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THE CHEMICAL NEWS.
VOLUME LVIX.
EDITED BY WILLIAM CROOKES, F.R.S., &c.
No. 1519.—JANUARY 4, 1889.

ON SOME NEW FOSSIL RESINS FROM THE COAL MEASURES.*

By W. IVISON MACADAM, F.R.S.E.,
Professor of Chemistry, New Veterinary College, Edinburgh.

My attention was directed some time ago by Mr. R. Kidston, F.G.S., to certain brown scales found in some coals. On treating these scales with solvents I found them to be of a resinoid nature. Mr. Kidston was of opinion that the substances might have been secreted by the carboniferous Lycopods (*Lepidadendros sigrellari*), as it is now pretty well proved that the two lateral cicatricules of the vascular scar of the leaf are secretary glands, only the central cicatricule being that of the vascular bundle. There is another source, however, from which the resin might have been derived, viz., macrospore, which so largely enter into the composition of some coals. At present, so far as our observations go, the source of the resins cannot be definitely determined, but it appears most probable that they have been derived from one of the two, or both the sources suggested.

The coals experimented on were obtained from the neighbourhood of Kilmarnock and Methil. In these two districts the resins are found in layers in the coals, and can be readily detected by the eye. In the Methil district the resins are found in largest quantity in the "Chemise" coal. This seam, although not the thickest in the coal measures of Fife, is probably the finest and most valuable seam in the series. Its maximum thickness is about ten feet; the lower portion being rough or steam coal, the upper part splint and household coal. The resins are most largely found in the upper portion. We are, however, aware that resins are distributed throughout the whole of the coal measures, and I have already isolated many of these substances, and am now proceeding with the analyses.

In this communication I only deal with four resins; two of which were derived from the Kilmarnock coal and two from the Chemise seam.

In our first experiments the solvent employed was chloroform, but after tests showed that the material so obtained was *partially* soluble in ether. In our latter work we have first extracted with ether and then treated the residue with chloroform. In this manner the resinoid substances are divided into two distinct portions. We have not yet determined whether the ether resin or the chloroform soluble resin can be further sub-divided, but we propose to determine this point. The ether soluble resins are, not only in the substances now specially treated, but in materials derived from other coals, partially volatile at temperatures much below 100° C., and we argue from this fact either that the bodies are complex, or that they are broken up at comparatively low temperatures. We specially mention this fact, as it has a direct bearing on an informal communication made by Professor Bedson to the Society of Chemical Industry at a meeting of the Newcastle Section, held in the Durham College of Science on November 8 this year, and reported in the *Journal* of the Society for that month (p. 729). In that communication Professor Bedson, referring to certain gases occluded by coal, states that he has obtained such by placing the coals "in suitable vessels and exhausting them by a Sprengel pump, and at the same time heating the coal at 100° C. (212° F.), drawing off the released gases by the continual flow of mercury." We would point out that many, if not all, coals, when heated to these temperatures, have a portion of their resins either volatilised or broken up, and we have found that the pure resins, when heated, do give off gases of the CH_4 and C_2H_4 series. We are also aware that the composition of coal dust has much to do with its explosive power, and I many years ago demonstrated that certain samples of coal dust were explosive in the presence of air and in the absence of fire-damp.

The results of the analyses of the four resins are as follows:—

	Kilmarnock Coal.		Chemise Seam Coal	
	Soluble in Ether.	Soluble in Chloroform.	Soluble in Ether.	Soluble in Chloroform.
Carbon ..	84·275	74·281	57·497	66·700
Hydrogen ..	9·361	6·515	7·527	7·315
Oxygen. ..	6·364	19·204	34·976	25·985
	100·000	100·000	100·000	100·000

The only substances already described that we are aware of, and which are nearly of the same composition, are the mineral resins anthracoxenite and schlanite, as given in Dana's "Mineralogy" (pp. 745 and 746), and the analyses of which are:—

	Anthracoxenite. (Insoluble in Ether).	Schlanite. (Soluble in Ether).
Carbon ..	75·274	81·47
Hydrogen ..	6·187	8·71
Oxygen. ..	18·539	9·82
	100·000	100·00

Both substances are from the coal beds of Brandeisl, near Schlan, in Bohemia.

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* Read before the Royal Physical Society of Edinburgh on Dec. 19, 1888, and illustrated by specimens.

This preliminary notice has been rendered necessary by the informal communication above quoted, and the author is now proceeding with the investigations of the resins obtainable from the coal measures.

PTOMAINES AND THEIR GENESIS, IN RELATION TO THE SEPSIN OF PANUM.

By JOHN M. WYBORN, F.C.S.

F. Coppola, while avoiding the conclusion that putrefaction is in no case sufficient of itself to cause the formation of the ptomaines, maintains that his researches have tended to show on the one hand that arterial blood contains no such alkaloids, and on the other that the processes, such as Dragendorff's, used for their extraction, are in themselves sufficient to produce them. These results are said to have been confirmed by the experiments of Marino, who was able to extract only traces of neurine and lecithin from various physiological products, and of Mosso and Guareschi, who state that in the extraction of alkaloids by sulphuric acid (Dragendorff's process), the substances owe their formation for the most part to the decomposing action of the acid.

Recently, however, it has been shown by V. Oliveri that the most dilute acids, even without the application of heat, cause the production of these substances from the decomposition of the lecithin and proteids present in the preparations. Moreover, the putrid solutions employed by investigators have been found to contain various acids, especially during the first fourteen days of the putrefactive process, and thus it would appear that this process itself is capable of producing the cadaveric alkaloids.

In 1865 Professor Panum, of Copenhagen, had demonstrated that albuminous substances yield by putrefaction a poisonous body soluble in water, insoluble in alcohol, and capable of withstanding a temperature of 100°. Bergmann has since confirmed this, and described the compound, *sepsin*, as generated by putrefaction.

By treating putrid infusion of muscle with strong alcohol, this substance has been obtained by Professor Burdon Sanderson* (who describes it as pyrogenous, or fever producing), Dr. Drysdale,† and others, and its poisonous characters have been verified.

In order to obtain a supply I proceeded as follows:— Lean beef, finely minced, was macerated in twice its weight of drinking water, without free access of air, but exposed on the sill of a window facing south to the heat and light of the sun during sixteen days (from 30th June, 1888) of dull, stormy weather with occasional sunshine. The strained liquid was then precipitated by an equal bulk of absolute alcohol. The precipitate was collected, boiled for five minutes in the same quantity of the alcohol as that first used, again collected and washed withboiling alcohol, and dried in a warm air chamber.

It was then extracted with distilled water and immediately filtered and evaporated to dryness on a water-bath. The residue, representing only 0·067 per cent. of the beef used, was found to consist of (1) a brownish red extract, rather heavy and freely soluble in water, (2) a pale greenish extract, very light and sparingly soluble in water, and (3) brilliant white crystalline plates.

Each grain (0·0648 grm.) of this residue was treated with 100 minims (5·9 c.c.) of a mixture of one volume of distilled water with two volumes of glycerin, forming, after standing, an amber coloured solution with a brown precipitate.

After keeping the solution one month, 5½ to 6 minims (0·324 c.c. to 0·354 c.c.), or less than $\frac{1}{18}$ grain of the extract, administered subcutaneously, was found to be fatal to mice in about an hour.

The filtered solution is at first nearly neutral to test-paper, but after exposure to the air it becomes strongly acid and acquires the odour of stale pepsin.

With platinic and auric chlorides precipitates are obtainable, but I regret that the quantity at my disposal is insufficient to admit of an analysis being made. It also gives precipitates with tannic, picric, phosphotungstic, and phosphomolybdic acids, that with the last named being sparingly soluble in ammonia.

With potassium ferrocyanide it gives a blue precipitate on the addition of ferric chloride, appearing after some time.

It also gives white precipitates with mercuric chloride and lead acetate, a yellow precipitate with potassium cadmium iodide, and a red precipitate with potassium bismuth iodide, and when boiled with potassium hydroxide an impure ammoniacal odour is observable.

Moist silver oxide digested with it is reduced to the metallic state.

With Nessler's reagent it yields a yellowish precipitate insoluble in dilute hydrochloric acid, and with Millon's reagent a white precipitate. Argentic nitrate causes a white precipitate insoluble in nitric acid, soluble in ammonia.

With acetic acid and potassium ferrocyanide a precipitate is obtained which is partially soluble in nitric and hydrochloric acids.

The dry residue when treated with sulphuric acid and potassium dichromate yields only a faint rose tint, which quickly vanishes. It is coloured yellow by nitric acid after standing for several hours.

From these reactions it would appear that while this body possesses many of the characters of the peptones, it also affords evidence of the presence of one or more of the cadaveric alkaloids, and such alkaloids must either be insoluble in alcohol themselves or in combination with some substance which renders them so, and, unless the alcohol were alone sufficient to produce them in the putrid solution, their pre-existence may be reasonably inferred.

SPECTRUM ANALYSIS OF CADMIUM.*

By A. GRÜNWALD,
Professor of Mathematics in the Imp. Roy. German Polytechnic University at Prague.

Introduction.

I.

Professor W. N. Hartley, of Dublin, being informed of my spectrum analysis of magnesium and carbon, drew my attention to the close relation existing between zinc, cadmium, and magnesium (pointed out in his paper "On the Homologous Spectra"), which seems to give evidence that these elements may be similarly composed. It might therefore be expected that my calculations for magnesium might easily be extended to zinc and cadmium.

This hint induced me to investigate the spectra of the latter elements. I began with the more complicated spectrum of cadmium, because I was convinced that the spectrum analysis of zinc would not cause me any further difficulty if I could succeed with the spectrum analysis of cadmium, as zinc takes the middle place between magnesium and cadmium in Mendeleeff's table of the chemical elements.

My investigations were successful in a degree I could never beforehand have ventured to hope. I succeeded not only with the analysis of cadmium here given, and later with the analysis of zinc in a relatively very short time, but I was also led by induction from these results to the

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* *British Medical Journal*, Feb., 1875, p. 201. *Ibid.*, Dec., 1877 p. 913.

† *On Pyrexin or Pyrogen.* By Dr. Drysdale. Baillière and Co.

* A paper read before the Royal Society, December 13, 1888.

discovery of a very important relation between the structure of the elements and their position in Mendeleeff's table.

The analysis of cadmium and zinc showed first of all that these bodies, at least so far as their known spectra allow a conclusion, are composed of condensation forms (different states of condensation) of the primary elements "*a*," "*b*," and "*c*," which I first found in hydrogen [: volume formula : $H = ba_4$:], and in oxygen [: volume formulæ : $O = H' \cdot O'$, $O' = b_4 O''_5$, $O'' = b_4 c_5$; $O = H' \cdot b_4 (b_4 c_5)_5$:], then in magnesium and in carbon. (See *Astronomische Nachrichten*, 1887, No. 2797, or *Philosophical Magazine*, 1887, and my paper "Mathematische Spectralanalyse des Magnesium's und der Kohle" in the *Sitzungsberichte der Wiener Akademie*, 1887.

Between the divers condensation forms of the primary body "*b*" in cadmium and in zinc there is relatively one which is the strongest. The strongest condensation form of "*b*" in cadmium is $\frac{7}{6}$ times more condensed than that in which "*b*" occurs in the hydrogen bound in aqueous vapour, while the strongest condensation form of "*b*" in zinc is $\frac{5}{4}$ times as strong. As zinc belongs to the 5th, cadmium to the 7th series of Mendeleeff's table (but together with magnesium to the IInd group of it) the suggestion arises that the elements of the *n*th series of Mendeleeff's table (except perhaps the so-called "typical elements" of the 1st and 2nd series) may contain the primary element "*b*" in a state of condensation (probably the strongest amongst several condensation forms of "*b*" in the secondary element referred to), in which it may be $\frac{n}{n-1}$ times more strongly condensed than in the hydrogen of aqueous vapour.

Supposing this induction to be correct, there must occur amongst the rays of the secondary elements, especially amongst the most refrangible of them, some rays whose wave-lengths λ by multiplication with $\frac{n}{n-1}$ could be transformed in corresponding wave-lengths, $\frac{n}{n-1}\lambda$, of water vapour, at least for $n > 2$, and in the case that there are rays of sufficiently high refrangibility amongst those known. These rays, $\frac{n}{n-1}\lambda$, would belong to the primary body "*b*" in the same chemical state as in the hydrogen of aqueous vapour.

Well, the induction above mentioned could be proved in a clear manner by a great number of elements, viz., by the elements Al, Si of the 3rd series ($n=3$), the element Fe of the 4th series ($n=4$), the elements Cu, Zn, As, of the 5th series ($n=5$), Sr ($n=6$), the elements Ag, Cd, In, Sn, Sb, Te, of the 7th series ($n=7$), Ba ($n=8$), and the elements Au, Hg, Tl, Pb, Bi, of the 11th series.

According to this inductive law discovered by me, the secondary element, magnesium of the 3rd series, for instance, must possess, besides the four groups of rays already analysed by me, a hitherto unknown group of rays whose wave-lengths λ ($\lambda < 2605$) by multiplication with $\frac{3}{2}$ [: $\frac{n}{n-1}$ for $n=3$:] will be reduced to wave-lengths $\frac{3}{2}\lambda$ of the water spectrum, forming a special group of the very numerous group (H_2O, O, *b*), due to the primary body "*b*" in the hydrogen of aqueous vapour. A similar prediction can be made concerning the rays λ of the other elements of the 3rd series, viz., Na (Al, Si, see above), P, S, and Cl ; each element of the 4th series ($n=4$), viz., K, Ca, Sc, Ti, V, Cr, Mn (Fe, see above), Co, Ni, will have respectively one group of more refrangible rays, the wave-lengths of which will be transformed by multiplication with $\frac{4}{3}$ $\left(\frac{n}{n-1} \text{ for } n=4\right)$ to wave-lengths, $\frac{4}{3}\lambda$ of the water vapour, forming also different partial groups of the group (H_2O, H, *b*) above mentioned, and so on.

"The wave-lengths due to homologous groups of different elements of the same group in Mendeleeff's table are connected, as I have further found, with their atomic weights, generally three and three, by very remarkable relations." The full exposition of those relations is reserved for a later special publication, which will be accompanied by very extended tables giving the evidence of them. I hope that in the meantime the predictions above made upon the ground of the fore-mentioned inductive law will be at least partially confirmed by future measurements, and that I shall be thus enabled to complete the induction by a further set of elements.

II.

But still in another direction scarcely less important, the spectrum analysis of cadmium, and especially that of zinc, together with the comparison of their spectra, have been of great consequence for the progress of my researches, as they confirmed me in the suggestion that the primary element "*c*" of oxygen (found also in Mg and in C, besides the primary element "*b*") "might be no other than a certain condensation form of the primary element '*a*' of hydrogen $H = ba_4$)."

(*a*) The electropositive character of the elements of the first of Mendeleeff's groups, and the same character of the primary body "*a*," the chemical analogy of the latter with the former and with the radicle "ammonium," NH_4, seemed to me to give some ground for the inference that condensation forms of the primary body "*a*" with and besides condensation forms of the primary body "*b*" might take a prominent part in the building up of the elements of Mendeleeff's first group in such a way that these elements might be looked upon as ammonium-like compounds of radicles, viz., of one radicle pentavalent (relatively 3-valent) and of four radicles monovalent, which might be, in general, compounds of the primary bodies "*a*" and "*b*," if not identical with the latter.

(β) The close relations which exist according to the inductive law above mentioned between the primary element "*b*" and the most refrangible rays of the secondary elements, together with the chemically different, nay contrarious, character of the bodies "*a*" and "*b*," made it probable that there might be also close relations between the primary element "*a*" and the least refrangible rays of the secondary elements.

Both reflections [: quoted above sub (*a*) and (β) :] induced me to examine whether the least refrangible rays of Li, Na, K, &c., at present known belong or do not belong to condensation forms of the primary element "*a*," and whether they are due directly or not to certain condensation forms of the primary element "*c*." Suppose the answer to be affirmative in each case—then it could not be difficult to determine the reduction factor for the transformation of the wave-lengths due to the primary body "*c*" into wave-lengths due to the primary body "*a*" in a definite chemical state, for instance, in that occurring in free hydrogen.

Success justified and confirmed my suggestion. The red rays of kalium, for instance, observed by Kirchhoff, Mascart, Huggins, Lecoq, Liveing and Dewar, Roscoe and Schuster, belong for the most part at the same time to a certain condensation form of the primary element "*a*," and to another definite condensation form of the primary element "*c*," their wave-lengths being rhythmically connected with the wave-lengths of "*c*," and with the wave-lengths of "*a*" in the same chemical state as in free hydrogen.

"The primary element '*c*' of oxygen, magnesium, and carbon is therefore no other than a definite condensation form of the primary element '*a*' of hydrogen, $H = ba_4$."

Now in all secondary elements, the spectra of which I have hitherto analysed, in O, Mg, C, Cd, and Zn I have met, besides the primary bodies "*a*" and "*b*," only with the primary body "*c*" occurring in different chemical states.

As "*c*" is recognised to be a certain condensation form of "*a*," the fore-mentioned secondary elements will only be composed of condensation forms of the two primary elements "*a*" and "*b*." This result leads us to the empirical induction that perhaps all the known and unknown secondary elements of Mendeleeff's table may be built up (besides the all-penetrating ether) of condensation forms of the two primary bodies "*a*" and "*b*," and may therefore (in the last instance) be only compounds of the latter.

If this inductive law should be proved true by further researches, Prout's hypothesis (*Annals of Philosophy*, by Th. Thompson, 1815 (6), 321) would have to be replaced by the following law:—

"The atomic weights of all secondary elements can be derived from the atomic weights of the two primary components "*a*" and "*b*" of hydrogen, $H = ba_4$, by integral numbers; the atomic weight of a secondary element, which consists in the last instance of α-atoms "*a*" and β-atoms "*b*," being given by the expression $\alpha a + \beta b$.*

The above results open up a magnificent prospect upon a very wide field for further research, and point to very important objects—immeasurably distant, it is true, but well defined in their outlines—for the co-operation of physics, chemistry, and astronomy (astrophysics).

The full exposition of the interesting relations here briefly sketched I reserve for a later publication.

III.

I have found by my spectrum analyses, that to the same condensation form of a primary element, occurring in different secondary elements, belong different partial groups of wave-lengths; these groups being in the same rhythmical relations to other comparison spectra, especially to that of aqueous vapour, but having besides almost nothing in common one with another.

With regard to the great importance of the forementioned partial or special groups for the comparison of the spectra, produced by different bodies, I may be permitted to elucidate their intrinsic meaning by a plain comparison:—

When an element occurs in two different bodies in the same chemical state [for instance, the primary body "*b*" in the state (H,*b*), such as it occurs in free hydrogen, in the magnesium and in carbon], the physical state of it is nevertheless by no means the same in the different bodies.

The various physical states of the same chemical condensation form in various bodies can be compared in a very striking manner with the various physical states or modifications a plate of the same metal undergoes, if it is wrought into different forms, variously supported and then variously rubbed or beaten.

As plates of the same kind of matter by such varied manner of treatment can be put into various systems of vibrations, with various systems of nodes, consequently in various physical modifications, while in the same chemical state, so the same chemical condensation form of an element can be set in various peculiar systems of vibrations, if it is combined with various other elements in different bodies, and therefore rubbed by various systems of waves excited in the surrounding ether or variously beaten by the atoms (or molecules) of the other components; systems of vibrations, which in return will be impressed on the surrounding ether, and brought to our knowledge by the latter.

I call the whole of all possible vibrations that a gaseous element in the same chemical state, but under various physical circumstances may assume, "the vibration complex due to that chemical state or condensation form;" and the whole of correspondent waves produced by it in the surrounding ether, "the complex of rays due to it."

This comprehension of all possible special groups, due to a certain condensation form of a gaseous element, into a "complex," is, however, only an ideal one; and it is therefore to be noted, that the mentioned condensation form cannot synchronously execute all the vibrations of the complex ideally (in imagination) due to it; in so far as the various physical conditions, which determine the appearance of the various special groups contained in the "complex," can either not exist together, or can only partly and under special conditions exist simultaneously. The foregoing exposition characterises in a sufficient manner the actual state of my spectral-analytical researches concerning the application of my theory to the discussion of the spectra.

IV.

The present paper on cadmium is a very remarkable link in the chain of publications intended to give an account of my results. It contains only a further instructive and interesting application of the criteria already known for the recognition of the primary elements "*a*," "*b*," and "*c*," which I have published in my paper, "Ueber die merkwürdigen Beziehungen zwischen dem Spectrum des Wasserdampfes und den Linienspectren des Wasserstoffs und Sauerstoffs, &c.," in the *Astronomische Nachrichten*, 1887, No. 2797, (also *Phil. Mag.*, 1887), and which I have arranged together in my paper, "Mathematische Spectralanalyse des Magnesium's und der Kohle," pp. 2—5.

