sponge readily dissolves when merely boiled with either a solution of bromine in bromhydric acid or of iodine in iodhydric acid.

DISCUSSION.

Dr. COLLIE mentioned, as an instance of a volatile metallic derivative, that he had recently had occasion to notice that the copper derivative of the double ketone diacetylmethane, $(Ac_2CH)_2Cu$, was volatile.

PHYSICAL SOCIETY.

June 12th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

MR. W. H. DINES, B.A., was elected a member of the Society.

Prof. W. G. Adams then took the Chair, whilst Prof. AYRTON read a paper on "*Alternate Current and Potential Difference Analogies in the Methods of Measuring Power*, by himself and Dr. SUMPNER.

In a paper read before the Society in March last, the authors pointed out that for every method of measuring power in which readings of volts and ampères were taken, other methods in which ampères were read instead of volts, and volts instead of ampères, could be devised. More recently Dr. Fleming had, by a transformation of a formula given by the authors in a communication made to the Royal Society on the measurement of power by three voltmeters, given the analogue in which three ammeters were employed. The two arrangements are represented in Figs. 1 and 2, whilst Fig. 3 shows a modification of Dr. Fleming's method (Fig. 2), in which the current in the non-inductive resistance, *r*, is measured by the aid of a voltmeter, V, across its terminals. This obviates the necessity of putting an electromagnetic instrument in what should be a non-inductive circuit. The formula for the mean watts spent in the circuit *a b*, Figs 1 and 2, are respectively—

$$W = \frac{1}{2r}(V_3^2 - V_1^2 - V_2^2) \text{ and } W = \frac{r}{2}(A_3^2 - A_1^2 - A_2^2).$$

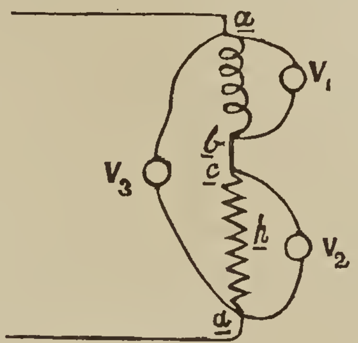


FIG. 1.

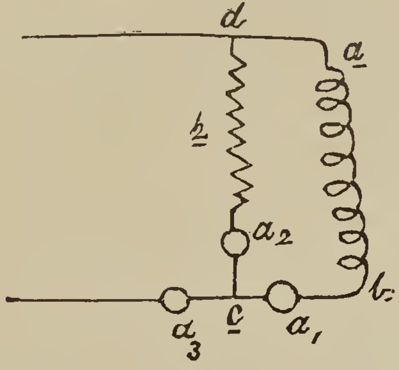


FIG. 2.

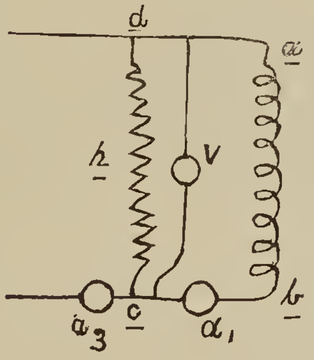


FIG. 3.

Mr. Blakesley's method of measuring power by a split dynamometer was shown to be analogous to the original electrometer method in which the difference of two readings was proportional to the power, and Blondlot and Currie's double electrometer method was shown to be the analogue of the ordinary wattmeter. The wattmeter was defective in the fact that a solenoidal coil was inserted in a nominally non-inductive circuit. The error thus introduced is, as was shown by one of the authors some years ago, expressed by the formula—

$$\frac{\text{Apparent watts}}{\text{True watts}} = \frac{1 + \tan\theta\tan\phi}{1 + \tan^2\phi}$$

where θ is the phase angle between the current and E.M.F. in the circuit in which the power is to be measured, and ϕ thephase angle for the approximately non-inductive circuit. It is now proved that the same formula expresses the error in any of the methods where resistances not wholly non-inductive are used.