The scale to which all wave-lengths in my paper are referred is that of Angström when no other scale is especially indicated. The numbers given on Angström's scale can easily be reduced to the corresponding numbers given on Rowland's or on Müller and Kempf's scale by the comparison of the relative wave-lengths of the solar lines E_1, E_2; at least so far only the systematic relations of the three scales are taken into consideration.

The wave-lengths of the above mentioned lines E_1 and E_2 are according to Angström ("Recherches sur le spectre solaire, spectre normal du soleil," Upsala, 1868); Henry A. Rowland ("On the Relative Wave-lengths of the Lines of the Solar Spectrum," *Phil. Mag.*, vol. xxiii., 1887); and Müller and Kempf ("Publikationen des Astrophysikalischen Observatorium's zu Potsdam," 1886):—

⊙	Angstrom's scale.	Rowland's scale.	Müller and Kempf's scale.
E_1	5269·59	5270·43	5270·53
E_2	5268·67	5269·65	5269·80

From these numbers we derive—

$$\left.\begin{array}{l}\text{For } E_1 : 5270{\cdot}43 : 5269{\cdot}59 = 1{\cdot}00016 \\ \text{For } E_2 : 5269{\cdot}65 : 5268{\cdot}67 = 1{\cdot}00018\end{array}\right\},$$

therefore in the mean—

$$\frac{1{\cdot}00016 + 1{\cdot}00018}{2} = 1{\cdot}00017 = 1\frac{1}{6000}$$

is the systematic reduction-factor for the transformation of the numbers on Angström's scale into the corresponding numbers on Rowland's scale, and $1 - 0{\cdot}00017 = 1 - \frac{1}{6000}$ is the reduction-factor for the change of the latter to the former:—

Further for—

$$\left.\begin{array}{l}E_1 : 5270{\cdot}53 : 5269{\cdot}59 = 1{\cdot}00018 \\ E_2 : 5269{\cdot}80 : 5268{\cdot}67 = 1{\cdot}00022\end{array}\right\},$$

thus, in the mean $\frac{1{\cdot}00018 + 1{\cdot}00022}{2} = 1{\cdot}00020$ is the systematic factor for the reduction of the numbers on Angström's scale into the corresponding numbers of Müller-Kempf's scale, and *vice versâ*: $1 - 0{\cdot}00020$ is the factor for the transformation of the latter into the former.

We can express hereafter the systematic relations between the three scales (with an accuracy sufficient for our purposes) by the equations:—

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* Prout, not knowing hydrogen to be a compound, suggested that this element, on account of its physical and chemical properties, especially its low atomicity and its almost exact multiple relations with many elementary substances, might be the ponderable base of all the others. *Annals of Philosophy*, vol vi., p. 330 (1815); vol. vii., p. 113 (1816).

$$\begin{cases} \lambda \quad (R)=\lambda(A)+\frac{1}{6000}\lambda(A)\,;\ \lambda(A) \quad =\lambda(R)-\frac{1}{6000}\lambda(R), \\ \lambda \ (M.K)=\lambda(A)+0{\cdot}00020\,\lambda(A)\,;\ \lambda(A)=\lambda(M.K)\ -0{\cdot}00020\,\lambda(M.K), \\ \lambda \ (M.K)=\lambda(R)+0{\cdot}00003\,\lambda(R)\,;\ \lambda(R)=\lambda(M.K)-0{\cdot}00003\,\lambda(M.K), \end{cases}$$

where λ (A), λ (R), (λ M.K) denote relatively the wave-length of one and the same ray on Angström's, Rowland's, and Müller-Kempf's scales.

The symbols used by me to denote the various condensation forms of the primary bodies occurring in H and O, &c., and the groups of wave-lengths due to it, are the same as in my paper on Magnesium and Carbon.

Thus denote, for instance, by—

(H, *b*) the group of wave lengths due to the primary body "*b*" in the chemical state, in which it occurs in free hydrogen.

(O, O′, *b*) the group emitted by the primary element "*b*" in the chemical state, in which it occurs in the component $O' = b_4O''_5$, contained in free hydrogen $O = H'O'$; H′ being the modified hydrogen which produces the second or so-called compound spectrum (H′) of hydrogen.

(O, O′, O″, *b*) the group, emitted by "*b*" in the same chemical state as in $O' = b_4c_5$, a component of $O'=b_4O_5$ in free oxygen $O=H'O'$.

(O, O′, O″, *c*) the group, emitted by the primary body "*c*" in the chemical state, in which it occurs in free oxygen, producing there the rays—

6146·0	H. H. Vogel.	4754·0	Plücker.
5205·4	Schuster.	4750·1	Schuster.
5190·0	,, (Plücker, Huggins).	4711·0	Plücker.
		4709·0	Schuster.
5175·4	,,	4705·0	Schuster, Huggins.
5159·3	,,	4699·0	Huggins (4698·5 Schuster).
5144·0	Plücker.	4695·5	Schuster.
4953·0	Huggins.	4690·0	Plücker.
4942·2	Schuster.	4677·0	Huggins.
4940·2	,,	4675·4	Schuster.
4923·7	,,	4660·7	,,
4907·0	Huggins.	4649·3	,,
4892·0	,,	4640·6	,,
4890·0	Schuster.	4639·0	Plücker.
4884·0	Plücker.	4600·0	,,
4871·0	Schuster.	4595·1	Schuster.
4866·0	Plücker.	4588·0	Huggins.
4864·0	Schuster.	4475·0	Salet.
4863·0	H. C. Vogel.	4469·2	Schuster.
4860·2	Schuster.	4465·0	,,
4856·2	,,	4455·0	Salet.
4853·0	Huggins.		&c.,
4848·0	Plücker.		

As it is very probable that several wave-lengths, found by calculation in the course of my discussion of the cadmium spectrum, and due to various condensation forms of the primary elements (especially of "*b*" in hydrogen or oxygen) may be met with in certain spectra—it is worth while to compare them with the latter. Thus, I should recommend—

(1). The comparison of the calculated wave-lengths due to the group (H, *b*) with the hydrogen spectrum, with the solar spectrum, with the star spectra (especially with that of the white stars), and with the spectrum of the oxyhydrogen flame.

(2). The comparison of the calculated wave-length belonging to the groups (O, O′, *b*), (O, O′, O″, *b*), O, O′, O″, *c*) with the oxygen spectrum, the air spectrum, the spectrum of the oxyhydrogen flame, &c.

For the sun and the stars possessing a light of their own (principally the white stars), contain in their outer atmospheres immense masses of burning and glowing hydrogen; they contain, and emit therefore certainly also, the most rays due to the primary bodies "*a*" and "*b*" in the same chemical states as in hydrogen, amongst the rays of their spectra.

The oxyhydrogen flame contains, at least among the rays less refrangible rays than λ 3300, several rays of incandescent hydrogen and oxygen amongst the mass of rays due to the aqueous vapour though of very small intensity, and in general quickly fading away as the refrangibility increases.

I have for this reason made the fore-mentioned comparisons, and have expressed their results in the tables.

The lines of the water spectrum (principally used as a comparison spectrum) are taken partly from the observations of Huggins (*Proceedings of the Royal Society of London*, 1880), "On the Spectrum of the Hydrogen Flame," partly from the *Report of the British Association*, 1886, pp. 169—171; for the most part, however, from the epistolary communications of Professor G. D. Liveing, of Cambridge.

During the elaboration of my paper on magnesium and carbon these communications reached only to the 13th September, 1887, but I was afterwards, by means of a communication of 24th January, 1888, enabled to use also the most recent measurements of Messrs. G. D. Liveing and J. Dewar, by which the former have been partly corrected and amplified; still this was antecedent to their publication in the *Philosophical Transactions of the Royal Society*, 1888, pp. 27—42 ("On the Spectrum of the Oxyhydrogen Flame").

In some cases where the rays of the water spectrum are too weak to act upon the photographic plate, I carried the comparison with the very numerous group of wave-lengths $\frac{H'}{2}$, corresponding to the wave-lengths H′ of the second or so-called "compound line spectrum of the hydrogen," the former being the halves of the latter. The wave-lengths H′ used were those measured by Dr. B. Hasselberg, of Pulkova, with great accuracy and with exemplary circumspection, originally in 1882, then with better instruments, and therefore with still greater accuracy and more in detail, 1883 and 1884. (See the *Mémoires de l'Academie de St. Pétersbourg*, "Untersuchungen über das II. Spectrum des Wasserstoffs," 1. Abhandlung 1882, 2. Abhandlung 1883, and "Zusatz zu meinen Untersuchungen," &c., 1884.

It may be still especially remarked that the most refrangible section of the water spectrum from λ=2448·4 to λ=2268·0, as also the least refrangible from λ=3673·3 to λ=4265·0 are so faint that Liveing and Dewar are compelled to expose the photographic plate up to five hours in order to make the whole of the lines visible and measurable, and to prove the existence of several lines predicted by me. The wave-lengths thus found are therefore liable to greater errors of observation than the others. These circumstances account also for some gaps occurring in some comparisons corresponding to certain criteria, and caused by the rays being too faint to be measurable, though the existence of such rays is notwithstanding ascertained by their satisfying other criteria.

Spectrum Analysis of Cadmium.

The lines corresponding to the rays of cadmium hitherto known can be distributed into six groups, whose wave-lengths can be characterised by their rhythmical relations to other spectra, especially to the water spectrum.

Each wave-length λ of this group can be reduced by multiplication with $\frac{2}{3}$ to wave-length $\lambda'=\frac{2}{3}\lambda$, which can be recognised as due to the primary body "*c*" in the same chemical state as in oxygen or in magnesium by the criteria given in my paper, *Mathematische Spectralanalyse des Magnesium's und der Kohle*, p. 4, sub. III., and p. 5, sub. VI., viz.:—

$\frac{3}{5}$ λ′ is a wave-length of a ray of aqueous vapour, produced by the primary body "*c*" in the chemical state in which it occurs in the oxygen of water vapour; thus a wave-length of the group (H_2O, O, O′, O″, *c*) [first chief criterion]; further—

The Ist group of cadmium-rays is—

$\lambda = \begin{cases} 6742{\cdot}0 \text{ Kirchhoff.} \\ 6740{\cdot}0 \text{ Huggins.} \end{cases}$
6726·5 Kirchhoff.*
$\lambda = \begin{cases} 6468{\cdot}0 \text{ Kirchhoff.} \\ 6466{\cdot}0 \text{ (?) broad, Thalén's, seems to be too small by two units.} \\ 6462{\cdot}0 \text{ Huggins.} \end{cases}$
6056·5 Thalén.†
5958·0 Huggins.†

$\frac{5}{8}\lambda'$ is a wave-length of the group (H_2O, O, O′, O″) of the water spectrum, produced by the body $O'' = b_4c_5$ in the same state as it occurs in the oxygen ($O = H'{\cdot}b_4O''_5$) of the aqueous vapour (second criterion); finally—

$\frac{2}{3}\lambda'$ is one of those wave-lengths of the water spectrum into which the wave-lengths of oxygen can be transformed by multiplication with $\frac{2}{3}$, the mean condensation factor of O and H in their union to form water vapour (third criterion).

Table I. gives a view of the characteristic relations just mentioned. The first column contains the wave-lengths λ of the Ist group; the second, the wave-lengths of the "*c*" rays rhythmically corresponding; the third and fourth, the fifth and sixth, finally the seventh and eighth columns give evidence of the accuracy with which the single rays of the group satisfy relatively the first, second, and third criterion. The wave-lengths satisfying all criteria with great accuracy, give first-rate evidence of the real existence of the group.

The Cd ray $\lambda = 6740$ (Huggins), which satisfies only the first and third criterion, leads by the second criterion to a new, very faint, still unknown line of aqueous vapour about $\lambda = 2808{\cdot}3$. The Cd ray $\lambda = 6056{\cdot}5$ (Thalén) is an empirical nodal ray (or ray of ramification) of the Ist and IInd group. Also the Cd ray about 5958 (Huggins) could be considered as an empirical nodal ray of the first two groups, but it seems to me to be more probable that it is only one of two faint rays lying close together and forming the nebulous ray of Thalén about 5957·5, and having the approximate wave-lengths 5958 and 5957·5, due respectively to the Ist and the IInd group. For while $\lambda = 5958$ satisfies the criteria of the Ist group very well, $\lambda = 5957{\cdot}5$ answers better to the most part of the criteria of the IInd group. (See the latter).

The wave-length $\lambda = 6466$ of the broad cadmium-ray of Thalén, answering evidently to the Cd ray $\lambda = 6468$ of Kirchhoff, seems to be too small by almost two units, as Kirchhoff's 6468 answers exceedingly well to the three criteria of the Ist group, while Thalén's $\lambda = 6466$ does not satisfy the first and the third criterion.

Cadmium contains, therefore (according to my well-known fundamental theorem), the primary body "c" *in a chemical state, dilated in the ratio* 3 : 2 *in comparison with the state in which* "c" *occurs in the oxygen or in magnesium.*

The wave-lengths λ of the above group are changed by multiplication with $\frac{2}{3}$ into wave-lengths $\lambda' = \frac{2}{3}\lambda$, which answer to the criteria for the wave-lengths (H, *b*), due to the primary element "*b*" in the same chemical state as in hydrogen, and given in my paper, *Mathematische Spectralanalyse des Magnesium's und der Kohle*, on p. 3, sub. II., and on p. 5, sub. VI.; they form, therefore, a special group of the wave-lengths complex (H, *b*).

According to these criteria there corresponds rhythmically to each wave-length λ, due to that group (H, *b*), four wave-lengths:—

$\frac{4}{5}\lambda'$, $\frac{23}{32}{\cdot}\frac{46}{41}\lambda'$, $\frac{21}{32}{\cdot}\frac{70}{59}\lambda'$, and $\frac{2}{3}\lambda'$ of the water spectrum, and two wave-lengths, $\frac{46}{71}\lambda'$ and $\frac{70}{59}\lambda'$, of the oxygen spectrum, answering to the second and third of the four above-stated wave-lengths.

(1). $\frac{4}{5}\lambda'$ is a wave-length due to the condensation form H, *b*) of the primary body "*b*," in the same state as in hydrogen in water vapour (first or chief criterion).

(2). $\frac{23}{32}{\cdot}\frac{46}{41}\lambda'$ is a wave-length which proceeds from the condensation form (H_2O, O, O′, *b*) of the primary body "*b*" in the compound O′ of O, bound in H, O vapour (second criterion).

(2*a*). $\frac{46}{41}\lambda'$, being a wave-length due to the chemical state (O, O′, *b*) of "*b*," as contained in the component O′ of free oxygen (first accessory criterion).

(3). $\frac{21}{32}\cdot\frac{70}{59}\lambda'$ is a wave-length belonging to the chemical condensation form (H_2O,O,O′,O″,*b*), thus produced by the primary body "*b*" in the state in which it occurs in $O'' = b_4c_5$, and with it in the oxygen of aqueous vapour (third criterion); while—

(3*a*). $\frac{70}{59}\lambda'$ is a wave-length generated by the primary element "*b*" in the chemical state (O,O′,O″,*b*), occurring in the component $O'' = b_4c_5$ of $O' = b_4O''_5$, in free oxygen, $O = H'O'$, under proper physical conditions (second accessory criterion; finally—

(4). $\frac{2}{3}\lambda'$ is one of those wave-lengths of aqueous vapour, to which the wave-lengths of hydrogen [therefore, also the wave-lengths of the condensation form (H,*b*)] can be reduced by multiplication with $\frac{2}{3}$, the mean reduction factor of H by its union with oxygen to form aqueous vapour.

The rays of the IInd group have, therefore, the character of helium-rays, being produced by the primary body "*b*" in the chemical state into which it comes when the hydrogen begins to be dissociated and simultaneouly expanded in the ratio 2 : 3.

The IInd group of the cadmium-rays contains the rays—

λ=
6438·0 very strong, Thalén.
*6056·5 very strong, nodal ray of the Ist and IInd group.
6004·0 Huggins (6003·5 Thalén).
5957·5 nebulous, Thalén.
5913·5 mean value of $\begin{cases} \text{5914 Huggins.} \\ \text{5913 Thalén.} \end{cases}$
$\left.\begin{array}{l} 5790{\cdot}0 \text{ nebulous} \\ 5687{\cdot}0 \text{ nebulous} \\ 5489{\cdot}0 \text{ nebulous} \\ 5471{\cdot}0 \text{ nebulous} \end{array}\right\}$ Thalén.
$\begin{cases} 5379{\cdot}9 \text{ Kirchhoff} \\ 5378{\cdot}0 \text{ very strong, broad, nebulous, Thalén.} \\ 5377{\cdot}0 \text{ Huggins, Mascart.} \end{cases}$
$\begin{cases} 5339{\cdot}0 \text{ Kirchhoff.} \\ 5337{\cdot}5 \text{ very strong, very broad, nebulous, Thalén.} \\ {**}5337{\cdot}0 \text{ Kirchhoff, nodal ray of the IInd and IVth group.} \end{cases}$
5304·5 Thalén (5304 Huggins).
**5153·0 Thalén, Huggins; nodal ray of the IInd and IVth group.
$\begin{cases} 5086{\cdot}0 \text{ (better than 5085 Thalén).} \\ 5084{\cdot}0 \text{ (?) Mascart.} \end{cases}$
4799·0 Hartley and Adeney.

The Tables II., II.*a*, II.*b*, II.*c*, show in how great a degree the criteria above mentioned are satisfied by the rays of this group, and especially by those due to the wave-lengths.

It should be particularly noted that the first columns of the Tables II.*a*, II.*b*, II.*c*, coincide with the second column of the Table II., forming thus branches of the latter. The ray $\lambda = 6056{\cdot}5$ (Thalén) is a nodal ray of the Ist and IInd groups; the ray $\lambda = 5337$ (Kirchhoff) and 5153 (Thalén) are nodal rays of the IInd and IVth groups. Thalén's $\lambda = 5085$ seems to be only the mean of two closely united lines at $\lambda = 5086$ and $\lambda = 5084$, appearing as one very strong line, as the latter satisfies with great accuracy the first three criteria; presupposing that

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* Probable value. Kayser in his *Lehrbuch der Spectralanalyse*, Berlin, 1883, p. 254, gives for this ray $\lambda = 6726$, whereas the *British Association Report*, 1887, p. 368, gives for it $\lambda = 6727$.

† The lines 6050 and 5959 given by Kayser, as obsezved by Huggins, are not to be found in the original paper of Huggins, "On the Spectra of Some Chemical Elements," *Phil. Trans.*, 1864; but instead of those, there occur the lines 6056 and 5958. The two former may therefore be misprints.

Mascart's 5084 is not also an erroneously determined value of $\lambda=5086$.

"Cadmium contains thus, according to the above discussion, the primary body "*b*" of hydrogen in the same chemical state as in helium, *id est*, in the state into which "*b*" comes when free hydrogen begins to be dissociated by sufficiently elevated temperature (and perhaps also by at the same time suitably diminished pressure), expanding itself simultaneouly in the ratio 2 : 3."

(To be continued).

UNIFORM METHODS FOR THE ANALYSIS OF FERTILISERS, CATTLE FOODS, DAIRY PRODUCTS, SUGAR, AND FERMENTED LIQUORS.*

In accordance with the call of the Secretary, the Association met in the library of the Department of Agriculture at 10 o'clock on Thursday, August 9, the President, Mr. P. E. Chazal, in the chair.

The President, in calling the meeting to order, said that he would omit the usual address, as there was a desire to proceed at once to business, with the view of accomplishing the objects of the convention in as short a time as possible.

On a call for reports of committees, Mr. Richardson, in the absence of the chairman, presented the report of the Committee on Cattle Foods.

Dr. Wiley then presented the Report of the Committee on Dairy Products, as follows:—

Report of the Committee on Dairy Products.

Mr. President—I found it impracticable to secure a meeting of the committee appointed at the last meeting to consider the subject of dairy products, and have therefore no report considered by all of the members of the committee to present. In the absence of such a document I thought it best to submit a brief résumé of the work which has been done in dairy products during the year since our convention last met. The methods proposed at our last meeting for the analysis of dairy products have given fairly good satisfaction, and I therefore recommend that they be continued unchanged for another year. Many points which are now in dispute will have been settled by that time, and at our next annual meeting any necessary changes in methods of analysis can be made.

With this introduction I beg to submit the following abstracts of the progress made in the analysis of dairy products during the year just past.

Milk Analysis.

Use of Asbestos Cloth Instead of Blotting-Paper in the Adams Method.

Johnstone has reported to the Society of Public Analysts favourable results attending his experiments in substituting asbestos paper for blotting-paper in the Adams method of fat estimation.—(Abstract from the *Analyst*, December, 1887, p. 234.)

(Note.—I called attention to the use of asbestos paper for this purpose two years ago, as will be seen on page 81 of *Bulletin* No. 13, Part 1.)

An Instrument for Calculating Milk Results.

Richmond has described an instrument for calculating milk analyses based on the relations existing between fat, solids not fat, and specific gravity in milk as established by the paper of Hehner and Richmond, published in the *Analyst*, vol. 13, p. 26. The instrument consists of a slide rule, on one side of which a scale, of which one division equals 1 inch, represents total solids. The other scale, one division of which equals 1·164 inches, represents the fat; while the scale representing specific gravity has a division equal to 1·254 inches.

The instrument is based upon the formula $T-0{\cdot}254\,G=1{\cdot}164\,F$. To use the instrument the lines indicating total solids and specific gravity found by analysis are placed together. The fat is then read off by an arrow on the other side. Where many analyses are to be made the instrument is especially valuable, since it eliminates all chances of error in calculation.—(Abstract from the *Analyst*, 1888, vol. 13, No. 144, p. 65.)

Estimation of Fat in Milk and Cream.

Werner Schmid proposes the following method of estimating milk fat: A test-tube of about 50 cubic centimetres capacity is graduated in tenths of a cubic centimetre; 10 cubic centimetres of milk or 5 cubic centimetres of cream are placed in the tube, and 10 cubic centimetres concentrated hydrochloric acid. The contents of the tube are boiled with constant shaking until the liquid is dark brown. After cooling in water add 30 cubic centimetres ether; shake, allow to stand until the ether solution has separated, measure its volume and remove 10 cubic centimetres with a pipette; place in a porcelain crucible, evaporate, and dry at 100° in air-bath. Calculate to total volume of the ether solution. The results are said to be exact.—(*Zeit. Anal. Chem.*, 27, p. 464.)

The Relation of Specific Gravity, Fat, and Solids not Fat, in Milk.

Hehner and Richmond have made an exhaustive study of the relations existing between the specific gravity, fat, and solids not fat, in milk. Three sets of determinations of the fat were made, viz., extraction from a paper coil, from plaster of Paris, and the direct extraction of the dried total solids. All previous formulæ relating to the above relations have been based upon imperfect methods of fat extraction. The work of Hehner and Richmond is therefore especially valuable on account of being based upon the Adams method of extraction. Forty-two analyses of various kinds of milk were made. For discussion of the formulæ the original paper is cited. The working formula obtained is $T-0{\cdot}254\,G=1{\cdot}164\,F$.

A table accompanying the paper gives the percentage of fat, calculated for specific gravities ranging from 1024·0 to 1034·0, and for total solids from 10 per cent to 15 per cent, inclusive.

The author strongly recommends that no milk analyses be accepted as correct which do not correspond closely with the calculated results.—(Abstract from the *Analyst*, vol. 13, No. 142, p. 26.)

Sources of Error in Soxhlet's Method of Estimating Fat in Milk.

Weinwurm has determined the error which may arise by allowing the ether fat solution obtained by Soxhlet's method to stand for varying lengths of time before its specific gravity is determined. As a result of his experiments, it appears that the apparent percentage of fat is raised by allowing the solution to stand for a long time. For the first twenty-four hours, however, this increase is only small, the amount, at most, being a few hundredths of a per cent. By standing a long time the apparent percentage of fat gradually increases, and appears to reach a maximum at the end of ten days. The amount of increase in that time may be 0·25 of 1 per cent.—(Abstract from Repertorium No. 19 of the *Chemiker Zeitung*, 1888, p. 151, and *M. Zg.*, 1888, 17, p. 401.)

Estimation of Dry Substance and Fat in Milk by Means of Wood Fibre.

Gantter proposes the use of wood fibre for the estimation of fat in milk, which he uses as follows:—

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* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

Two grms. of wood fibre are dried at 105° to constant weight in a dish containing a small glass rod. The total weight of the dish, glass rod, and fibre is noted. After weighing the dish, which is covered with a neat-fitting cover to prevent the absorption of water, 5 to 6 grms. of the milk are poured upon the wood fibre, and the exact amount taken determined by re-weighing the bottle. During evaporation the mass of fibre is pressed from time to time against the sides of the dish, so that no particles thereof remain attached thereto. The final drying is made in an air-bath, and the whole time required for the evaporation and drying should be about two hours and a half. From the increase in weight the amount of dry substance is determined. The mass of fibre is now transferred to a Soxhlet extraction apparatus, and, if necessary, the dish rinsed with petroleum ether. The extraction of fat and the weighing thereof are carried on in the usual way. The author has also used this method for the determination of water in butter and other fats and oils.—(Abstract from the *Zeitschrift für analytische Chemie*, vol. 26, No. 6, p. 678.)

The Chemical Action of Some Micro-Organisms in Milk.

Warington has studied the effect of certain micro-organisms on the curdling of milk. This curdling is effected either by the formation of a rennet-like ferment or by the production of lactic acid. The amount of lactic acid required to curdle milk depends on the temperature, the amount growing less as the temperature rises. Five different organisms were examined which had the power of curdling milk, but in very different degrees. They were *Staphylococcus candidus; B. termo; M. gelatinosus, B. fluorescens liquescens*, and *M. ureæ*.

Some of them readily curdled milk at a temperature as low as 10°. They do not, however, at that temperature produce an appreciable acidity. They therefore act plainly as a ferment. A large quantity of gas is evolved during the action of the same on milk.

Five organisms were also found to act as peptonisers; they are, *B. subtilis, B. anthracis, B. floccus, B. toruliformis*, and Finkler's comma. The milk treated with these organisms at 22° becomes clear after a few days. The clear fluid is rich in pepton. A few organisms render milk after a time decidedly alkaline; two of these are, *B. fluorescens non liquescens* and the *Bacillus of septicœmia*.

Cultivation in milk is an excellent method of distinguishing micro-organisms. — (Abstract from the Chemical News, June 22, 1888.)

Reduction and Rotation Power of Milk Sugar.

Deniges and Bonnans have reviewed the literature concerning the reduction of copper solution by milk sugar. As compared with pure glucose the reducing power of lactose is as 96 to 136. The copper solution employed contained 34·65 grms. of pure crystallised copper sulphate and 10 cubic centimetres pure sulphuric acid per litre. The alkaline solution was composed of 250 cubic centimetres of soda lye of 36° strength, in which was dissolved 150 grms. of crystallised Rochelle salts. Ten cubic centimetres of this solution was added to each 10 cubic centimetres of the copper solution.

For the determination of the rotatory power of lactose the author used a pure sugar, obtained by three crystallisations. The specific rotatory power for the anhydrous sugar at 20° was 55·30 for concentrations varying from 4 to 36 per cent; for the crystallised sugar the specific rotatory power in the same condition is 52·53. The general formula for the crystallised salt would be $[a] = 52{\cdot}53+(20—T)\times 0{\cdot}055$. The number 0·055 is the correction to be applied for each variation of 1° in temperature. The numbers obtained by the authors are exactly those given by Schmöger.—(Abstract taken from the *Journal de Pharmacie et de Chimie*, April and May, 1888, pp. 363 and 411.)

Estimation of Sugar in Milk by the Polariscope.

Vieth discusses the method adopted by the Association of Official Agricultural Chemists for the estimation of sugar in milk, which was originally described by me in the *American Chemical Journal*, vol. vi., No. v. The author is of opinion that acetic acid and subacetate of lead can be used with equal advantage with mercuric nitrate and nitric acid for preparing the milk for polarisation. He, however, prefers the use of the mercury salt. He calls attention to the correction which should be made in the reading of the polariscope for the volume of the precipitate. According to Vieth this correction in the method adopted by the Association is too small. The volume of the precipitate is equal to the combined volumes of the precipitated casein and fat carried down with it. The method employed by Vieth for making the correction for the volume of the precipitate is illustrated by the following example:—

Given a milk with a specific gravity of 1·0325 which contains 3·72 of fat. Add to 50 cubic centimetres of this milk 1½ cubic centimetres of the mercuric nitrate solution. The polarisation of the filtrate shows 5·1 milk sugar. The necessary calculations for the correction of this number are as follows:—

$$93 : 100 :: 372 : X \text{ whence } X=4$$

the volume occupied by the fat.

$$103{\cdot}25 : 96 :: 51 : X \text{ whence } X =4{\cdot}74.$$

The number 96 in the above formula represents 100 c.c. of the liquid less 4 c.c., the volume of the fat. The number 4·74 represents the percentage of crystallised milk sugar. The percentage of the anhydrous milk sugar would therefore be 4·5.—(Abstract from the *Analyst*, vol. xiii., No. 144, p. 63).

Short's Method of Determining Fat in Milk.

(Bul. Wis. Ag. Ex. Station, No. 16.)

The process depends on the following facts: That when a mixture of milk and a strong alkali is heated to the temperature of boiling water for a sufficient time the fat of the milk unites with the alkali and forms a soap which is dissolved in the hot liquid; at the same time the casein and albumen are disintegrated and become much more easily soluble. After the heating has continued for about two hours the mixture of milk and alkali becomes homogeneous and of a dark brown colour. On the addition of an acid the soap is decomposed, the fatty acids are set free, and rise to the surface, while the albumen, casein, &c., are first precipitated and then dissolved. The insoluble fatty acids thus obtained constitute very nearly 87 per cent. of the total fat of the milk.

Apparatus.

The process requires the following apparatus:—

(1) Tubes made of soft lead glass about one-sixteenth inch thick. The lower part of the tube is about 5 inches long and fifteen-sixteenths of an inch in diameter. The upper part of the tube 5 inches long and one-fourth inch inside diameter.

(2) Three pipettes, one holding when filled up to the mar7 on the neck 20 cubic centimetres (about two-thirds of an ounce), this being the exact amount of milk to be taken for analysis; the other two pipettes, holding 10 cubic centimetres each, for measuring the alkali and acid used.

(3) A scale, divided in millimetres, for measuriug the column of fat when the analysis is finished. The one used by the writer is a folding boxwood rule, but any rule divided in millimetres will answer the purpose.

(4) A water-bath made of sheet copper. It is provided with a rack to hold the tubes while being heated; also a feed and overflow to keep the water in the bath at a constant level.

(5) A wash bottle to hold hot water.

Solutions Required.

The solutions required for the process are as follows:—

No. 1.—8·75 ounces (250 grms.) caustic soda and 10·7 ounces (300 grms.) caustic potash dissolved in 4 pounds (1809 grms.) water. Use 10 cubic centimetres for each analysis.

No. 2.—Equal parts of commercial sulphuric and acetic acids. The acetic acid should be of 1·047 specific gravity. Use 10 cubic centimetres of the mixed acids for each analysis.

Directions for Analysis.

Taking Samples.—Mix the milk thoroughly by pouring from one vessel to another, avoiding as much as possible the formation of air bubbles; warming the milk to 80° or 90° Fahrenheit will prevent frothing to a large extent. After mixing allow the milk to stand one or two minutes to permit the air bubbles to escape before taking samples. Fill the 20 cubic centimetre pipette by placing the lower end in the milk and sucking until the milk rises in the tube above the mark on the side. Place the finger quickly on the top of the tube and allow the milk to run out slowly until it falls to the mark on the side of the tube; then let the contents of the pipette run into one of the analytical tubes, blowing out the last few drops.

Adding the Alkali.—Fill one of the 10 cubic centimetre pipettes to the mark on the side with alkali, and allow the solution to flow into the milk just measured. Place the finger on the top of the tube and shake the tube until the milk and alkali are well mixed. A rubber cot on the finger will protect it from the action of the alkali. Treat all samples in the same way. Place the tubes in the rack, set the rack and tubes in the water-bath, and heat the bath until the water boils: continue boiling for two hours, or until the contents of the tube become homogeneous and of a dark brown colour similar to that of sorghum molasses. After the tubes have boiled for one hour remove the rack and tubes from the bath and examine the tubes to see if the contents are well mixed. If a whitish layer of casein and fat is found floating on the surface of the liquid, gently shake and roll the tubes until the contents are well mixed. Return tubes to water-bath and boil one hour. The tubes are then ready for the addition of the acid.

Adding the Acid.—Remove the rack with the tubes from the water and allow them to cool to about 150° Fahrenheit. Then, by means of the pipette add 10 cubic centimetres of the acid mixture to each tube slowly, so as not to cause the contents of the tube to froth over. Mix the acid with the contents by running a small glass tube to the bottom of the mixture and blowing gently. Place the rack and tubes again in the bath and heat to boiling for one hour. Remove the tubes from the water, and then, by means of the water-bottle, fill the tubes with *hot* water to within 1 inch of the top. The fat will then rise to the top of the water. Replace the tubes in the bath and allow them to stand in the hot water, without boiling, for one hour. At the end of this time remove the tubes from the bath, one at a time, and measure while hot.

Measuring the Fat.—The analyst will observe that the lines representing the upper and lower limits of the column of fat do not extend straight across the tubes, but are slightly curved. In measuring the column of fat place the rule on the tube so that the lower line will come opposite the lowest part of the curved line of the fat; then read up the scale to the division coming opposite the lowest part of the upper curved line. The number of divisions on the rule is the length of the column of fat in millimetres. The per cent of fat in the milk is then calculated from the following formula and data:—

Amount of milk taken, 20 c.c.
Specific gravity of milk, 1·032.
Specific gravity of insoluble fatty acids, 0·914.
Per cent of insoluble fatty acids in butter fat, 87.

From the above data we have the following formula:—

$$100 \frac{a \times b \times c}{d \times e} = x.$$

Where a = the length of the column of fat in m.m.
b = the value of one linear m.m. of measured fat expressed in c.c. The value of b will vary according to the size of the tube used.
c = specific gravity of the insoluble fatty acids.
d = 20·64 grms. or the volume of milk taken for analysis multiplied by its specific gravity.
e = per cent of fat present in sample of milk taken for analysis.

Substituting the figures obtained by an actual analysis, the formula would be—

$$100 \frac{30 \times 0{\cdot}027 \times 0{\cdot}914}{20{\cdot}64 \times 0{\cdot}87} = x = 4{\cdot}12$$

per cent of fat in sample of milk analysed.

(Note.—The neck of the tubes can be graduated in c.c., removing the necessity of the troublesome measurements mentioned above.—H. W. W.).

If the process has been conducted according to the above directions the column of fat will be free from impurities, and the line of separation between the water and fat will be perfectly clear. On first rising to the surface the fat is slightly turbid owing to the presence of a small quantity of water. Although this will make no appreciable difference in the measurement of the fat, it may, if desired, be obtained perfectly clear by removing the tubes from the bath and allowing them to cool slowly. The crystallisation of the fat causes the finely divided water, which is distributed through the fat, to collect in drops, which sink to the bottom when the tubes are again heated, leaving the fat perfectly clear.

The analyst may fail to obtain correct results from the following causes:—Either the column of the fat may contain flecks of undecomposed casein, which would increase the volume of fat, thereby giving too high a per cent, or a small quantity of butter fat may remain unsaponified, which will also give too high results. These errors are both caused by insufficient heating of the milk with the alkali, and may be easily obviated by taking care to heat the mixture of milk and alkali for two hours at least. If not pressed for time it is better to heat two and a half hours, and thereby remove all risks of the above errors. If milk containing more than 6 per cent is to be tested, the mixture of milk and alkali should be heated at least three hours. In such case it would be better perhaps to take 10 c.c. in place of the usual amount.

Before adding acid the tubes and contents must be allowed to cool to 150° Fahrenheit at least. If added at a higher temperature the contact of the strong acid with the hot alkali solution will generate sufficient heat to cause the contents of the tube to boil with explosive violence, throwing out the contents of the tube and spoiling the analysis. If after the addition of hot water the tubes are allowed to stand in boiling water, small bubbles of gas are given off by the continued action of the acid on the casein. These bubbles rise through the column of fat, rendering it turbid and causing difficulty in meauring. The bottles containing the solutions of acid and alkali should be kept corked when not in use. If the acid bottle be left open the acetic acid will evaporate and the acid will not dissolve the casein. The alkali bottle should be kept closed to prevent absorption of carbonic acid and consequent weakening of the solution.

(Note.—The method of Short has been compared in my laboratory with the anhydrous copper method of Piggott and Morse. A mean of 12 determinations gave by the anhydrous copper method 3·20 per cent of fat, and by the Short method method 3·18 fat. The same samples treated by the Adams method gave results considerably higher. The process of Short has also been improved by graduating the neck of the tube into tenths of a c.c.

For use at stations where expensive chemical apparatus cannot be had, the method appears to have great value.—H. W. W.).

Bicarbonate of Sodium in Milk.

Proust makes an energetic protest against the addition of bicarbonate of sodium to milk for the purpose of preserving it. His principal objection to the use of the above salt is based upon its action on lactic acid, the lactate of soda being a salt injurious to children.—(Abstract from *Chemisches Central-Blatt*, No. 24, 1888, p. 837).

(To be continued).

NOTICES OF BOOKS.

Pictures in Black and White; or, Photographers Photographed. By George Mason (Mark Oute). London: Greenwood and Co.

Here is a book which carries the reader back to the time before photography was enlisted in the service of astronomical and biological research, and when it was confined almost exclusively to taking portraits. The author places before us the village fair with its travelling *ateliers*, got up in the style of the showman's caravan, where the curious rustic, half suspicious of necromancy, was invited to have his likeness taken on glass. Not a few of the operators, it must be admitted, were ex-showmen, innocent of physics and chemistry, as of art, who saw in the new invention an easy way of filling their pockets. Nor were they mistaken, for imperfect as might be their results, the public was satisfied and paid cheerfully prices which would now be considered exorbitant.

The careers of these itinerant photographers have been widely different; some of them not content with the little empirical knowledge which they had at their command, studied the principles and practice of their art, and have gradually developed, if not in their own persons, yet in those of their successors, into the qualified photographers whose studios we encounter in all towns of any pretensions.

Others, in whose veins the showman's blood was predominant, lived on the "lightly come, lightly gone" principle, and spent their money as quickly as it was earned, until their art lost the attractions of novelty, and could be exercised to advantage only by men of special taaining. Some of them accordingly returned to their original callings as mountebanks, cheap jacks, comic singers, and what not. Some remained faithful to the camera, and may still be seen in summer time in the outskirts of Epping Forest and other popular resorts ready to "take" the British public for the small fee of sixpence per head. In the good old times half-a-crown would have been paid ungrudingly. What these poor survivals do in the winter is an unsolved problem, which makes us think that the power of hybernation might be a desirable boon to many of the human race.

This book, though it does not in the least touch upon the history of photography as an art, throws an instructive light upon its early career as a profession.

Basic Slag; its Value as a Fertiliser, together with a Short Account of the Principles of Phosphatic Manuring. By C. M. Aikman, B.Sc., F.R.S.E., F.I.C., F.C.S. Edinburgh: *North British Agriculturist.*

This pamphlet is a reprint of certain articles inserted in the *North British Agriculturist.* The author considers that three constituents only of plant food need engage the attention of the farmer, viz., nitrogen, phosphoric acid, and potash, the other minerals taken up by plants being always present in soils in sufficient proportion. Here Mr. Aikman differs from M. Ville, who holds that lime is also requisite, even in the most calcareous soils. The consumption of basic slag, which it is the author's object to recommend as a source of phosphoric acid, is, so far, much less extensive in Britain than in Germany, where it now reaches six million hundredweights yearly. The author points out that the solubility of basic slag is very much greater than that of natural phosphatic minerals, and that its rapidity of action upon the crop is consequently much greater.

According to varied culture experiments its phosphoric acid is about half as valuable as that in soluble phosphates, and it is best adapted to plants of the leguminous kind. Farmers are especially warned against mixing it with sulphate of ammonia, and in like manner with Peruvian guano, since the free lime which it contains will drive off and waste the ammonia.

Catalogue of Standard Second-hand and New Books, English and Foreign, on Chemistry and the Allied Sciences. W. F. Clay, 2, Teviot Place, Edinburgh.

This catalogue has an especial claim on the attention of students, professional men, and scientists generally. It includes many complete sets of journals, of the transactions of learned societies, and of the works issued by publishing clubs. Many of these books are extremely scarce, being out of print, and having been, in the first place, issued to subscribers only. Thus we see here announced a complete set of the Cavendish Society's publications, and a complete set of the *Berichte* of the German Chemical Society, which have never been circulated through the trade. There are also sets of *Liebig's Annalen*, of the *Journal of the Chemical Society*, of the *Reports of the British Association*, and of the *Proceedings of the Royal Society*, and many other series valuable for reference.

A few errors in printing are to be met with which may occasionally puzzle the reader. Thus there is here mention of a "Short Text-book of *Morganic* Chemistry," by Prof. Kolbe, a branch of the science which some compositor has evidently evolved out of the depths of his own consciousness.