As is well known, Mr. Blakesley has applied his split dynamometer to the measurement of phase differences between two currents; and an analogous method of finding the phase difference between two potential differences is described in the paper. In this method a high resistance split dynamometer, such as suggested by Mr. Rimington for measuring power, is employed. Blondlot and Currie's electrometer could also be used for the same purpose. Numerous diagrams illustrating the various analogies accompany the paper.

Prof. S. P. Thompson enquired whether hot-wire voltmeters could be employed to measure the various potential differences without introducing error.

In reply, Prof. Ayrton said that, although no great error was introduced by the self-induction of these instruments, yet the fact that they required considerable current was a disadvantage, and as these currents were not always in the same phase as those in other circuits, troublesome corrections were sometimes necessary. Electrostatic instruments were preferable.

Prof. Adams said he was glad to hear the inductance of Cardew voltmeters introduced no serious error, for they were very convenient instruments to use.

Prof. O. Lodge, F.R.S., exhibited and described *A Clock for Pointing Out the Direction of the Earth's Orbital Motion in the Ether.*

After mentioning the various motions to which a point on the earth's surface is subjected, he pointed out that the orbital motion was the largest component, and its direction at any instant not easy to conceive. An apparatus for pointing out this direction was therefore convenient when dealing with problems requiring a knowledge of the motion of a point through the ether. In one of two clocks shown, one spindle representing the earth's polar axis and another the axis of the ecliptic were inclined at an angle $23\frac{1}{2}^{\circ}$ and coupled by a Hooke's joint. The latter axis was capable of rotating round the former. At its upper end the ecliptic axis carried a tube and a pointer, both being perpendicular to the axis and to each other. The clock keeping solar time rotated both axes, and when properly set, the tube pointed in the direction of the sun, and the pointer therefore indicated the direction of the earth's orbital motion.

Some Experiments with Leyden Jars were then shown by Dr. Lodge.

The first one was with resonant jars, in which the discharge of one jar precipitated the overflow of another when the lengths of the jar circuits were properly adjusted or tuned. The latter jar was entirely disconnected from the former, and was influenced merely by electro-magnetic waves emanating from the discharging circuit. Lengthening or shortening either circuit prevented the overflow. Correct tuning was, he said, of great importance in these experiments, for a dozen or more oscillations occurred before the discharge ceased. The effect could be shown over considerable distances. In connection with this subject, Mr. Blakesley had called his attention to an observation made by Priestley many years ago, who noticed that when several jars were being charged from the same prime conductor, if one of them discharged, the others would sometimes also discharge, although they were not fully charged. This he (Dr. Lodge) thought might be due to the same kind of influence which he had just shown to exist. The word *Resonance*, he said, was often misunderstood by supposing it always had reference to sound, and, as substitutes, he thought that *symphoning* or *symphonic* might be allowable.

The next experiment was to show that wires might be tuned to respond to the oscillation of a jar discharge just as a string could be tuned to respond to a tuning fork. A thin stretched wire was connected to the knob of a jar, and another parallel one to its outer coating, and by varying the length of an independent discharging circuit, a glow was caused to appear along the remote halves of the stretched wires at each discharge; each of the wires thus acted like a stopped organ pipe, the remote ends being the nodes at which the variations of pressure are greatest. By using long wires he had observed a glow on portions of them with the intermediate parts dark; this corresponded with the first harmonic, and by measuring the distance between two nodes he had determined the wave-length of the oscillations. The length so found did not agree very closely with the calculated length, and the discrepancy he thought due to the specific inductive capacity of the glass not being the same for such rapidly alternating pressures as for steady ones. He also showed that the electric pulses passing along a wire could be caused, by tuning, to react on the jar to which it was connected and cause it to overflow even when the distance from the outside to the inside coating was about eight inches. During this experiment he pointed out that the noise of the spark was greatly reduced by increasing the length of the discharging circuit. The same fact was also illustrated by causing two jars to discharge into each other, spark gaps being put both between their inner and outer coatings, so as to obtain "A" sparks and "B" sparks. By putting on a long "alternative path" as a shunt to the "B" spark gap, and increasing that gap, the noise of the "A" spark was greatly reduced. He had reason to believe that the "B" spark was a quarter phase behind the "A" spark, but the experimental proof had not been completed.