This catalogue is calculated to be of service to many who are in search of rare or curious scientific works.

CORRESPONDENCE.

WATER ANALYSIS.

To the Editor of the Chemical News.

Sir,—My book on Water Analysis has reached a seventh edition, and entered on its twenty-first year. The widespread and enduring acceptance of the book throws responsibility on its author which he fully recognises.

In sending forth the new edition, the question as to how far modifications and extensions were called for has been very carefully considered.

That portion of the book which deals with the pollution of water by organic matters has not been changed in any way. The second and third sections of the book have, however, undergone alteration and enlargement.

The natural history of water—apart from all considerations of pollution by human intervention—is very interesting, and falls within the scope of the book on water analysis.

The close of part III. is occupied with a sketch entitled "The Classification of Natural Water." Beginning as invisible vapour in the atmosphere water condenses and assumes the liquid or the solid form, and falls to the ground.

It afterwards either sinks into the ground and becomes spring-water, or it remains surface-water. In virtue of its powers of solution it records its own history in its contents, and natural waters possess an identity which they retain until they are evaporated or merged in the ocean.

In former editions reference has been made to the specific gravity of drinking-water. In the present edition is published a research into the specific gravity of drinking-waters, and for the first time a real connection between the contents of an ordinary drinking-water and its specific gravity is established.

The question of the solution of lead by certain kinds of water is also discussed.—I am, &c.,

J. Alfred Wanklyn.

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. cvii., No. 25, December 17, 1888.

On Certain New Properties of Ethyl Fluoride and on its Analysis.—H. Moissan.—This compound can be prepared in a state of purity by the reaction of ethyl iodide and anhydrous silver fluoride. If heated for several hours to dull redness in a glass bell it yields a complex mixture of carbides containing mere traces of silicon fluoride. Under the action of a weak induction spark it expands greatly, yielding hydrofluoric acid, a small quantity of acetylene, and especially ethylene, without any deposit of carbon. The action of ethyl fluoride upon animals is different from that of ethyl chloride. It produces at first, not anæsthesia, but excitement quickly followed by death.

Compounds of Nitric Oxide with Chloro-ruthenites and the Atomic Weight of Ruthenium.—A. Joly.—The salts described by Claus are not chloro-rutheniates, and compounds of the type $RCl_4,nMCl$ are hitherto unknown both in the case of ruthenium and rhodium. From his numerous and concordant analyses the author deduces for ruthenium the atomic weight 101·5. He adds that the determination of the vapour density, which he previously undertook in concert with H. Debray, leads to an atomic weight lower than 102.

The Use of Hydrogen Peroxide for the Determination of Metals of the Iron Group: (1) Chrome; (2) Manganese; (3) Iron.—Ad. Carnot.—This paper will be inserted in full.

Reproduction of Zircons.—MM. Hautefeuille and Perrey.—Zircons may be obtained at a temperature not exceeding 700° by the action of lithium dimolybdate upon a mixture of zirconia and silica.

Action of Mercury Cyanide upon the Salts of Copper.—Raoul Varet.—Mercury cyanide is not decomposed by the oxy-salts of copper, but by the haloid salts. There is then, as with the alkaline cyanides, an escape of cyanogen, and a formation of cuprous cyanide, which enters into combination with the mercury salt just formed. With the cuprous salts the result is the same, but there is no escape of cyanogen.

On a Diquinolic Base.—Albert Colson.—The base in question is a white solid, of a cotton-like appearance, sparingly soluble in water, soluble in six times its weight of dilute hydrochloric acid, and in ten parts of alcohol at 92°. It is deposited from its solution in ether in the form of long, flattened needles, strongly double refractory. It turns green with concentrated ferric chloride and forms a yellow chloroplatinate and chloraurate; its composition is $C_{22}H_{18}N_2O_3$.

The Combustion-heats of the Camphors and the Borneols.—W. Louguinine.—This memoir does not admit of useful abstraction.

Moniteur Scientifique, Quesneville.
Series 4, Vol. ii., September, 1888.

Researches on Porcelain.—Ch. Lauth and G. Dutailly.—The completion of a series of valuable papers, too extensive for reproduction.

Researches on Allo-Isomerism.—A. Michael.—Translated from the *American Chemical Journal*.

On Portland Cement.—Charles Spackman.—From the *Journal of the Society of Chemical Industry*.

The Distinction to be Established between the Mono- and Di-refractive Bodies having a Rotatory Power.—Dr. G. Quesneville.—This purely mathematical paper requires the accompanying diagrams.

Contributions to the Theory of the Vitriol Chambers.—G. Lunge.—From the Chemical News.

Detection and Determination of Selenium in Meteoric Iron.—Mr. Warren.—From the Chemical News.

Academy of Medicine.—Session of July 17th, 1888.—A report on new procedures in vinification proposed as substitutes for "plastering." The conclusions reached are that the introduction into the must of calcium phosphate or of calcium tartrate is open to no objections. Both increase the proportion of the tonic and ferruginous matters, and are besides useful in impeding the formation of the higher alcohols.

The Analysis of Butters and the Determination of the Soluble Fatty Acids.—V. Planchon.—The author proposes a method founded on the following principle:—If we saponify a known weight of fatty matter with a known excess of alkali we may, on neutralising the mixture with a standard acid, determine the proportion of alkali which has combined with the fatty acids. The figure thus obtained called in Germany "Kœttsdorfer's number" has a relation to the quantity of glycerin originally combined and displaced by the alkali. If in place of ceasing to add the standard acid at the moment when neutrality is reached, we continue to drop in this acid so as to employ exactly the quantity corresponding to the alkali which has served for saponification, the soap will be decomposed and the fatty acids will float on the surface. The acids thus isolated may be completely insoluble. In this case, the liquid separated by filtration after cooling will be neutral. If, on the contrary, a portion of the acids is soluble, it will impart to the filtrate an acidity which may be easily estimated by means of a standard alkali. For this process the following solutions are necessary:—1. Semi-normal sulphuric acid very exactly titrated. 2. Normal alcoholic solution of caustic soda. It is prepared by dissolving 45 grms. of pure caustic soda in a minimum of hot water and making the solution up to 1 litre with alcohol at 97°. The standard of this solution is fixed by means of sulphuric acid, just mentioned, adding either alcohol, or a stronger alcoholic solution of caustic soda, so that 25 c.c. may correspond exactly to 50 c.c. of the semi-normal sulphuric acid. 3. Quinque-normal aqueous solution of caustic soda. The saponification is effected in ordinary flasks, with rather wide necks, holding 150 c.c. up to the beginning of the neck. Prior to the analysis we place in these flasks 150 c.c. of alcohol at 15 per cent and heat to 50°—55°. When the temperature is steady we mark with a diamond the level of the liquid, which is then thrown away. We then proceed to the actual analysis as follows:—The butter is first melted in the stove at 50° in a glass dish. As soon as the water and the curd are separated we examine if the fatty matter is clear; if so, the quantity necessary for the analysis is taken with a glass tube, drawn out narrow.

If not, the upper stratum is filtered, and the first portions which pass through are taken. The butter should be left in the stove for a very short time only. The flask being tared to a weight of 5 grms. the weight is removed and the melted butter is added from a pipette so as to re-establish the equilibrium. If we let the drops of liquid fall slowly towards the end we easily avoid exceeding the necessary quantity. We then run into the flask 25 c.c. of the normal alcoholic soda, and boil for twenty minutes with an ascending condenser, either on the sand-bath or over a very small gas flame. At the end of this time the saponification is completed; the source of heat is removed, the flask is let cool for some minutes, and about 60 c.c. of distilled water are then added and a few drops of phenyl phthaleine. The semi-normal acid is then run into the soapy solution by means of a burette with a glass cock, holding 50 c.c., and graduated to $\frac{1}{10}$ c.c. When the red tint disappears we read off the quantity of acid used, and note this first result. Without removing the flask we continue the addition of the semi-normal acid until the total volume used is 50 c.c. (or rather, a number bordering on 50 c.c., found necessary in blank experiments for the exact neutralisation of the 25 c.c. of soda). The flask is then set on the water-bath, heated to 50°—55°, when the insoluble fatty acids melt and separate. The flask is repeatedly agitated, and when the temperature is steady we add a quantity of luke-warm distilled water sufficient to raise the *lower* level of the stratum of fatty acids to the mark at the bottom of the neck. The flask is then closed with the finger and well shaken so as to break up the acids, and it is then left to cool. When the upper stratum is clear the flask may be set in cold water, when the fatty acids crystallise. When completely cold we filter and take, of the filtrate, 100 c.c. for titration with the quinque-normal alkali. We may here stop, as the two indications already obtained permit us to decide on the purity of the sample. But we generally determine also the proportion of the insoluble fatty acids, especially if the presence of margarine is evident. To this end, whilst the fatty acids are cooling we tare accurately a filter without folds, dried at 100°; the solution of the soluble acids is passed through this filter, which retains the small clots carried along with the liquid, and we set aside the first 100 c.c. of the filtrate for titration. The cake of fatty acids remaining in the flask is taken up with boiling water; its melting-point is determined, and the whole is poured into the tared filter. A few washings with boiling water suffice to cleanse the flask and to free the filter from sodium sulphate. The funnel and its contents are placed in cold water and after the crystallisation of the fatty acids the filter is placed in a tared platinum capsule set in a Gay-Lussac stove. The first weighing is effected after three hours of desiccation, and the further loss is verified from hour to hour. In case of pure butter the loss does not fall to 5—6 m.grms. per hour until after 6—7 hours. The operation is then stopped and the final weight taken.

Industrial Review, and Patents Taken.—A collection of specifications chiefly German and English.

New Process for the Volumetric Determination of Sulphates in Presence of other Salts.—D. Sidersky.—This method will be inserted in full.

October, 1888.

Chemical Action of Certain Micro-organisms.—R. Warington.—From the *Journal of the Chemical Society*.

Action of the Aldehyds upon the Phenols.—H. Causse.—In this paper the author studies the action of glyoxylic acid, ethylic aldehyd, of heat, of zinc-powder, potassa, acetic anhydride, and acetone upon resorcine.

Manufacture of Explosives by Nobel's Explosives Company.—From the *Journal of the Society of Chemical Industry*.

The Oxidation of Linseed Oil Considered as an Analytical Procedure.—A. Chenevier.—The author considers that the oxidation method proposed by M. Livache may constitute an industrial procedure capable, in certain cases, of superseding the boiling oils with litharge. It may also furnish indications on the drying quality of any oil by an observation of the time which it requires, when once prepared, to dry upon a plate of glass. We have thus the advantage of knowing the drying properties of the oil, independently of substances which may be mixed with it afterwards. But it is inaccurate to rely upon the increase of weight of the oil, for it is too variable according to circumstances which are independent of its quality. For a linseed oil the best index of quality is still the specific gravity. The higher the gravity of an oil the better it dries. This is the difference between oils from French and from foreign seeds (Bombay, Calcutta, La Plata, &c.) The specific gravity of the former is always at least 0·9325, whilst the oils from foreign seeds are often below 0·932.

Influence of the Composition of Glass upon the Slow Displacement of the Zero in Thermometers.—R. Weber.—From the *Journal of the Chemical Society*. (*Berichte*, xxi., 1086).

Synthetic Formation of Closed Chains of Carbon.—MM. Colman and Perkin.—From the *Journal of the Chemical Society*.

The Production of Indigo in China.—From the *Journal of the Society of Arts*.

Ultramarine by the Moist Way.—Dr. F. Knapp.—The author has examined the preparation of ultramarine with silica alone, with alumina alone, or blue of the ultramarine type prepared with sodium salts or with calcium phosphate, the sodium sulphide, and the black precipitate extracted from it, and black sulphur, which he considers identical with the black sulphur of Magnus. In preparing ultramarine by the dry way sodium carbonate is added to the clay and the sulphur. Potassium carbonate cannot be used either in the dry or the wet process. There is no analogy between the two alkalies as regards the special properties of their sulphides. The sulphide obtained by fusing potassium carbonate with an excess of sulphur is devoid of that green shade observed in the corresponding sodium compound, but is of a pure reddish brown. If dissolved in water it deposits no black matter, and the solution is never green, but reddish brown.

The Origin and the Transformations of Nitric Acid in Plants.—From the *Journal of the Chemical Society*, but originally abstracted from the *Proceedings of the German Botanical Society*.

The Azo-colours.—Paul Richard.—An important paper not capable of being compressed within our limits.

Determination of Nitrotoluene in Ortho- and Paranitrotoluene.—MM. Reverdin and De la Harpe.—The process is based upon the fact that sulphonised paranitrotoluene is easily transformed by boiling with soda into a stilbene derivative (dinitrodisulphostilbene), the strongly alkaline solution of which has a deep red colour, whilst the corresponding ortho-compound is not attacked under the same conditions, and its alkaline solution remains colourless. The authors dissolve in fuming sulphuric acid orthonitrotoluene containing a known proportion of paranitrotoluene, say 5 per cent. They heat slightly in the water-bath, and when the sulphonation is complete they pour the solution into water, neutralise with soda, and dilute with much water, so that 1 c.c. of the solution, if heated with a given and unvarying quantity of a solution of caustic soda, takes a pale rose shade. They then operate in the same manner with the sample under examination, and dilute progressively the neutralised solution until 1 c.c. of this solution heated with soda gives the same shade as the type. The volume of this solution, compared with that of the type, is directly proportional to the quantity of para in the sample.

The Reduction-products of Hematoxyline. — J. Hegler.—The author has reduced the acetylic derivative of hæmatoxylene by means of zinc-powder. The product which passes over below 300° is a yellow solid, soluble in alcohol, ether, glacial acetic acid, and benzol, from which it crystallises in small yellow needles. Below 300°, and chiefly between 250° and 260°, there passes over a yellow oil, of a strong odour and insoluble in alkalies.

The Contact of Carbon and Other Substances at High Temperatures and under Strong Pressures.—Ch. A. Parsons.—From the Chemical News.

MISCELLANEOUS.

The Late Professor Tuson.— The friends of the late Professor Tuson find, with deep regret, that his death, at the premature age of 56, leaves his widow, with two daughters in delicate health dependent on her, entirely unprovided for. The undermentioned have kindly consented to act as a Committee for the purpose of raising a fund for her benefit, and it is hoped that a sufficient sum may be subscribed to enable them to purchase an Annuity or make some other suitable provision for her. The Honorary Secretaries will be very pleased to receive the names of any other gentlemen who may be willing to join the Committee, and most earnestly solicit subscriptions to the fund. Any amounts forwarded to Richard A. N. Powys, Esq., Royal Veterinary College, Camden Town, N.W., will be duly acknowledged. Subscriptions may also be paid to Messrs. Herries, Farquhar, and Co., 16, St. James's Street, S.W., to the credit of the "Tuson Fund." *Committee.*—Sir F. A. Abel, C.B., F.R.S., Prof. Attfield, F.R.S., Prof. Axe, M.R.C.V.S., E. Bellamy, F.R.C.S., Prof. Bernays, F.I.C., F.C.S., Prof. Brown, C.B., Hon. Associate R.C.V.S., Lloyd Bullock, F.C.S., Michael Carteighe, F.I.C , F.C.S., Spencer Chapman, Edward Clark, William Crookes, P.C.S., F.R.S., Warren, De la Rue, D.C.L., F.R S., H. Favarger, Dr. J. H. Gladstone, F.R.S., H. A. Greig, G. Harley, M.D., F.R.S., C. W. Heaton, F.I.C., F.C.S., F. J. Honey, A. H. Hooker, F.I.C., F.C.S., David Howard, J.P., F.C.S., C. R. Lightbody, Dr. Rudolph Messel, A. F. Moens, L. Mond, F.I.C., F.C.S., Hugo Müller, F.R.S., G. Plater, Prof. Penberthy, F.R.C.V.S., Richard A. N. Powys, Prof. Pritchard, P.R.C.V.S., W. O. Robinson, Prof. Shave, M.R.C.V.S., Prof. Simonds, Hon. Associate R.C.V.S., Harold Simpson, S. Harman Sturgis, John Spiller, F.I.C., F.C.S., W. Walker, and F. Wragg, F.R.C.V.S. *Hon. Secretaries*—C. W. Heaton and Richard A. N. Powys.

MEETINGS FOR THE WEEK.

Monday, 7th.—Medical, 8.30.
—— Society of Chemical Industry, 8. "Notes on Explosives," by C. Napier Hake.
Tuesday, 8th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Royal Institution, 3. "Clouds and Cloudland," by Professor Dewar, M.A., F.R.S.
Wednesday, 9th.—Geological, 8.
—— Microscopical, 8.
—— Pharmaceutical, 8.
Thursday, 10th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
Friday, 11th.—Astronomical, 8.
—— Quekett Club.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Science and Art Department.—(Reply to "Student.")—The querist will find what he requires on p. 73 of Jarmain's "Qualitative Analysis" (fifth edition), and also on page 238 of Valentin's "Qualitative Analysis" (sixth edition, 1884). The latter does not include salicylic acid, but this could be specially tested for.—Young Analyst.

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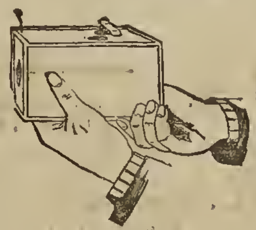

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January 4, 1889.

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THE RAPID AND SURE DETECTION OF ANTIMONY IN MINERALS.*

By ALEXANDER JOHNSTONE.

(Additional Note).

By adding a drop of ammonium sulphide to the white incrustation of Sb_2O_3 obtained by heating the antimoniferous mineral with fusion mixture in the inner blowpipe flame, I have shown how antimony can be rapidly and surely detected. When the antimony is present in *very* small quantity, the charcoal method must be the one adopted. In other cases, however, when the metal is more abundant, it can be quickly and very satisfactorily identified by heating the substance, with the addition of fusion mixture, in a glass tube (having about ¼″ bore) *open at both ends*. A little of the mixture of pounded mineral and flux is placed in a glass tube at a distance of about a quarter of an inch from the end. The tube is inclined slightly, and heat by means of a blowpipe flame is applied. Dense white smoke is produced, and a white sublimate deposits on the upper and sometimes also on the lower side of the tube. Touch this white sublimate with a *single* drop of ammonium sulphide, and at once the highly characteristic orange sulphide of antimony is produced very distinctly. No other white sublimate obtained in the open tube in the manner described than Sb_2O_3 is converted into an orange-coloured substance on the application of ammonium sulphide.

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ON THE
COLOURATION OF A COAL FIRE BY COMMON SALT.

By NORMAN LEONARD, B.Sc.

It is probable that many readers of the Chemical News have, like myself, been questioned as to the cause of the blue flame produced when a pinch of ordinary table salt is thrown into a coal fire. I have, however, never met with anyone who could explain the phenomenon, which appears to contradict the results of the usual experiments on flame colourations, in which a spirit or gas-lamp is used. Among the attempts at explanation which I have heard suggested are:—(1) That the vapours arising from the salt prevent complete combustion, the blue flame of carbon monoxide being the result. (2) That the sodium flame cuts off the yellow light emitted by the glowing coals, and only allows the red and blue to pass. (3) That the colouration is due to the chlorine of the salt, which may perhaps combine with the carbon and hydrogen of the fuel to form compounds, such as chloroform and tetrachloride of carbon, which are, in their turn, decomposed and oxidised, with production of the colouration in question.

The blue colouration seems to me to be of too purple a shade to admit of the truth of the first theory. The second theory seems rather far-fetched, but the third is pretty well borne out by the following facts, the result of some experiments which I have recently made.

1. The blue flame is not produced when sodium chloride is projected on to a red-hot platinum capsule.

2. The colouration produced by throwing sodium chloride into a coal fire is produced equally well by potassium chloride and less readily by the chlorides of barium, calcium, and ammonium.

3. The colouration is not produced by the carbonate, phosphate, or sulphate of sodium.

4. Chloroform, carbon tetrachloride, and ethylene dichloride, when thrown into a coal fire, produce blue colourations, similar to that produced by sodium chloride.

THE USE OF HYDROGEN PEROXIDE FOR THE DETERMINATION OF METALS OF THE IRON GROUP:
(1) CHROME; (2) MANGANESE; (3) IRON.

By ADOLPH CARNOT.

(1) *Chrome.*—The author has shown that oxygenated water rapidly and completely reduces chromic acid in a cold acid solution. In a hot alkaline or ammoniacal solution it effects the inverse transformation, and may be used for entirely peroxidising chromic oxide. The reaction presents a peculiar interest in an ammoniacal solution, differing from all the methods employed for the peroxidation of chrome, in as far as it dispenses with the use of fixed reagents, which are always undesirable in analyses.

A dilute solution, *e.g.*, of chromium chloride, heated to 100^c with the addition of a few c.c. of oxygenated water, then supersaturated with ammonia and heated anew to ebullition, becomes at first brown and turbid, then clear and pale yellow, passing to the state of ammonium chromate. The reaction is promoted by agitation, during which there is an escape of oxygen. If there remains a little chromium oxide not transformed, it must be let settle, separated by decantation, re-dissolved in an acid, and again treated with oxygenated water and ammonia.

When the peroxidation is complete the chromic acid may be determined volumetrically either with hydrogen peroxide or some other reducing agent in a standard solution. It is merely necessary for this determination that no trace of the first reagent may remain. But this is an easy precaution, as the hydrogen peroxide disappears completely after a few minutes' boiling in presence of a sufficient excess of ammonia. There is also sufficient indication of its presence, for on acidifying the cold liquid we see appear the blue tint characteristic of hydrogen peroxide in presence of chromic acid. It should then be boiled again with ammonia and a little hydrogen peroxide. The same reagent may also be used in gravimetric analyses, but its purity must be first ascertained. The presence of hydrochloric or sulphuric acid does not in general occasion any inconvenience.

Chrome may be thus peroxidised in an ammoniacal liquid and separated in one or two such operations from oxides which are precipitated by ammonia or ammonium carbonate. The solution of chromate can then be reduced by hydrogen peroxide in presence of a slight excess of acid, and heated to boiling. If we supersaturate with ammonia there will be partial peroxidation of the chrome by any peroxide of hydrogen which has not been destroyed, and the liquid will remain yellow. To avoid this inconvenience a current of sulphuretted hydrogen is passed for a few moments into the hot liquid, saturating it then with ammonia and letting it boil. The precipitation of the oxide of chrome is thus quite complete.

Chrome may be also determined very well by adding to the slightly acid solution, just reduced with hydrogen peroxide, first phosphate and then sodium or ammonium acetate, and boiling for ten to fifteen minutes. As the liquid remains acid, there is no peroxidation, and we obtain the precipitate of hydrated chromium phosphate of a fine green.

These two methods, volumetric and gravimetric,

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* See Chemical News, vol. lviii., p. 296.

furnish simple solutions for various problems of chemical analysis. If, *e.g.*, we wish to determine the proportions of chromic acid and of chromium sesquioxide in a mixture, the chromic acid is determined volumetrically with oxygenated water, and the total chrome is then precipitated as oxide or phosphate.

If we have a mixture of alkaline chromate and aluminate, like that found after chrome iron has been attacked with an alkaline flux and the silica has been separated, we determine the chromic acid with oxygenated water and then precipitate together and weigh the chromium and aluminium phosphates; knowing the chromium, the aluminium is calculated as the difference. If we have a solution containing iron and chrome as sesquioxide, we peroxidise with hydrogen peroxide and ammonia, boiling for five to ten minutes. We then re-dissolve in a slight excess of acid and determine the chromic acid and ferric oxide as indicated for alumina in the previous case.

(2) *Manganese.*—In an acid liquid manganese, like chrome, is reduced by hydrogen peroxide, and in an ammoniacal solution it is peroxidised. We need not enlarge on the former reaction, which is well known and is utilised in the determination of oxygenated water with potassium permanganate. The second reaction may claim some attention on account of the facility which it offers for the determination of manganese. If we pour a few c.c. of oxygenated water and afterwards ammonia into a solution containing a manganous salt, there is at once produced a dark brown precipitate containing the total manganese. On heating to a boil the precipitate collects together, but it retains a portion of the bases which existed in the liquid, and which can only be removed by a series of similar precipitations, which may, however, be executed very rapidly. The volumetric determination can always be effected satisfactorily. The author has ascertained that the manganese is entirely precipitated as peroxide, whether it exists alone or along with lime, baryta, oxide of zinc, or ferric oxide. The solution is made ammoniacal and boiled for about ten minutes in order completely to remove any excess of hydrogen peroxide. The oxygen of the peroxide, and consequently the manganese itself, is determined volumetrically; for instance, by means of oxalic acid, sulphuric acid, and potassium permanganate.

(3) *Iron.*—It is well known that iron, unlike the two former metals, is peroxidised by hydrogen peroxide in an acid solution. The conversion is immediate, even in the cold, and is effected more easily than with any other oxidising agent.—*Comptes Rendus*, vol. cvii., p. 997.

SPECTRUM ANALYSIS OF CADMIUM.*

By A. GRÜNWALD,

Professor of Mathematics in the Imp. Roy. German Polytechnic University at Prague.

(Continued from p. 7).

The IIIrd group of the cadmium-rays embraces the rays observed principally by Hartley and Adeney.

λ =
*4414·5 } nodal rays of the IIIrd and IVth group.
*4115·2
*3986·0 Mascart
3976·3
3974·5
3940·0
3851·0
3810·0
3682·6 (?) { of doubtful origin, like an impurity, as it proceeds from one electrode only.
3611·8 strong.
3609·6 very strong.
3608·0 Mascart.
3535·0
3466·8 strong.
3465·4 very strong.
3402·9 very strong.
3384·7
3288·0 Mascart.
**3233·6 nodal ray of the IIIrd and Vth group.

The wave-lengths λ of these rays belong to the group (H, *b*), or to that condensation form of the primary body "*b*" in which it occurs in free hydrogen, and (besides other condensation forms) also in the vapour of magnesium and of carbon.

They satisfy, indeed, according to the Tables III, III*a*, III*b*, and III*c*, more or less completely the known criteria of such rays, which I have already mentioned in the discussion of the IInd group, and given for the wave-lengths (λ′) there occurring.

They can be summarily expressed by the following symbolic equations:—

$\frac{4}{5}(H, b) = (H_2O, H, b)$ water spectrum (first chief criterion).
$\frac{23}{32}\cdot\frac{46}{41}(H, b) = (H_2O, O, O', b)$ water spectrum (second criterion).
$\frac{21}{32}\cdot\frac{70}{59}(H, b) = (H_2O, O, O', O'', b)$ water spectrum (third criterion).
$\frac{2}{3}(H, b) = (H_2O, H)$ water spectrum (fourth criterion).

and—

$\frac{46}{41}(H, b) = (O, O'b)$ oxygen (first accessory criterion).
$\frac{70}{59}(H, b) = (O, O', O'', b)$ oxygen (second accessory criterion).

The wave-lengths λ, in the first column of the tables, which satisfy simultaneously the seven criteria with great accuracy, proving thereby the existence of this group.

The rays λ = 4414·5, 4115·2, 3986, connect the IIIrd and IVth, the ray 3233·6 the IIIrd and Vth group as nodal rays.

"Cadmium contains, therefore, the primary body "*b*" in the same chemical state as in free hydrogen, but in another physical modification."

The IVth group of the cadmium-rays is composed of the following rays:—

λ =
*5337·0 very strong, Kirchhoff } empirical nodal rays of the IIIrd and IVth.
*5153·0 Huggins
4798·0 strong, Huggins.
4677·6+Liveing and Dewar.
4676·7 Hartley and Adeney.
4416·0 Huggins (4415·5, strong, Thalén).
**4414·5 { Hartley and Adeney, nodal ray of the IIIrd and IVth group.
4215·3 Hartley and Adeney.
4158·0 (?) ,, ,,
4141·0 ,, ,,
4127·4 ,, ,,
**4115·2 ,, ,, nodal ray of the IIIrd and IVth group.
3987·6 ,, ,,
**3986·0 Mascart, nodal ray of the IIIrd and IVth group.
3498·2 Hartley and Adeney.

The cited rays are "*c*" rays, due to the primary body "*c*" in the same chemical state as in free oxygen or in magnesium vapour. For the wave-lengths λ give (see Table IV.), by multiplication with $\frac{3}{5}$, $\frac{5}{8}$, and $\frac{2}{3}$, corresponding wave-lengths, $\frac{3}{5}\lambda$, $\frac{5}{8}\lambda$, $\frac{2}{3}\lambda$ of the water spectrum, and answer thereby to the known criteria of the "*c*" rays, which can be shortly expressed by the following symbolical equations:—

$\frac{3}{5}(c) = (H_2O, O, O', O'', c)$ (first or chief criterion).
$\frac{5}{8}(c) = (H_2O, O, O', O'')$ (second criterion).
$\frac{2}{3}(c) = (H_2O, O)$ (third criterion).

The physical modification in which "*c*" occurs in cadmium seems to be similar to that in which it occurs

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* A Paper read before the Royal Society, December 13, 1888.

in oxygen; as several "c" rays of cadmium, viz., $\lambda = 4476 \cdot 7$, 4416, 4414·5, and 4158·0 (?) agree almost completely with corresponding "c" rays of oxygen.

The group under discussion is connected with the IInd group by the nodal rays $\lambda = 5337$, 5153, and with the IIIrd group by the nodal rays $\lambda = 4414 \cdot 5$, 4115·2, and 3986. The wave-lengths λ of those rays, which satisfy all three criteria, and are therefore characteristic of this group. Cadmium contains consequently the primary body "c" also in the same chemical state as in oxygen or in magnesium, and in physical modifications similar to that of the "c" in oxygen.

The Vth group of the cadmium-rays (see the Tables V., V.a, V.b, V.c), is a very numerous one. Their wave-lengths are, according to Hartley and Adeney (st. = strong, v. st. = very strong, f. st. = fairly strong)—

$\lambda =$

3285·3
3282·9
3276·4
3264·1 nebulous.
3260·2 st.
3251·8
3249·5 st.
*3233·6 empir. nodal ray of the Vth and IIIrd group.
3222·6
3219·9
3216·0
3211·8
3200·6
3196·8
3194·9
3185·1 st.
3181·5
3176·1 (?)
3172·9 st.
3161·0 st.
3156·6
3152·7
3132·5
3129·4 st.
3123·6
3120·9
3117·8 f. st.
3112·0
3095·0 st.
3090·5
3087·7
3084·3 st.
3080·2
3076·7
3073·2
3067·8 f. st.
3064·0 st.
3058·4 f. st.
3052·3 f. st.
3048·2 f. st.
3034·9
3023·8
3016·1
3013·8
3002·2
2994·8
**2986·1 empir. nodal ray of the Vth and VIth group.
2979·9 st.
2970·2
**2964·5 empir. nodal ray of the Vth and VIth group.
2951·4
2947·1 f. st.
**2909·9 empir. nodal ray of the Vth and VIth group.
2880·1 st.
**2868·0 empir. nodal ray of the Vth and VIth group.
2833·0
2832·3
**2807·3 empir. nodal ray of the Vth and VIth group.

$\lambda =$

**2804·0 empir. nodal ray of the Vth and VIth group.
2774·5
2766·5
**2763·1 empir. nodal ray of the Vth and VIth group.
**2726·9 empir. nodal ray of the Vth and VIth group.
**2706·0 empir. nodal ray of the Vth and VIth group.
**2677·2 empir. nodal ray of the Vth and VIth group.
**2645·4 empir. nodal ray of the Vth and VIth group.
2632·3
2630·2
2618·0
2614·0
**2611·0 empir. nodal ray of the Vth and VIth group.
2600·8
**2598·8 empir. nodal ray of the Vth and VIth group.
**2574·2 Mascart, empirical nodal ray of the Vth and VIth group.
**2563·2 empir. nodal ray of the Vth and VIth group.
2551·6
**2547·2 empir. nodal ray of the Vth and VIth group.
2499·6
**2488·2 empir. nodal ray of the Vth and VIth group.
**2469·3 f. st.; empir. nodal ray of the Vth and VIth group.
**2376·6 empir. nodal ray of the Vth and VIth group.
2329·5 st.
{ 2313·6 v. st., broad; Hartley.
{ 2313·5 Cornu.
** { 2288·9 v. st., broad } empir. nodal ray of the Vth and
{ 2288·5 Cornu } VIth group.
2268·6
2265·9 v. st., broad.
**2227·0 empir. nodal ray of the Vth and VIth group.
2206·0
2111·5

The foregoing numbers agree almost completely with corresponding wave-lengths of the water spectrum. They are transformed by multiplication with the factor $\frac{5}{4}$ into numbers $\lambda' = \frac{5}{4}\lambda$, which possess, unmistakably, the characteristic marks of wave-lengths due to the group (H, b).

The wave-lengths λ belong, therefore, to the very large group of wave-lengths (H_2O, H, b) which the primary body "b" produces in the chemical state in which it exists in the bound hydrogen of aqueous vapour.

The Tables V., V.a, V.b, V.c, which form in reality only one table, but divided into several branches, because the first columns of Tables V.a, V.b, V.c, coincide with the third column of Table V., give us a plain idea of the remarkable relations and agreements which the Vth group shows in regard to the criteria quoted summarily below. The wave-lengths are also here, and in the tables, those which satisfy most completely and exactly the criteria.

Criteria of the Vth Group.

*Cd $\lambda = (H_2O, H, b)$ water spectrum (first chief criterion).
$\lambda' = \frac{5}{4}\lambda = (H, b)$ hydrogen (accessory criterion).
*$\frac{23}{32} \cdot \frac{46}{41}\lambda' = (H_2O, O, O', b)$ water spectrum (second criterion).
$\frac{46}{41}\lambda' = (O, O', b)$ oxygen (accessory criterion).
*$\frac{21}{32} \cdot \frac{70}{59}\lambda' = (H_2O, O, O', O'', b)$ water spectrum (third criterion).
$\frac{70}{59}\lambda' = (O, O', O'', b)$ oxygen (accessory criterion).
*$\frac{2}{3}\lambda' = (H_2O, H)$ water spectrum (fourth criterion).

Among the rays of the Vth group occur, besides the empirical nodal ray 3233·6 already mentioned in the IIIrd group, a series of rays which satisfy not only the criteria of that group, but also that of the VIth group, being, therefore, empirical nodal rays of the Vth and VIth group.

These rays are—

λ = 2986·1 ·, 2964·5 ·, 2909·9 ·, 2868·0, 2807·3 ·, 2804·0 ·, 2763·1, 2726·9 ·, 2706·0 ·, 2677·2, 2645·4 –, 2611·0 –, 2598·8 –, 2574·2, 2563·2 –, 2547·2 –, 2488·2, 2469·3, 2376·6 +, 2288·9, 2227·0 –.

The wave-lengths λ = 2574·2 (Mascart), 2288·9 (Hartley and Adeney), answer on the photographs to certain points of very broad and strong lines; λ = 2469·3 is a fairly strong line. The wave-lengths followed above by short lines or thick points belong, according to Hartley and Adeney, to short relatively to very short lines. The forementioned lines may, for the most part, be only seemingly, and not truly nodal rays; if they be not really nodal rays, they may be either double rays, one of which belongs to the Vth, and the other to the VIth group, or such rays as might be proved, by more accurate measurements of the wave-lengths of Cd, H_2O vapour, and of the other comparison spectra, to belong only to one of the two groups, (thus probably 2807·3, 2726·9, 2488·2, 2376·6, only to the Vth, and 2909·0, 2804·0, 2706·0, 2677·2, 2611·0, 2598·8, 2574·2, 2563·2 only to the VIth group).

The rays of the IIIrd group, λ = 3402·9, 3288, and the ray λ = 3176·1, belong, according to the criteria, probably also to the Vth group, though they (perhaps from their faintness) have not hitherto been observed amongst the rays of the water spectrum.

"Cadmium contains, in consequence of the above explanation, the primary body "*b*" in that chemical condensation form in which it occurs also in the hydrogen bound in aqueous vapour, being at the same time in a very similar physical state."

Peculiarly related to the structure of cadmium, and therefore of great importance as a point of departure for new researches, which throw an unexpected light upon the structure of the bodies hitherto looked upon as elements (see the Introduction), is the VIth group of the cadmium rays, (Tables VI., VI.*a*, VI.*b*, VI.*c*). It includes the rays observed (with few exceptions) by Hartley and Adeney (st. = strong, v. st. = very strong, f. st. = fairly strong, bd. = broad):—

λ =	
3209·0	
3177·9	
*2986·1	empir. nodal ray of the Vth and VIth group.
*2964·5	empir. nodal ray of the Vth and VIth group.
*2909·9	empir. nodal ray of the Vth and VIth group.
*2868·0	empir. nodal ray of the Vth and VIth group.
2836·1	f. st.
*2832·3	empir. nodal ray of the Vth and VIth group.
*2807·3	empir. nodal ray of the Vth and VIth group.
*2804·0	empir. nodal ray of the Vth and VIth group.
2779·8	
*2763·1	empir. nodal ray of the Vth and VIth group.
2747·7	v. st., bd.
2743·0	Mascart.
*2726·9	empir. nodal ray of the Vth and VIth group.
*2706·0	empir. nodal ray of the Vth and VIth group.
*2677·2	empir. nodal ray of the Vth and VIth group.
2658·5	
2649·4	
2645·4	
2639·7 +	
2639·5 –	
2635·3	
2632·7	
2629·1	
2624·8	
*2611·0	empir. nodal ray of the Vth and VIth group.
*2598·8	empir. nodal ray of the Vth and VIth group.
2595·3	
2592·0	
2587·8	
2585·0	
2574·2	Mascart; empir. nodal ray of the Vth and VIth group.
2572·2	v. st., bd.
*2563·2	empir. nodal ray of the Vth and VIth group.
2557·4	
2555·0	
*2547·2	empir. nodal ray of the Vth and VIth group.
2544·5	
*2488·2	empir. nodal ray of the Vth and VIth group.
*2469·3	f. st.; empir. nodal ray of the Vth and VIth group.
2418·5	
2377·3	
*2376·6	empir. nodal ray of the Vth and VIth group.
2321·6	v. st.
2321·8	Cornu.
2318·0	Mascart.
2312·5	value of L. Bell's 2312·83 on Rowland's scale reduced to Angström's scale.
2307·0	st.
*2288·9	v. st., bd. } empir. nodal ray of the Vth and VIth group.
2288·5	Cornu.
2249·2	
2241·4	f. st.
*2227·0	empir. nodal ray of the Vth and VIth group.
2217·1	(?) Mascart.
2196·4	st. bd.
2194·5	Cornu.
2146·8	st., bd.
2144·1	Cornu.

The wave-lengths λ of this group are transformed by multiplication with the factor $\frac{7}{6}$ to wave-lengths $\lambda' = \frac{7}{6}\lambda$ belonging to the group (H_2O, H, *b*), which can be recognised and proved to be such by the known criteria, quoted summarily and used already in the discussion of the Vth group, which forms also a partial group of (H_2O, H, *b*). We have only to write there λ' instead of λ, and λ'' instead of λ', to adapt the criteria formerly used to the present conditions.

The criteria of the VIth group are therefore shortly—

$*\frac{7}{6}$ Cd. $\lambda = (H_2O, H, b)\lambda'$ water spectrum (first or chief criterion).

$\lambda'' = \frac{5}{4}\lambda'$ hydrogen (accessory criterion).

$*\frac{23}{32} \cdot \frac{46}{41}\lambda'' = (H_2O, O, O', b)$ water spectrum (second criterion).

$\frac{46}{41}\lambda'' = (O, O', b)$ oxygen (accessory criterion).

$*\frac{21}{32} \cdot \frac{70}{59}\lambda'' = (H_2O, O, O', O'', b)$ water spectrum (third criterion).

$\frac{70}{59}\lambda'' = (O, O', O'', b)$ oxygen (accessory criterion).

$*\frac{2}{3}\lambda'' = (H_2O, H)$ water spectrum (fourth criterion).

The reader will find the comparisons prescribed by the above cited criteria, carried out in the Tables VI., VI.*a*, VI.*b*, VI.*c*, the three latter of which are only three different combinations of the first (VI.), as the first columns of VI.*a*, VI.*b*, VI.*c* are identical with the fourth column of VI.

The special arrangement of the single tables is easily understood without further explanation. The figures here also are those which satisfy in the best manner the most part of the given criteria (including the chief criterion), or rather those for which the proofs referred to are the most conclusive with the measurements known at present.

The empirical (and perhaps for the most part only seeming, not real) nodal rays of the Vth and VIth group have already been treated in detail in the discussion of the latter. Finally it may be remarked that the signs + or – annexed at the right hand to several wave-lengths indicate that the true values of them might be, having regard to the criteria, relatively greater or smaller.

With regard to my previously established fundamental theorem (*Astronomische Nachrichten*, 1887, No. 2797), the above discussion shows that cadmium contains the primary body "*b*" also in a chemical state, $\frac{7}{6}$ times more condensed than in the chemical states corresponding to the Vth group, viz., $\frac{7}{6}$ times more condensed than in the bound hydrogen of aqueous vapour.

This condensation form is therefore the strongest of all condensation forms of "*b*" occurring in cadmium; and the primary element "*b*" forms in this chemical state the kernel, upon and around which the other condensation forms of the primary bodies "*b*" and "*c*" have been stored in the original formation of the cadmium. Summing the results of all our former discussions, we can enunciate as the chief result of our spectrum analysis of cadmium the following statement:—

Cadmium is a compound that behaves itself in all chemical processes hitherto known as a radical or relative element.