He next described some experiments on the screening of electromagnetic radiation, in which a Hertz resonator was surrounded by different materials. He had found no trace of opacity in insulators, but the thinnest film of metal procurable completely screened the resonator. Cardboard rubbed with plumbago also acted like a nearly perfect screen. In connection with resonators he exhibited what he called a *graduated electric eye* or an *electric harp* made by his assistant, Mr. Robinson, in which strips of tin-foil of different lengths are attached to a glass plate, and have spark gaps at each end which separate them from other pieces of foil. One or other of the strips would respond according to the frequency of the electromagnetic radiation falling upon it.

Mr. Blakesley asked whether the tuning of the resonant jars needed re-adjustment when the distance between their circuits was varied, for, according to theory, the mutual induction should diminish the self-induction of the primary, and cause its oscillations to be more rapid. If this was true the method might be used for getting rapid oscillations. He also inquired whether the glow would appear in the same position on the two stretched wires if their ends were joined.

Dr. Sumpner wished to know how the resistances, inductances, and capacities of the circuits and jars were determined, and whether any evidence of irregular distribution of the charges on the tin-foil had been noted. With reference to the overflowing of a jar caused by using a certain length of discharging circuit, he asked whether the overflow did not prove the existence of a higher potential than that which originally existed between the coatings of the jar, and, if so, where did the excess energy come from?

Dr. Thompson asked if it would be possible to make a wire circuit analogous to an open organ pipe by putting sheets of metal on the ends of the wires.

Dr. Lodge, in reply, said Mr. Blakesley's suggestion was an important one, but he had not observed that any change in the adjustment was necessitated by varying the distance between the resonating circuits. Neither had he noticed any glow on wires joined to form a single loop, but this might be possible if the wires were long enough to give harmonies.

In answer to Dr. Sumpner, he said that the capacities were difficult to determine, for with much rapid oscillations the coatings were virtually enlarged. Lord Rayleigh had shown how to calculate the inductances, and the resistances he had practically measured by his alternative path experiments. The overflow of jars he thought was caused by the charges in some way concentrating on the edges of the foil, thus causing a kind of flood tide at which the overflow occurred.

The **President** asked Dr. Lodge what his views were as to the cause of the opacity of ebonite to light. Was it due to a selective absorption which cut off only the rays to which the eye was sensitive, or was the ordinary explanation that it contained impurities which were conducting and hence acted as screens likely to be correct? Another possible explanation was that the motion of the ether particles may be in three dimensions, and light be due to the projection of this motion on a plane perpendicular to the ray, whilst electro-magnetic induction might be due to the other component.

Dr. **Lodge** said he believed that ebonite was not opaque because of conducting particles being present, and was inclined to think that it acted more like ground glass, in which the opacity was due to internal reflections. Such a substance would only be opaque to vibrations whose wave-lengths were comparable with the size of the particles.

A Note "On the Construction of Non-Inductive Resistances," by Prof. W. E. Ayrton, F.R.S., and Mr. T. Mather, was postponed until next meeting.

CORRESPONDENCE.

THE RELATION BETWEEN THE CHEMICAL CONSTITUTION OF CERTAIN ORGANIC COMPOUNDS AND THEIR ACTION UPON THE ULTRA-VIOLET RAYS.

(A Correction).

To the Editor of the Chemical News.