It contains, according to the analysis of its line spectrum as at present known, the primary element "*b*" of hydrogen ($H = ba_4$) in four, and the primary element "*c*" of oxygen and magnesium in (at least) two different chemical states, viz.:—

I. *The Primary Element* "c."

(α). In the same chemical state as in oxygen, magnesium, and carbon, and in a physical modification similar (partly at least) to that in which it occurs in oxygen; it emits in this state the IVth group of the cadmium rays.

(β). In a state more dilated than the former in the ratio 2 : 3, producing the Ist group of the cadmium rays.

II. *The Primary Element* "b."

(α). In a chemical state as in "helium," that is to say in the state into which it comes when hydrogen ($= ba_4$) begins to be associated by sufficiently elevated temperature, and perhaps also by simultaneously suitably diminished pressure, expanding itself at once in the ratio 2 : 3; it emits in this state the IInd group of the cadmium rays.

(β). In the same chemical condensation form as in free hydrogen ($= ba_4$), but in another physical modification, originating the IIIrd group of the Cd rays.

(γ). In the same chemical condensation, and at the same time in a physical modification, very similar to that in which it occurs in the bound hydrogen of aqueous vapour, giving out the rays of the Vth group; finally:

(δ). In a condensation form in which "*b*" is $\frac{7}{6}$ times more condensed than sub (γ), emitting the rays of the VIth group. In this state of relatively maximum condensation it forms the "kernel," upon and around which the other condensation forms of the primary bodies "*b*" and "*c*" have been stored in the original formation of the cadmium under circumstances hitherto entirely unknown.

"The primary substance '*c*' in the state cited sub I. (α), and the three condensation forms of '*b*' quoted sub II. (α), II. (β), and II. (γ), occur also in magnesium (see 'Mathematische Spektralanalyse des Magnesium's und der Kohle,' 1887, in the *Sitzungsberichte der Wiener Academie*), but evidently in less quantity by weight, according to the less atomic weight of magnesium, thus accounting for the near relation existing between cadmium and magnesium."

(To be continued).

UNIFORM METHODS FOR THE ANALYSIS OF FERTILISERS, CATTLE FOODS, DAIRY PRODUCTS, SUGAR, AND FERMENTED LIQUORS.*

(Continued from p. 10).

Butter Analysis.

Action of Alcohol on Butter Fat.

Cochran has made experiments on the solubilities of the different glycerides of butter in alcohol with reference to the quantity of volatile acid which the dissolved and undissolved portions would yield when treated by Reichert's method. As a result of the work it is seen that that portion of the glycerides dissolved by ethyl or methyl alcohol is richer in volatile acids than the undissolved portions. The iodine number of the dissolved fat is less than the undissolved fat. The melting-point of the fats dissolved by alcohol is less than that of the undissolved fats.

The above facts would be of importance in the examination of butters, to which it is suspected artificial butyrates may have been added.—(Abstract from the *Analyst*, vol. xiii., p. 55).

A Quick Method of Distinguishing Oleomargarine in Butter.

Dubernard has proposed the following method for a qualitative examination of butter for oleomargarine. The method rests upon the observation that pure butter vigorously shaken with ammonia at a temperature of from 70° to 80° and afterwards heated to 100° produces only a small amount of foam, which does not last a long time. Margarine, on the contrary, produces a large quantity of lasting foam. In order to distinguish butter from margarine by this method, the following manipulation is pursued.

In a test-tube place about 3 grms. of the butter to be examined. Heat to 95° or 100° in a water-bath, and then allow to cool to about 80°. Add to the melted substance 5 c.c. of ammonia, shake vigorously, and place again in the water-bath and heat to 95° or 100°. The ammonia is volatilised with the formation of foam. The foam in the tube rises more or less according as the butter contains a larger or smaller quantity of oleomargarine. In mixtures of pure butter with known quantities of margarine the tube can be graduated and the relative quantities of butter and margarine thus approximately determined.—(Abstract from *Chemiker Zeitung*, 1888, No. 46, p. 760).

Detection of Adulterations in Butter.

Bockairy proposes the following method for the detection of adulterations in butter which rest upon the different solubilities of fats in toluene:—

Place in a test-tube 15 c.c. of pure toluene, add 15 c.c. of the filtered fat and 40 c.c. of strong alcohol at 18°; the toluene holding in solution the fatty matter remains at the bottom of the tube. By means of a water-bath the tube is heated to 50° and thoroughly shaken. If the sample is of butter fat or a mixture of butter fat and some other kind, there is no turbidity; but if no butter be present a turbidity is at once manifested. The tube is placed in water at a temperature of 40° for half an hour; pure butter gives no turbidity at the end of that time, but if other fats are present the mixture will appear turbid.—(Abstract taken from the Chemical News, July 6, 1888, p. 11, and *Bul. de la Société Chimique de Paris*, vol. xlix., No. 5, p. 331).

Difference Between Natural and Artificial Butter.

C. J. van Lookeren proposes the following for a characteristic test between pure and falsified butter:—

A small amount of butter is melted in a teaspoon, and a drop thereof placed in boiling water contained in a watch-glass. If the butter be pure a thin film of fat is formed upon the hot water, which breaks up into numerous fat globules, which tend to collect quickly at the periphery. With oleomargarine, &c., a thin film of fat is formed in the same way, which, however, breaks up into only a few large drops, which remain distributed over the whole surface of the water. The conditions for the success of the experiment are that the water be perfectly pure and clear, and the melted butter fat very hot.—(Abstract in the Repertorium of the *Chemiker Zeitung*, No. 18, 1888, p. 143, from the *Milchztg.*, 1888, No. 17, p. 562).

A Modification of Koettstoefer's and Reichert's Processes.

Lowe has proposed the following method of determining

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* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

the volatility and saponification equivalent of butter and other fats :—

About 2 grms. of the filtered fat are saponified with 10 c.c. of normal alcoholic potash in a stoppered flask. The alcohol is then boiled off and the soap dissolved in 50 c.c. of hot water. The excess of potash is then determined with semi-normal sulphuric acid solution. The saponification numbers having thus been determined, enough additional sulphuric acid is run in to make 25 c.c. in all. The flask is then connected to a condenser, and 50 c.c. distilled off, filtered, and determined in the usual way. The same flask is used throughout the whole process, one of 200 c.c. capacity answering the purpose very well. The whole process does not occupy more than two hours, and can be completed often in less time.

Tyrer, criticising the process of Mr. Lowe, was of the opinion that the quantity of fat taken, two grms., was too small, since it gave only about one-tenth of a grm. of volatile fatty acids. The alkali also dissolved some of the glass, thus introducing an error of which no account was taken. Carbonic acid, moreover, expelled by this method, increased the apparent estimate of filtered fatty acids.—(Abstract from the *Journal of the Society of Chemical Industry*, March, 1888, p. 185; May, 1888, p. 376).

Saponification Without the Use of Alcohol.

Mansfeld, in order to avoid the losses due to etherification during saponification in the presence of alcohol, has proposed to carry on the process of saponification, preparatory to the estimation of volatile acids in butter, without the use of alcohol. The method employed is as follows :—

Five grms. of the melted and filtered butter fat are taken; into the melted fat are allowed to run 2 c.c. of a potash lye containing 100 grms. caustic potash in 100 c.c. of water. The flask is closed with a stopper carrying a glass tube drawn out to a capillary point; the flask is then placed in an air-bath heated to about 100° and allowed to remain for two hours. At the end of that time the saponification is completed. One hundred c.c. of water are now added, the flask placed in a water-bath until the soap is dissolved, which is decomposed and subjected to distillation in the usual way.—(Abstract in *Chemisches Central-Blatt*, June 23, 1888, p. 870, from *M. Z.*, No. 17, pp. 281—83).

Wollny's Criticism of the Reichert-Meissl Method.

The method of determining volatile fatty acids devised by Reichert has, during the past year, been subjected to an extended criticism by Dr. R. Wollny, of Kiel. Dr. Wollny, as a result of 98 analytical tests, was convinced of the truth of the statement of Professor Fresenius, that the Reichert method was totally unreliable for the determination of very small quantities of butter in oleomargarine.

As a result of his analytical work Dr. Wollny was convinced that the chief source of error in the Reichert work was due to the absorption of carbonic acid. He asserts that the error which may arise from this source must amount to as much as 10 per cent butter, and renders the results obtained by the method quite inaccurate. It being very difficult to secure an alkali free from carbonate, the author decided to use a 50 per cent solution of caustic soda instead of potash, since in a solution of that strength the chloride, nitrate, sulphate, and carbonate of soda are quite insoluble.

An arrangement was also devised by which the solution of caustic soda could be kept and drawn off for use without risk of absorption of carbonic acid. Such a solution made and kept in this way gave for 3 c.c. treated by the ordinary process of Reichert's distillation, an amount of volatile acid sufficient to neutralise from 0·2 to 0·3 c.c. of the decinormal barium hydrate solution. The author's precautions to prevent absorption of CO_2 are wholly unnecessary when the saponification is carried on in closed flasks.

Dr. Wollny further discusses the errors due to the formation of butyric ethers during saponification and distillation, and also the error due to the mechanical translation of particles of insoluble fatty acids during the process of distillation, and the error due to the shape and size of the vessel in which the distillation is carried on and the time of its duration. The magnitude of these errors he states as follows :—

(1). Due to absorption of carbonic acid + 10 per cent (2 and 3). Formation of butyric ether − 13 per cent. (4). Cohesion of fatty acids − 30 per cent. (5). Shape and size of vessel + or − 5 per cent.—(*M. Z.*, 1887, Nos. 32, 33, 34, 35, and the *Analyst*, 1887, Nos. 139, 140, 141, 142).

Dr. Wollny further describes the exact methods to be employed in the examination and the results obtained, for the details of which I refer to the original papers.

As president of the butter commission of the German Dairy Association, Dr. Wollny has proposed the following method to be employed in the comparative examinations of butter for the forthcoming report of the commission (see *M. Z.*, No. 25, 1888). In the preparation of the decinormal barium solution each one of those taking part in the analyses has been furnished with samples of normal sulphuric acid, pure crystallised chloride of barium, and pure peroxalate of potash. In addition to this for testing the refractometer samples of olive oil, nitrobenzol and monobromnaphthalin have been sent. Following are the details given by Dr. Wollny for the preparation of the reagents and the conduct of the analysis.

METHOD PROPOSED BY DR. WOLLNY FOR THE EXAMINATION OF BUTTER FOR THE COMMISSION OF THE GERMAN DAIRY UNION.

(From the *Milch Zeitung*, 1888, No 25 et seq.).

1. *Proving the Weights and Burettes.*

The weights which are to be used must be carefully compared and the burettes calibrated.

2. *Estimation of the Strength of Normal Sulphuric Acid.*

A clean dry dropping-bottle of about 60 grms. content, the tip of which is touched with vaseline on the outside, is carefully weighed; 35 or 40 grms. of normal sulphuric acid are then placed in it, and it is again weighed. Afterwards five portions in duplicate of about 3 grms. are weighed in a beaker glass of 300 c.c. capacity. The drop-bottle being weighed after each portion, the exact weight of the normal sulphuric acid is determined. One hundred c.c. of recently boiled distilled water are added to each of the portions. One hundred c.c. of this distilled water must not require more than 2 drops of barium solution to give colour after 1 c.c. of the phenolphthalein solution has been added. The samples are heated in the water-bath to the boiling-point, and to each portion as many c.c. of dilute barium chloride solution added that for each grm. of the normal sulphuric acid there are present 10 c.c. of the $BaCl_2$. The barium chloride solution contains 15 grms. of the salt in 1 litre of distilled water. Afterwards the beakers are covered with watch-glasses and allowed to stand for fifteen minutes over the water-bath. The precipitates are to be collected upon ash free filters of 9 centimetres diameter, and washed with hot distilled water until the chlorine action disappears. After drying and incineration the weight obtained is to be multiplied by the factor 0·34331. The five duplicate portions, after the addition of one c.c. of phenolphthalein solution, are treated with barium solution until the red colour appears. The numbers obtained are to be calculated to 100 grms. of the normal sulphuric acid.

3. *Estimation of Saturation of the Normal Sulphuric Acid by the Barium Solution.*

From the results obtained by the above analyses the exact strength of the decinormal barium solution is to be determined.

4. *Titration of Barium Solution with Potassium Peroxalate.*

One grm. of the peroxalate of potassium, after drying for twelve hours in a desiccator over sulphuric acid, is placed in a weighing bottle similar to the one described above. Sixty grms. of hot distilled water are then added, and after the salt has been dissolved and the solution cooled the weighing-bottle is again weighed. About 12 grms. of the solution are now run into each of five beaker glasses, and the exact amount in each one determined by re-weighing the weighing-bottle. Ninety c.c. of recently boiled distilled water are now added, together with one c.c. of phenolphthalein solution. The barium solution is now added until the red colour, which at first disappears, remains for at least five minutes. The results are calculated to the strength of the barium solution according to the formula—

$$T = \frac{10000 \times p\ (b-t)}{84{\cdot}5\ n\ (l-t)},$$

in which

t = the weight of the weighing-bottle empty.
b = the weight of the weighing bottle + the peroxalate.
l = the weight of the weighing bottle + the peroxalate solution.
p = the weight of the portion of the solution employed.
n = the number of c.c. of barium solution used.

5. *Estimation of the Volatile Acids after Saponification with the Aid of Alcohol.*

Five grms. of the butter fat are weighed into an Erlenmeyer flask; 10 c.c. of alcohol at 96 per cent, and 2 c.c. of concentrated soda lye at 50 per cent, which has been preserved in an atmosphere free of carbonic acid, are added. The flask, furnished with a reflux condenser, is heated, with occasional shaking, in a boiling water-bath for one-quarter of an hour. The alcohol is then distilled off by allowing the flask to remain for three-quarters of an hour in a boiling water-bath. One hundred c.c. of recently boiled distilled water are then added and allowed to remain in the water-bath until the soap is dissolved. The soap solution is then immediately decomposed with 40 c.c. of dilute sulphuric acid (25 c.c. sulphuric acid to 1 litre), and the flask immediately connected with the condenser. This connection is made by means of a 7 m.m. diameter glass tube, which, 1 c.m. above the cork, is blown into a bulb 2 c.m. in diameter; the glass tube is now carried obliquely upwards about 6 c.m. and then bent obliquely downward; it is connected with the condenser by a not too short rubber tube. The flask is now warmed by a small flame until the insoluble acids are melted to a clear transparent liquid. The flame is now turned on with such strength that within half an hour exactly 110 c.c. are distilled off. 100 c.c. of the distillate are now filtered off, placed in a beaker glass, 1 c.c. of phenolphthalein solution added, and titrated with barium solution; when the red colour is shown the contents of the beaker glass are poured back into the measuring glass in which the 100 c.c. was measured, again poured back into the beaker, and again titrated with the barium solution until the red colour becomes permanent. The distillation should take place in as nearly thirty minutes as possible.

6. *Estimation of the Volatile Acids after Saponification without Alcohol.*

Five grms. of the butter fat are saponified with 2 c.c. of concentrated potash lye preserved from contact with carbonic acid. The lye solution is made by dissolving 100 grms. of the potash in 58 grms. of water. By gentle rotation of the flask the lye and fat are intimately mixed together; the flask is then placed in a vertical position over a boiling water-bath until the mixture becomes solid. It is then placed obliquely in the water bath. After it has remained here for two hours it is taken out and the remainder of the process continued as above.

7. *Estimation of the Mean Molecular Weight of the Volatile Fat Acids.*

The soap solution obtained by the titration of barium hydrate in No. 6 is placed in a weighed platinum dish, evaporated to dryness in the water-bath, dried in a drying oven for two hours, and again weighed.

8. *Estimation of Volatile Fat Acids by Distillation from Magnesium Salts.*

Eight grms. of butter fat are placed in an Erlenmeyer flask, treated with 3 c.c. of concentrated potash lye and 15 c.c. of alcohol, as in No. 5, and the alcohol then distilled off. The soap, dissolved in 100 c.c. of water, is washed with 250 c.c. of water in a measuring flask of 500 c.c. capacity, and cooled to the temperature of the room. Then, by means of a pipette, with constant shaking, 50 c.c. of magnesium sulphate solution, 15 per cent strength, are added, the flask filled up to the mark with water, and vigorously shaken. The mixture is now placed upon an 18 centimetre filter and 300 c.c. filtered into a measuring flask. The filtrate is brought into a flask holding about 500 c.c., which on the one side is joined with a steam generator and on the other with a condenser. 2 c.c. of strong sulphuric acid, together with two pieces of pumice stone, are added. 250 to 275 c.c. are now distilled off into a measuring flask of 500 c.c. capacity, the distillate being filtered into the flask through a moistened filter. The gas flame under the distillation flask is then turned down low and the distillation continued in a current of steam until the 500 c.c. flask is full. After the filter which has been used has been washed with a little water, the distillate is placed in a large flask of 1 litre capacity and 2 c.c. of phenolphthalein added and titrated.

9. *Estimation of the Volatile Fatty Acids from Copper Salts.*

The estimation is carried on exactly as in No. 8, substituting 50 c.c. of copper sulphate solution for the 50 c.c. of magnesium salts. In the present case the distillate may be collected directly in the one half-litre flask without filtration, since by precipitation with copper sulphate solution no insoluble fatty acids pass over during distillation.

10. *Estimation of Volatile Fatty Acids by Distillation in a Current of Steam, according to Goldmann.*

Five grms. of butter fat are weighed in a long-necked flask of about 300 c.c. capacity. 10 c.c. alcohol and 2 c.c. potash lye are added, and the flask connected, on the one hand, with a steam generator, and on the other with a condenser. The contents of the flask are now warmed with a small flame for twenty minutes, the condenser being directed obliquely downward, and, in a measuring cylinder, 6 c.c. distilled off. The steam is then directed into the flask and 50 c.c. more collected. The soap is now decomposed with 5 c.c. of sulphuric acid (20 c.c. strong acid diluted to 100 c.c.), the separated fat acids heated with a small flame until they form a clear solution, and in a current of steam the volatile acids distilled off into a 500 c.c. flask. The size of the flame is so regulated that the contents of the distillation flask remain constant at about 30 to 40 c.c., and the distillation is continued until each succeeding 500 c.c., after the addition of 2 c.c. phenolphthalein solution, require not more than 2 c.c. of the decinormal barium solution to produce the red colour.

12. *Estimation of the Fatty Acids Soluble in Ten Per Cent Alcohol.*

(*a*). *Rose's Method.*—12·5 grms. of butter fat are weighed into a graduated flask of 500 c.c. capacity, 50 c.c. of alcoholic potash lye (about 112 grms. of potassium hydrate dissolved in absolute alcohol and made up to 1 litre) are added and gently shaken. After five minutes as slight an excess of semi-normal sulphuric acid as possible is added. After two minutes dilute with water to 490 c.c.;

to destroy the foam, add 5 c.c. more absolute alcohol, fill up to the mark with water, aad then add as much more water as will correspond to the amount of fat taken. The flask is now shaken, contents filtered through a dry filter, and 250 c.c. of the filtrate titrated with decinormal potash lye.

(*b*). *Modification of the Above Process by Dr. Wollny.*—Weigh 6·25 grms. of the fat in an Erlenmeyer flask of 300 c.c. capacity. Add 25 c.c. of potash lye, made with absolute alcohol as described above, and then diluted with absolute alcohol until not more than 74 c.c. and not less than 73 c.c. of semi-normal sulphuric acid are required to neutralise it. The flask is then closed with a stopper which carries a glass tube 10 m.m. wide and 50 c.m. long; heat with a very small flame until the contents are near the boiling-point for about twenty minutes, and until the smell of the butter ether has entirely disappeared. The flask is then cooled in water and 150 c.c. of recently-boiled distilled water added. When the soap is dissolved and the whole mass cooled to about 15°, 75 c.c. semi-normal sulphuric acid are added. The flask is then closed with a rubber stopper and shaken vigorously for one minute. Filter through a strong dry-folded filter into a graduated flask holding 200 c.c., pour the 200 c.c. into a large beaker glass, and titrate with barium solution.

13. *Estimation of Insoluble Fat Acids.*

Treat 3 to 4 grms. of the butter fat with 2 c.c. concentrated soda lye and 10 c.c. alcohol in a porcelain dish on the water-bath and evaporate the soap to dryness. Dissolve the soap with 100 c.c. of hot water and 5 c.c. concentrated sulphuric acid, and heat the separated fatty acids for one hour on the water-bath. Pour the contents of the dish on a filter of 11 c.c. diameter, made of the best thick Swedish filter-paper, previously dried and weighed. Upon this filter the acids are washed with 1·5 litres of boiling water. The filter with the insoluble fatty acids, after they have been solidified, is placed in a weighed beaker glass, dried for two hours in an air-bath, and weighed.

16. *Estimation of the Free Fat Acids.*

Ten grms. of the butter fat are placed in a beaker glass with 20 c.c. of ether and 10 c.c. of alcohol and 1 c.c. phenolphthalein solution. The free acids are then titrated with decinormal alcoholic potash.

11, 14, 15, 17, 18, 19. *Combined Estimation of the Saponification Number, the Volatile, Soluble, and Insoluble Fat Acids.*

(*a*). *Saponification Number.*—Five grms. of the fat are weighed into an Erlenmeyer flask and 25 c.c. of alcoholic potash added. (25 c.c. alcoholic potash should saturate from 48 to 50 c.c. semi-normal sulphuric acid). The mixture should be warmed as in No. 5 for a full hour with the reflux condenser. Meanwhile, the same quantity of alcoholic potash should be exactly titrated with the semi-normal sulphuric acid, and later being titrated by the barium solution used and the number obtained noted. The alcoholic soap solution is taken from the water-bath, the solid parts adhering to the walls of the flask dissolved by gentle shaking, and, after the addition of 1 c.c. phenolphthalein solution, titrated with semi-normal sulphuric acid. The number obtained is subtracted from the number obtained in the blank experiment and calculated back to the corresponding number of c.c. barium solution.

(*b*). *Volatile Fat Acids.*—The alcohol is driven off from the exactly neutralised alcoholic soap solution obtained in the foregoing experiment, and then an additional amount of sulphuric acid added, amounting to 2 c.c. more than necessary to neutralise the original potash lye employed. The mixture is then diluted with 140 c.c. of recently-boiled distilled water/and two pieces of pumice stone added, and, as in No. 5, 110 c.c. distilled off, of which 100 c.c., after filtration, is titrated.

(*c*). *Soluble Fat Acids.*—After the end of the foregoing experiment the distillation flask is removed from the distillation tube and replaced by one filled with distilled water, and placed as a receptacle under the condenser. The condensation water is now allowed to flow from the condenser, and the condensed insoluble fatty acids driven over into the original distillation flask by a current of steam. In like manner the insoluble acids collected upon the filter are washed into the original distillation flask. After the fatty acids are solidified the whole of them are brought into a cylinder 3·5 c.m. wide and 15 c.m. long, which ends in a 6 m.m. wide tube carrying a goose-necked glass tube from its side; and on the lower end is closed with a rubber tube and pinch-cock. The lower contraction of the cylinder is stopped with a plug of glass wool, which forms a thick filter but allows hot water to run through easily. Under the goose neck of this wash vessel, which is held in a vertical position by a retort holder, is placed a graduated flask of 500 c.c. capacity, into which the excess of water flows. When the acids have been brought from the distillation flask, together with the pieces of pumice stone, into the wash-flask, any residue is washed out with the washing-bottle with boiling water. The above must be so conducted that no drops of the fatty acid pass through the glass wool, and that no fatty acid remains on the upper walls of the washing-flask. The washing-flask is furnished with a gum stopper carrying two holes. Through the one passes a tube for the inlet of steam: through the other a tube at least 8 m.m. in diameter, cut off obliquely at the lower end and divided above the stopper into two branches. By means of one of these branches it is connected with a perpendicular condenser, at least 8 m.m. wide, and through the other it is connected by means of a rubber tube and pinch-cock with a hot-water reservoir by means of a U-tube reaching to the bottom thereof. Through the steam-tube, which is somewhat bent at the end, so that the steam is directed obliquely downwards and outwards against the sides of the washing-bottle, a current of steam is conducted, which stirs up in a lively manner the surface of the fatty acids, which swim upon the top of the water, while the condensed water drops back out of the reflux condenser in a boiling hot condition, and the excess flows through the goose-neck into the measuring flask. The wash-water collected in the 500 c.c. flask is titrated with barium solution, with the addition of 2 c.c. phenolphthalein solution. This operation is repeated three times, in all, 1·5 litres of wash-water being collected. The total amount of barium solution required in the three operations is collected in one number.

(*d*). *Insoluble Fatty Acids.*—After the end of the foregoing experiment the wash-flask is cooled until the fatty acids are solidified. The pinch-cock closing the lower opening of the wash-flask is opened, the water allowed to flow off, and a current of air passed through the apparatus by means of an aspirator after the opening of the goose-neck is lightly stoppered and the steam generator removed. The wash-flask, together with the fatty acids and the glass-wool plug, are completely dried in this manner after, at most, half an hour. The steam generator is now replaced with a flask which contains ether free of water, alcohol, and acids. The ether is brought to the boiling-point by means of warm water, and its vapour, condensing in the washing-flask, dissolves the fatty acids and carries them into the weighed flask of about 100 c.c. capacity, placed below to receive them. When about 40 or 50 c.c. of ether have distilled over, the operation is broken, the outer end of the wash-flask washed with ether, and the weighed flask below is placed in a warm place in order to drive off the ether. The weighed flask containing the acids is now warmed in the water-bath and placed under the receiver of an air-pump. After the acids are completely freed from ether by this method the flask is again weighed and the weight of the acids noted

(*e*). *Mean Molecular Weight of the Insoluble Fat Acids.*—The fatty acids obtained in the foregoing experiment are melted at a low temperature and from 0·8 to 1 grm weighed in a beaker glass, dissolved in 50 c.c. of alcohol, 1 c.c. phenolphthalein solution added, and titrated with barium solution.

20. *Determination of the Iodine Number.*

Weigh out from 0·8 to 1 grm. butter fat in a flask of about 200 c.c. capacity, furnished with a glass stopper; dissolve in 10 c.c. chloroform and add 20 c.c. iodine solution. In case the liquid is not clear, more chloroform must be added. If the iodine colour should rapidly disappear, add from 5 to 10 c.c. more. The amount of iodine added should be sufficient to secure strong colourisation after standing two hours. Add 10 to 15 c.c. iodide of potassium mixture and 150 c.c, of water; titrate with thiosulphate of sodium solution until the iodine has almost disappeared. Add then a little starch solution, and continue titration until the blue colour has disappeared.

21. *Estimation of Refractive Index.*

Set the large Abbe refractometer with water at 18°, so that the index reads 1·3330. The instrument should then be placed in a room which is kept at a temperature of about 25°. The estimation of the refractive index of butter fats cannot be made below 25° on account of the solidification of the fat. The instrument is also to be tested at 20° with olive oil, nitrobenzol, and monobromnaphthalin.

25. *Determination of the Specific Gravity at Zero or 15°.*

A platinum crucible is supplied with a platinum wire handle, so that it can be suspended from the hook of the balance. It is then weighed empty, and afterwards its specific gravity taken in water at zero. The water is kept at zero by being placed in a small beaker glass, which in turn is put in a larger beaker, closed and surrounded with finely pounded ice. The crucible is then dried and 15 grms. of melted butter fat placed therein. The butter fat is allowed to solidify slowly at a temperature not below 15°. The crucible with its contents is then weighed in the air and placed in distilled ice-cold water for an hour. The whole is then weighed in water at zero as before. From these results the specific gravity of the fat at zero is determined. In the same way determine the specific gravity at 15°.

26. *Estimation of the Specific Gravity in Boiling Water by means of the Pyknometer.*

A small flask of 50 grms., the neck of which is drawn out to a narrow tube and marked at the narrow place, is weighed empty. It is then filled with distilled water to the mark and placed for an hour in finely pounded ice. The contraction of the water is restored by the addition of ice-cold water until the mark is reached; it is then dried, allowed to come to the temperature of the room, and weighed. The same flask is then filled to the mark with boiling water, and, after coming to the temperature of the room, weighed. The flask is then emptied, dried, filled with melted butter fat, kept in a boiling water-bath for an hour, the butter fat filling to the mark, afterwards cooled to the temperature of the room and weighed.

27. *Estimation of the Specific Gravity with Mohr's Balance.*

This is determined in the usual manner by the use of a specific gravity bob, the thermometer of which is arranged so as to show a temperature of 100°.

28. *Estimation of the Specific Gravity with the Areometer in Boiling Water.*

This is determined by means of spindles furnished by the firm of G. C. Gerhard, in Bonn. These spindles are graduated especially for specific gravity at a temperature of 100°.

29. *Estimation of the Melting-point.*

This is determined in straight or U-formed capillary tubes. They are filled with butter fat at 100° and placed in ice-water for a quarter of an hour. The capillary tube is then placed, with a thermometer, in a beaker glass with water at 20° and slowly warmed with a small flame.

30. *Estimation of the Solidifying Point.*

Place about 100 c.c. of the melted fat in a test-tube at 40°. Stir with a thermometer until the fat begins to solidify, the test-tube meanwhile being placed in a large vessel containing water at 20°. The temperature will rise slightly when the solidification begins, and the highest point reached is entered as the solidification point.

Note. Dr. Wollny has proposed in the above scheme an exhaustive study of butter fat. Many points appear to be superfluous and others elaborated into unnecessary detail. The method of determining insoluble fatty acids appears to be more objectionable than any other part of the scheme. The method of making the melting-point first described in the *Journal of Analytical Chemistry* (vol. i., No. 1, p. 39) appears to have escaped the notice of the German commission. I also note with regret the apparent ignorance of the existence of the Gooch crucible existing in Germany.

Points to be especially commended in these investigations are, sending samples and standard reagents, blanks for entering the analytical results, and minute printed directions for conducting the manipulation.

The numbers prefixed to the several paragraphs correspond to the number of the column in the blank in which the results are to be entered.—H. W. W.

(To be continued).

THE PROPOSED CHEMICAL LABORATORY AT THE UNIVERSITY OF SYDNEY.

We are indebted to the courtesy of Professor A. Liversidge, F.R.S., for a very full description of the projected laboratory. The matter, he tells us, was in contemplation as far back as 1873, but unfortunately certain makeshifts were found possible, and so the erection of a really suitable building has been proposed. Happily, says Professor Liversidge, such expedients are now no longer possible.

Funds do not allow of the erection of a palatial structure, and the University is right in not sacrificing practical utility to outside display.

The main laboratory, intended for all save the very junior students and for a select few who are sufficiently advanced to undertake original research, is 72 by 36 feet, and 22 feet high in the centre. Part of the roof will be left flat for experiments requiring direct sun-light. There will be no provision required for warming the rooms, as on the few days when artificial heat is desirable movable gas stoves will be placed in the lower part of the draught-cupboards.

At one end is a yard for out-door experiments, with a large sink, a good water-supply, and generators and a gas-holder for sulphuretted hydrogen. The floors will be of wood, varnished round the walls and the benches. All the interior wood work will also be varnished. On the roof or in a tower will be a large cistern to supply water under pressure. The gas and water-pipes, battery, telephone and electric light wires, are to be laid in channels along the floors and down the angles of the walls. A well, passing down from the tower to the basement, will serve for aspirator and compressed air tubes. Some of the windows are utilised as draught-cupboards by enclosing the outer side of the lower sash. Others can be used for microscopic work. There is at one end of a long slate bench a sink (Doulton ware) with the edges protected by wood and india-rubber, with a drying slope and rack. Next follows a self-feeding still for distilled water supplying ten gallons a day.

The principal lecture room is 34 by 47 feet, and is arranged for 180 students. The lecture table, 27 by 3 feet, is provided with gas and water, leads for the electric light, aspirators, air-blasts, oxygen, hydrogen, and coal-gas under water pressure from the cistern. There will be a lecture-preparation room, a collection-room and museum, a smaller lecture or class-room for 130 students, a demonstration room for juniors, 36 by 24 feet, and separate balance rooms, rooms for reference library, for gas analysis, spectroscopic and polariscope work, and a dark room.

The metallurgical and mineralogical laboratories are in the basement, fitted with a gas-engine and crushing and grinding apparatus, two 9-inch and two 12-inch furnaces, and two muffle furnaces on Percy's design. On the ground floor at the south end are the Professor's private room, 21 by 16 feet; a microscope and balance room of the same dimensions, and a private laboratory, 32 by 21 feet, where three or four advanced students can work under the immediate eye of the Professor.

From the very full description and the twelve accompanying plates we must conclude that the laboratory, if carried out as proposed, will be a credit to the University, and will give good scope both for instruction and for research. The space available seems to be well utilised, and there are all necessary appliances, without anything which the economist can denounce as luxurious or extravagant.

The new laboratory will be very near the biological, the physical, and the engineering laboratories, an arrangement which may often prove a mutual convenience.

NOTICES OF BOOKS.

The British Journal Photographic Almanack, and Photographer's Daily Companion, 1889. Edited by J. Traill Taylor. London: Greenwood and Co.

If anyone doubts the importance which photography has reached, a glance at this almanack, and especially at its advertising pages, will convince him of his mistake. If we leave out of consideration lenses, lamps, dry plates, sensitised papers, chemicals, and complete sets of apparatus, we find here no fewer than ninety cameras, each recommended as possessing some advantageous feature, or as being adapted for some special purpose. It has, in fact, been found so difficult to find out rational, appropriate names for these devices, that one inventor gives to his instrument the ill-omened name of "international."

In the almanack itself we find some very interesting matter. A sceptically disposed individual doubts if "detective" cameras have ever really detected or helped to detect a single evil-doer?

A little poem by Mark Oute, entitled "My Detective," reminds us that even in England the doings of the photographer may be annoyingly interfered with by Jacks-in-office.

A short paper on "Chemical Changes," by Mr. C. H. Bothamley, F.C.S., has a wide bearing; it may concern all, or most of the chemical arts. It brings forward facts which, though well known to professional chemists, are often overlooked by outsiders.

Mr. J. Hubert writes anent the intrusion of amateurs, one of whom had kindly offered to photograph a religious gathering at cost-price, *plus* a champagne supper!

In proof of the greater activity of the light in India, we find it mentioned that one twenty-fifth of a second was an amply sufficient exposure for obtaining a good seascape at Madras.

To all persons interested in photography this almanack will prove invaluable, but we trust that they will not be bewildered with choice among the multitudinous appliances here recommended.

Our Supply of Phosphates for the Manufacture of Superphosphate and other Manures. By Hermann Voss. London: Farquharson, Roberts, and Phillips, Limited.

This pamphlet comprises a paper read on December 10th last, before the Chemical Manufacturers' Association and the discussion which followed.

The author shows that the supply of mineral phosphates is by no means unlimited. Our imports from Canada do not exceed 20,000 tons yearly. The shipments of Norwegian apatite and Russian coprolites have almost ceased. The Estremadura phosphates are in great part of low quality, and the expense of transport is great. The largest importations have been of late from Carolina, whence, in 1887, we drew no less than 164,000 tons. Nor is an early exhaustion of the deposits probable. But, on the other hand, the demand for this material in America is fast increasing, and the freight is generally high.

The Belgian phosphate is described as abundant in quantity but very rich in calcium carbonate, a so-called "profligate" ingredient, since it involves the waste of a large amount of sulphuric acid. The total quantity of phosphates imported into the United Kingdom in 1887 was 283,415 tons.

We are glad to find that the author, in passing, enters his protest against the waste of fertilising matters, phosphates among others, going on in this country. The facts stated in the paper and in the discussion may, perhaps, convince some persons concerned, that this extravagance cannot go on for ever. Other countries are now rivalling us in the folly of pouring fertilising matter into the sea, heedless that the time must come when the Bank of Nature will no longer honour our drafts.

A New Patent Calendar for 1889. Thos. Fletcher and Co., Warrington.

Almanacks have already come into very general use as channels for advertisements. That of Messrs. Fletcher, now before us, present a novel feature. There is a page for every working day in the year, and on each we find a figure of one of Messrs. Fletcher and Co.'s devices for the production of heat by means of gas—scientific, technical, culinary, or generally domestic. For descriptions the reader is referred to the "Complete List" issued by the firm. At the foot of the page follow the day of the month and the week.

Letts's Diaries for 1889.

We have received a few of these useful publications from Messrs. Cassell, Petter, and Galpin, and perceive that they keep up to their usual style of excellence.

CORRESPONDENCE.

ELECTRIC SUGAR.

To the Editor of the Chemical News.

Sir,—The *Times* of Saturday, January 5th, contains an account from Philadelphia of the collapse of the "New York Electric Sugar Refining Company," in which the writer says—"Quantities of refined sugar, chiefly cubes, had been purchased by the operators and prepared in some secret spot with a chemical liquid which eliminated the ordinary impurities found in all sugars" . . . "the chemical used had crystallised the cubes to a large extent, and they had a finer appearance and a finer quality than sugar was ever known to possess."

From this latter statement it would appear that the chemical process contained some elements of value and apparently unique as to the results. Can any of your readers throw light on this particular process? or has the secret perished with the decease of the inventor?—I am, &c.,

G. A. Keyworth.

Hastings, January 7, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cvii., No. 26, December 24, 1888.

This issue contains merely an account of the Annual Public Session of the Academy on December 24, with a report of the "allocution" of the President, and notices of the prizes awarded.

Moniteur Scientifique, Quesneville.
Series 4, Vol. ii., November, 1888.

The Yeasts of Wines.—Louis Marx.—The author recapitulates the results of Hansen, who found in beer-yeast, previously regarded as pure, six ferments, *Saccharomyces pastorianus* I. II. III., *Saccharomyces cerivisiæ*, *Saccharomyces ellipsoideus* I. and II., distinguished by the time which they require for the development of their ascopores. In the lyes of certain wines he distinguishes no fewer than fifteen ferments, to which he does not assign names, as he has not yet decided whether the forms obtained from different wines are identical.

New Theory of the Double Elliptical Refraction of Quartz.—Dr. G. Quesneville.—This paper does not admit of useful abstraction.

Synthetic Formation of Closed Carbon Chains in the Aromatic Series.—W. H. Perkin.—From the *Journal of the Chemical Society.*

Improvements in the Manufacture and Use of Explosives.—Oscar Guttmann.—The author describes an improved method for making charcoal, patented by Güttler, of Reichenstein. He introduces hot carbon dioxide into the retorts during the process of charring, and cold carbon dioxide during cooling. The product from lime-kilns is sufficiently pure. He next notices the discrepancies observed in the analysis of gun-cotton, and points out the necessity of using absolutely pure reagents. He then describes the carbo-dynamite of Borland and Reid, which, it is said, can be exploded in a coal-mine without exploding fire-damp; a new explosive made by Schückher and Co., under the name of meganite; the "bellite" of Carl Lamm, of Rotebra; the "Security" of Schœneweg; the "Romite" of Sjöbrg (?); the "Roburite" of C. Roth; the explosives of R. K. Punsheon, of Sir F. A. Abel, and of Grüne, &c.

Industrial Review and Various Patents.—Abstracts of a number of German specifications, largely referring to colouring-matters.

Industrial Society of Mulhouse.—Session of September 12, 1888.—The principal feature of the session was a paper by P. Richard on the chemical constitution of wool, which he regards as an amidic acid.

Action of Sulphur upon the Oils.—C. A. Fawsitt, F.R.S.E., F.C.S.—From the *Journal of the Society of Chemical Industry.*

Thiophosphoryle Fluoride.—Prof. T. E. Thorpe, F.R.S., and J. W. Rodger.—From the *Journal of the Chemical Society.*

Resistance of Dressing to the Bleaching Processes, and on the System of H. Kœchlin and Mather and Platt.—Camille Kœchlin.—The essential feature of this process is the use of caustic soda at 25 grms. a litre, when a previous treatment with lime is unnecessary. He shows that sulphuric acid has a less injurious effect upon textile fibres than it is commonly supposed, and is more easily removed by washing than are the volatile acids.

Proportion of Ash in Human Bones at Different Ages.—W. P. Mason.—From the Chemical News.

New Method for the Purification of Alcohol or the Production of Non-poisonous Alcohol.—Emile Reboux.—The author passes in review the methods of Godefroy (use of a mixture of zinc-powder with copper and a hypochlorite), that of Bowick, Bang, Ruffin, and Philippart. P. F. Tettelin, instead of transforming or eliminating existing impurities at the risk of destroying at the same time the peculiar aroma of each spirit, professes to prevent the formation of furfurols, aldehyds, superior alcohols, and alkaloids.

Test for Essential Oils.—"Eck" founds a process for detecting the oil of pine when used for sophisticating the oil of juniper berries upon the power of the latter of at once decolourising a very dilute alcoholic solution of juniper, whilst many essential oils do not show this reaction. The method of applying the test is to dissolve a drop of the oil in question in 3 c.c. of alcohol at not less than 90 per cent, and to add a drop of the tincture of iodine. In a check experiment, in which he added directly oil of turpentine to oil of juniper and applied the iodine test as above described, the iodine was nevertheless decolourised. In consequence he distils the oil on the water-bath and applies the test to the first drop which comes over. Iodine is instantly decolourised by oil of peppermint (Mitcham); in a minute by the oils of ginger and juniper; in two minutes by oils of pepper and cardamum; in three to eight minutes by oil of mace. The oils of coriander, carraway, turpentine, rue, sassafras, roses, rosemary, orange, aniseed, fennel, angelica, and wormwood do not decolourise iodine.