Sir,—Having carefully perused the communications of Dr. Gerhard Krüss, which are of particular interest to me, I remark that in his paper entitled "Beziehungen Zwischen Zusammensetzung und Absorption-Spektrum organischer Verbindungen" (*Zeits. für Physikalischen Chemie*, vol. ii., p. 312) he very properly refers to papers on the subject by MM. Soret and Rilliet, *Comp. Rend.*, lxxxix., 747 (1879), and of J. L. Schönn, *Ann. Phys.* (2), vi., 267; but he has attributed the original work of Prof. Huntington and myself to Mr. W. R. Dunstan, who has merely made use of abstracts of the following papers by us:—(1) "Researches on the Action of Organic Substances on the Ultra-Violet Rays of the Spectrum." Parts I. and II. (*Phil. Trans.*, 170, p. 257, Part I., 1879); and (2) "Researches on the Action of Organic Substances on the Ultra-Violet Rays of the Spectrum," Part III.; "An Examination of Essential Oils" (*Proc. Roy. Soc.*, xxxi., p. 1, 1880). Also (3) the memoirs by myself entitled "Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra" (*Journ. Chem. Soc.*, xxxix., p. 153, Parts I. to V., 1881). These communications were read on June 3rd and December 2nd, 1880. My later investigations, published under the same general title, in 1882, 1885, and 1887, are not mentioned, and have probably been overlooked by Dr. Krüss, though the last communication (Part VIII., *J. Chem. Soc.*, 51), "A Study of Coloured Substances and Dyes," deals with the effect of NH_2 and OH groups in the molecules of such substances upon the absorption spectrum. I do not desire to draw attention to any accidental omission on the part of Dr. Krüss, but rather to point out the inconvenience to authors which may arise from the publication of communications such as that which Prof. Dunstan prepared. It is headed "Report on Organic Chemistry," to which is given the specific title "The Relation between the Chemical Constitution of certain Organic Compounds and their Action upon the Ultra-Violet Rays."

Owing to the manner in which this Report is reproduced in the *Pharmaceutical Journal* (xi., p. 54, 1881) it is by no means evident that the matter contained therein is not original. In point of fact it reads as if the deductions were drawn by Prof. Dunstan, after a study of our memoirs in the *Phil. Trans.*, *Proc. Roy. Soc.*, and *Journ. Chem. Soc.*

Dr. Krüss thus appears to have been misled into attributing the authorship of the above-mentioned work to the author of the title only. By this Report being quoted and referred to as an original contribution I also was misled, and put to the trouble of consulting it. I then found that it was published actually prior to my papers entitled "Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra," for, although they had been verbally communicated to the Chemical Society as early as June 3rd, 1880, and in writing on December 2nd of the same year, they were of necessity not published in the Journal until March, 1881, while Prof. Dunstan's Report upon them appeared in January. He thus appears to be entitled to priority in respect of these matters, and I am under the necessity of requesting you to be so good as to allow me to make this correction.—I am, &c.,

W. N. Hartley.

Royal College of Science for Ireland,
Stephen's Green, Dublin, June 5, 1891.

EXAMINATIONISM.

To the Editor of the Chemical News.

Sir,—The latest edition of the Directory issued by the Department of Science and Art of the Committee of Council on Education contains the following section relating to the quantitative portion of the Honours Stage Examination in Practical Inorganic Chemistry (Subject X.p.):—"II.—A practical examination in quantitative analysis, in which the candidate will have to make a quantitative determination of one of the following bodies: lead, silver, iron, calcium, potassium, ammonium, hydrochloric acid, sulphuric acid, carbonic acid."

At the examination on May 30th last, the exercise set in quantitative analysis was an alloy containing *copper*, the percentage of which was to be determined gravimetrically.

There is, I am aware, much to be said for and against examinational tests of capability; but there can scarcely be two opinions as to the unfairness of issuing a definitively worded syllabus, and then setting, or permitting to be set, an exercise absolutely outside it. Why issue the syllabus at all? In a case within my own immediate observation, a candidate who (if the syllabus had been adhered to) would certainly, as far as could be foreseen, have obtained a first-class, was so taken aback by having an alloy set before him composed of metals not included in the list published for his guidance that he omitted the quantitative portion of the examination altogether, although I believe he performed the qualitative work very well, and know that he could have accurately made any of the quantitative estimations provided for in the syllabus. What the results in his own case may be I do not know but there must have been many similar cases. No doubt it may be said, in deprecation of criticism, that the exercise set was easy, and that with the directions given (which, by the way, were not complete), the candidates' knowledge of quantitative manipulation should have been sufficient to carry them through. This, I submit, would be no defence: the point being whether the detailed syllabus should or should not, in fairness, have been adhered to.

I see that this matter has already called forth some strong remarks from the lynx-eyed editor of *Truth*, but as I have observed no reference to the subject in the scientific journals to which I have had access I venture to trouble you with this letter.—I am, &c.,

E. Godwin Clayton, F.I.C., &c.

Chemical Laboratory,
43 and 44, Holborn Viaduct, London, E.C.,
June 16, 1891.

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. cxii., No. 23, June 8, 1891.

Action of Ammonia upon certain Compounds of the Halogen Salts of Mercury.—M. Raoul Varet.—The author has examined the action of aqueous ammonia upon the compounds of mercury iodide with the cyanides. He has particularly studied the double mercury and cadmium iodocyanide; the mercury and potassium iodocyanide, a salt which dissolves in aqueous ammonia, heated to about 40°, is deposited again on cooling, without having fixed any ammonia. Gaseous ammonia is taken up by mercury cyanide with difficulty, forming a white amorphous body, $HgCy.NH_3$, which rapidly loses ammonia if exposed to the air and absorbs water, which may be again expelled by re-treatment with a current of NH_3. Mercury and barium chlorocyanide takes up 3 equivs. NH_3 if treated with a current of gaseous ammonia at 100° until completely dehydrated and then for 8 hours longer in the cold.

A New Method of Preparing Silicon Chloroiodides.—A. Besson.—The three chloroiodides which are theoretically possible are easily obtained by allowing chlorine and silicon iodide to act upon each other simultaneously in the nascent state.

Revue Générale des Sciences Pures et Appliquées. Vol. ii., No. 8, March 15, 1891.

Chemical Equilibria. Part Second. Application of the Principles of Thermodynamics.—H. Le Chatelier and G. Mouret.—The authors announce the following general laws as governing the transformation of all chemical systems whatsoever:—

1. The chemical transformation effected at fixed tensions without the intervention of foreign energies other than those exchanged with the medium is that which answers to a decrease of potential, a quantity expressed by the formula $\pi = u - st + vp$, where u, s and v are the internal energy, the entropism, and the volume of the system, t and p are the temperature and the pressure of this medium.

2. In order that a chemical system may be in equilibrium, it is necessary and sufficient that the potential is maximum, minimum, or constant.

3. When the tensions of dissociation vary from dp and dt the transformation effected is that for which the utilisable chemical energy is positive, *i.e.*, that for which we have the relation—

$$L\frac{dt}{t} + N\frac{dp}{p} > 0,$$

where L and N are the energies of chemical transformation, latent heat, and work, p and t are the tensions.

4. In order that there may be isodissociation, *i.e.*, in order that the simultaneous variations of the tensions of dissociation may not modify the chemical state of the system supposed free from any connection, the variations must satisfy the relation—

$$L\frac{dt}{t} + N\frac{dp}{p} = 0.$$

5. In order that a chemical system which is homogeneous, or has fixed tensions, may be in equilibrium it is necessary and sufficient that the potentials of its elements referred to the unit of mass may be equal.

Revue Universelle des Mines et de la Metallurgie. Vol. xiii., No. 3.

This issue does not contain any chemical matter.

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