Archives Neerlandaises des Sciences Exactes et Naturelles.
Vol. xxiii., Part iii.

This number contains no chemical matter.

MISCELLANEOUS.

Society of Arts.—The following arrangements have been made for the Wednesday Evening Meetings of the Society of Arts after Christmas. On the 16th January, a paper will be read by Colonel Hozier, on the "Channel Tunnel;" on the 23rd one by Professor George Forbes, on "Electric Meters for Central Stations;" and on the 30th one by Mr. Conrad Beck, on the "Construction of Photographic Lenses." Papers for which dates have not yet been fixed will also be read on the "Status of the County Council," by Mr. G. L. Gomme; on the "Forth Bridge," by Mr. B. Baker; on "Salt," by Mr. P. L. Simmonds; on the "Manufacture of Aluminium," by Mr William Anderson; on "Secondary Batteries," by Mr Preece; on "Automatic Selling Machines," by Mr. J. G. Lorrain; on "Arc Lamps and their Mechanism," by Professor Silvanus Thompson; on the "Irish Lace Industry," by Mr. Alan Cole; and on the "Use of Spirit as an Agent in prime Movers," by Mr. A. F. Yarrow.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Science and Art Department.—Mr. W. E. Youle, in answer to the query of "Student" ("Science and Art Department"), advises examination of filtrate "after separation of the inorganic bases *as usual*," that the organic acids may be detected in it. What is the *usual* method of separation pursued? If it involves (1) use of hot acids or mixtures of acids to effect solution, (2) concentration with HNO_3 and gentle ignition to ensure peroxidation of Fe, &c., (3) complete ignition preceeding separation of alkalies, it is to be feared that the amount of unaltered organic matter surviving for "Student's" examination will be small indeed. May I suggest the adoption of the, to me, usual method of decomposing original solution with excess of sodic carbonate, and examining the filtrate—after neutralisation by acids appropriate to test to be applied—for acids organic or inorganic (if required to be determined)? If difficulty occurs, owing to incomplete precipitation of metals by $NaCO_3$ in presence of organic acids, the accurate and careful method recommended by Fresenius ("Qualitative Analysis," 10th English Edition, from 15th German Edition, pp. 325 and 281) should be followed. "Student should pay great attention to odours evolved by the organic acids and their salts when subjected to destructive distillation in a hard glass tube, and observe closely the effect of warming with dilute and concentrated hydric sulphate.—W. Popplewell Bloxam.

MEETINGS FOR THE WEEK

Monday, 14th.—Medical, 8.30.
Tuesday, 14th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
Wednesday, 16th.—Society of Arts, 8. "The Channel Tunnel," by Colonel Hozier.
—— Meteorological, 7. (Anniversary).
Thursday, 17th.—Royal, 4.30.
—— Chemical, 8. "On a Cubical Form of Bismuthous Oxide," by M. M. P. Muir and Arthur Hutchinson. "On the Iodides of Copper," by Douglas Carnegie. "On the Periodates; No. II.," by C. W. Kimmins. "On Compounds of Arsenious Oxide and Antimonious Oxide with Sulphuric Anhydride," by R. H. Adie. "On a Compound of Boron Oxide with Sulphuric Anhydride," by R. F. Davey.

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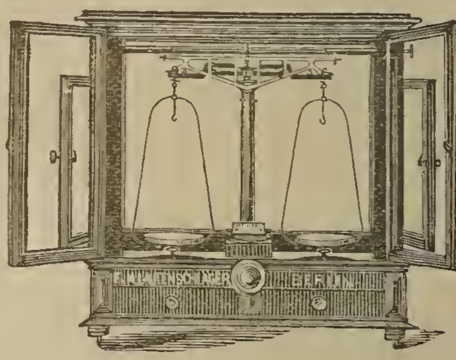

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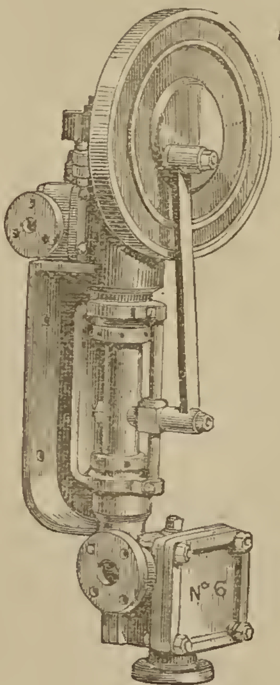

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THE CHEMICAL NEWS.

Vol. LIX. No. 1521.

ON THE ESTIMATION OF TITANIUM IN NATURAL SILICATES.

By PHILIP HOLLAND.

As it is often necessary in the analytical course for silicates to take account of the titanic oxide, since it occurs in some rocks in notable amount, it may be useful to give the details of a few experiments lately made on the commonly accepted plan of separating titanic oxide from the oxides of iron and aluminium.

A pure specimen of TiO_2 was prepared in the first place by converting the commercial article into potassic fluo-titanate. This, after several crystallisations, was decomposed by ammonia, and the product well washed and ignited. So made from a fairly pure commercial sample, the titanic dioxide was found free from aluminium and iron. On ignition it became yellow, but regained its original perfect whiteness when cold.

As the practice of decomposing silicates by HF in the presence of H_2SO_4 is now more common than formerly, it was desirable to learn if titanic oxide is quite stable under these conditions, for as Riley has shown (*Journal of the Chemical Society*, xii., 13) there is considerable loss in the absence of oil of vitriol. Another point, bearing directly on the estimation of titanic oxide, was the conditions of complete precipitation when the solution of a bisulphate fusion of such oxide is boiled, this being a method much in vogue for parting titanic oxide from the oxides of aluminium and iron.

To settle the first question, viz., the fixity of titanic oxide when digested with HF and a little H_2SO_4, a few experiments were made as follows:—

Into a weighed platinum crucible, already containing a known weight of recently ignited titanic oxide, was put 2 c.c. of a dilute H_2SO_4, to be presently described. Next was added, at three stages, as much re-distilled HF (not the commercial article) as in a blank trial sufficed to volatilise 1 grm. of pure silica. After each addition of the acid the contents of the covered crucible were carried to dryness, and, before weighing, ignited, at first gently and then strongly with the blast-lamp. Below are the weights of the TiO_2 before and after the treatment:—

Wt. of TiO_2. Grms.	Wt. after treatment. Grms.	Error.
0·0340	0·0340	—
0·0414	0·0413	0·0001
0·0520	0·0520	—
0·0352	0·0352	—

There appears to be no loss in the presence of vitriol. In the absence of vitriol, however, a single experiment made on 0·0466 grm. gave, after treatment, 0·0340 grm. as the weight of the residue, showing a loss of 25·3 per cent of the TiO_2 taken. In this experiment the oxide was only once treated with HF before ignition. Further treatments in the same way would obviously have removed the whole.

Passing now to the complete separation of titanic oxide by boiling the acid solution of the bisulphate fusion, the fact is well known that incomplete separation attends the use of too much free mineral acid. My own experiments confirm those of Gooch and others in this respect.

For the test experiments to show the plan of separating titanic oxide from iron and aluminium the following solutions were made up:—

(*a*). Dilute acid, of which 5 c.c. contained 0·8 grm. of SO_3.

(*b*). Solution of ferrous sulphate and potash alum, of which 100 c.c. contained alum equal to 0·26 grm. Al_2O_3, and iron salt equal to 0·026 grm. of Fe_2O_3.

(*c*). Solution of titanic oxide (made by fusing TiO_2 with potassium acid sulphate), of which 100 c.c. contained 10 m.grms. of TiO_2.

Solution "*b*" was assumed to represent per 100 c.c. the weight of $Al_2O_3+Fe_2O_3$ extracted from 1 grm. of an average fire-clay that had been subjected to the fluoric treatment. The dilute acid "*a*" contained in 5 c.c. rather more than sufficient SO_3 to combine with the 0·286 grms. of the mixed oxides present in 100 c.c. of solution "*b*."

In the experiment to be now described 100 c.c. of "*b*" was made *just* alkaline with ammonia, 5 c.c. of "*a*" was next added, as also 50 c.c. of a saturated solution of SO_2, and finally boiling water till the vol. was about 900 c.c. On boiling the contents of the covered beaker for twenty minutes the solution remained perfectly clear. In the next place an addition of 10 c.c. of "*c*" was made equal to 1 m.grm. of TiO_2 and the boiling continued for twenty minutes longer. This addition did not appear to cause any change, still, on allowing the beaker to stand for twelve hours still covered, it was easy on decanting nearly all the fluid, to see a slight opalescence in what remained when this was shaken round. I assume the opalescence to have been due to titanic oxide, since it did not disappear on adding more acid, as it should have done if caused by basic aluminium sulphate. This experiment afforded then some evidence as to the conditions favourable to the precipitation of small amounts of titanic oxide.

In the next four experiments 100 c.c. of "*b*" and the same of "*c*" were mixed, made just alkaline as before, re-acidified with 5 c.c. of "*a*" and 50 c.c. of solution of SO_2 in the order given. The whole, further diluted to 900 c.c. with boiling water, was boiled for twenty minutes. The collected precipitates, when washed, ignited, and weighed, were in all cases slightly coloured. They were therefore fused with bisulphate and the precipitation repeated. In the third column are the results of this treatment.

TiO_2 taken.	First Precipitation.	Second Precipitation.
10 m.grms.	9·8 m.grms.	9·0 m.grms.
,,	11·1 ,,	8·8 ,,
,,	10·3 ,,	9·6 ,,
,,	10·0 ,,	8·9 ,,

A further experiment was made as before, taking, however, 200 c.c. of the titanic solution, equal to 20 m.grms. TiO_2. The numbers were:—

1st precipitation .. .. .. 20·2 m.grms.
2nd , ... 19·7 ,,

The titanic oxide, after the second precipitation and ignition, was not *absolutely* white, thus showing the tendency the precipitate has to carry down iron and doubtless alumina also.

I will now give in outline a scheme, with an example of the analysis of a silicate to which a known weight of titanic oxide was added. The rock chosen was granite, the specimen being part of a drift boulder from the Ribble Docks excavation at Preston. A qualitative analysis proved it to contain TiO_2, CaO, and MgO, in addition to the usual constituents of granite. The TiO_2 amounted to 0·62 per cent. Now, as some basalts contain 3 per cent and more of TiO_2, and as I had recently met with 1·94 per cent in a specimen of igneous rock from the Isle of Man, it seemed enough for the purposes of the test experiments to make up an artificial sample by adding to the granite a known additional weight of TiO_2. The rock was powdered, ignited, and sifted through fine muslin, and the TiO_2, also in fine powder, was added to the extent of 3 per cent over and above that already in the sample. The mixing of the TiO_2 with the silicate was done in a dry and warm wide-mouthed bottle. After mixing, the sample was gently ignited and put in a closed tube ready for work. The plan of analysis was this. Into a somewhat large platinum crucible was put 2 grms. of the sample, which was then moistened throughout with dilute H_2SO_4, a little re-distilled HF was next added, and the mixing promoted by careful shaking. As much heat is evolved when silicates are treated with strong solution of HF, often causing violent effervescence; this acid should be added by degrees. When 5 grms. or so had been added, the crucible covered with its lid was heated in an air-bath of the following construction, which has been found convenient for such operations. It consists of a moderately thick unglazed iron dish of 20 c.m. diameter, with a cone-shaped sheet-iron cover open at top and bottom, and serrated at its bottom and wider end, which rests just inside the dish when in use. The cover, 16 c.m. high and 9 c.m. diameter at its apex, has projecting slips at two sides which serve as handles. A few stout wire tripods of different heights and some porcelain triangles support crucible dishes, &c., whilst a clamp at the top of the cover carries a thermometer whenever this is required. Two such air-baths were made for me some time ago, which appear to answer all the purposes of the more costly forms, usually of copper.

To return to the analysis. The air-bath was heated to about 100° C., when the thermometer was removed and the crucible or crucibles, for two can be heated at one time, were placed on one of the supports; as the operation progressed, the temperature of the bath was raised until the residues appeared dry. At this stage concentrated HCl was added and the crucibles heated anew. Provided enough HF had been used in the first instance, the residues dissolved with the exception of a little TiO_2. Any undissolved TiO_2 was caught on a filter, washed, and the filtrate collected in a half-litre flask, in which it was oxidised by a few drops of chlorine-water. The small filter and residue were ignited, fused with a little bisulphate, and the solution of the fusion, after filtration, added to the contents of the flask, which were now diluted to the mark, mixed, and divided into portions D and E.

Portion D, = 1 grm. of sample, was diluted somewhat, and in it were the Al_2O_3, Fe_2O_3, and TiO_2, co-precipitated by the ammonium acetate plan, repeating the operation and uniting the two filtrates for the MnO, CaO, and MgO estimations. Before, however, proceeding to separate these, the united filtrate was treated for a little Al_2O_3 it frequently contained, which was weighed along with the major portion in the mixed precipitate. The latter, after weighing, was finely powdered, collected in a tared platinum crucible to learn its proportion to the whole, and fused with recently ignited bisulphate. The fusion, if properly managed by carefully rotating the crucible over the flame, should be quite clear and free from suspended particles of TiO_2 or undissolved bases. The fusion was next quickly extracted at 80° C. with water containing a little vitriol, transferred to a large beaker, and treated with ammonia, &c., just as in the earlier experiments. At the end of the twenty minutes' boiling the solution was filtered and the precipitate, after drying and igniting, fused afresh, repeating the remaining operations as above, before final weighing. Turning to portion E of the original solution: in it, the iron precipitated first by ammonium sulphide in the presence of the tartrate was washed, re-dissolved in HCl, oxidised, and re-precipitated as ferric oxide by ammonia.

It will be observed the scheme so far has given the united weights of the $Al_2O_3+Fe_2O_3+TiO_2$, as also the weight of the TiO_2 and that of the Fe_2O_3. The Al_2O_3 was estimated by difference. As regards the silica and alkalies, these were estimated on fresh portions of the original sample; the alkalies by Smith's lime fusion plan.

The following are the numbers for the several constituents of the sample, which was analysed precisely in the way described. The TiO_2 assumed to be present was 3·62 per cent:—

		1.	2.	3.	4.	Mean.
SiO_2 .	..	65·62	65·48			65·550
Al_2O_3.	..	17·57	17·21	17·32	17·43	17·382
Fe_2O_3	..	4·64	5·08	4·76	4·82	4·825
TiO_2 .	..	3·47	3·52	3·58	3·49	3·515
MnO .	..	0·18	0·23			0·205
CaO .	..	0·12				0·120
MgO .	..	0·10				0·100
K_2O..	..	5·73	5·75			5·740
Na_2O.	..	2·66	2·50			2·580
						100·017

Before closing this paper I would call attention to a plan of separating titanic oxide from alumina and ferric oxide, ascribed to G. Roussel at p. 113 of "Select Methods in Chemical Analysis." He takes the acid solution containing them and adds solution of SO_2, sodium sulphate, and thiosulphate, and boils. By this means the alumina and titanic oxide are thrown down, ferrous iron remaining in solution. The mixed precipitate containing sulphur is washed, gently heated to drive off sulphur, and then digested in a sealed tube with hot concentrated HCl, which extracts the Al_2O_3, leaving the TiO_2 sufficiently pure to wash, ignite, and weigh. The process failed in my hands. It was tried on 1 grm. of the silicate sample, when the numbers were:—

		Per cent.
TiO_2 undissolved by the HCl	.. ..	2·27
,, recovered from the acid	.. ..	1·27
		3·54

As ignited TiO_2, *per se*, is insoluble in hot HCl, I attributed the failure to the fact that in driving off the sulphur by heat some of the TiO_2 had combined with the Al_2O_3 to form a titanate which dissolved in strong HCl, just as some natural titanates are known to do.

In support of the hypothesis that combination might have occurred from heating the oxides too strongly, I took 0·1415 grm. of Al_2O_3, 0·0834 grm. Fe_2O_3, and 0·0382 grm. of TiO_2. The two first were disssolved in HCl and the TiO_2 in water after fusion with bisulphate. To the mixed solutions ammonia was added in not too great excess, and the whole boiled. The resulting precipitate was then collected, washed, and *ignited*. It was next powdered and digested with HCl at 100° C. in a sealed tube, when the whole dissolved with the exception of 3·8 m.grms., showing that over 90 per cent of the TiO_2 had passed into solution. In carrying out Roussel's process, wherein success may depend on the temperature at which the sulphur is expelled, it would appear preferable to extract the latter with CS_2 and then treat the residue with HCl to remove Al_2O_3, or better perhaps with dilute H_2SO_4, which would be less likely to dissolve any TiO_2.

The method of full analysis here set out has given good results for granites, basalts, felstones, and the like. Where, however, a qualitative examination reveals P_2O_5 and TiO_2, a somewhat different course for the separation of the TiO_2 must be pursued, for, as Blair has shown, each one of these two, when both are associated in a mineral, interferes with the correct estimation of the other, owing to formation of titanic phosphate.

In silicates where ferrous iron occurs this is found by digesting in a sealed tube, at 120° C., 2 to 4 grms. of the rock in fine powder with chlorine-free HCl. The solution is titrated with bichromate. The more accurate plan is to treat the silicate with HF, in which the SO_2 present in commercial samples has been first oxidised by permanganate, carrying out the extraction in the way recommended by Fresenius.

From the foregoing experiments it will be seen that but relatively small weights of TiO_2 have been taken. It was found easier to obain aluminium and iron-free precipitates when the weight of titanic oxide was only 2 to 5 centigrms. than when it reached 1 to 1·5 decigrms. There is no difficulty in recovering small amounts of TiO_2

from the beaker in which the precipitation is made, provided a little concentrated HCl be heated in it for a short time. This, though it does not always entirely dissolve the strongly adherent oxide, so far loosens it as to allow of its recovery with the feather. Any TiO_2 dssolved in the acid is thrown down by ammonia.

DECOMPOSITION OF NICKEL AND COBALT.

The Vienna correspondent of the *Times*, telegraphing on the 14th inst., says that Dr. Krüss, the well-known chemist, of Munich, has succeeded in decomposing the metals cobalt and nickel, hitherto believed to be elements. He finds that both metals have one constituent in common, and one in which they differ.

[We hope to give further particulars in our next number.—*Ed.* C. N.]

THE PHYSICAL PROPERTIES OF THE GRAPHITES OBTAINED FROM VARIOUS METALS AFTER THE SEPARATION OF THE SAME BY MEANS OF DILUTE ACIDS.

By H. N. WARREN, Research Analyst.

The metals of the third group, and especially iron, undoubtedly furnish graphite most readily when maintained at an elevated temperature in contact with carbon; the scales thus separated from the cast metal being possessed of larger magnitude than those obtainable from either nickel or cobalt, both these metals producing graphite of a much finer quality, and in many instances, unless viewed by the aid of a microscope, being indistinguishable from lamp-black, while in all other respects both their varieties closely resemble each other. But on further following the group to manganese, a considerable variance is observed; for on dissolving a portion of ferromanganese containing a high percentage of that metal, a graphite is obtained consisting of much thinner scales than by similarly treating cast-iron, and possessed of a distinct brownish tint, being at the same time less readily oxidised. Further, if commercial black oxide of manganese be reduced by means of carbon at a high temperature, and the metallic manganese thus obtained be dissolved by the aid of dilute acids, a graphite is produced presenting a perfectly brown colour, the dimension of the scales being somewhat considerable. I have also frequently observed, after carefully selecting the same, that several of the scales appear decidedly translucent and still less combustible than that obtainable from ferromanganese. Chromeisen thus treated usually gives much brighter scales, and at the same time harder, than those obtainable in the case of iron, whereas those produced by the dissolution of cast chromium in appearance approach more closely to silicon, being entirely destitute of any brownish tinge and possessing a semi-metallic lustre, being less energetic to combine with oxygen, unless when heated in a current of the pure gas.

The above mentioned graphites thus produced may be undoubtedly influenced by the difference of the fusion points of the various metals employed for their production; thus, for instance, chromium being the most difficult of fusion tends to produce a graphite possessing a more stable form than that produced by either iron, nickel, or cobalt. Strange to say, however, each modification may be inverted in the same manner as silicon behaves towards allotropy; thus, if a small quantity of pure iron be maintained in the liquid form by the aid of an oxhydrogen flame, and a quantity of the brown modification obtained by treating manganese with dilute acids be introduced into the liquid iron, and the graphite afterwards separated in the usual manner, it will be found on examination to correspond in every respect with the graphite usually produced by such means.

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SPECTRUM ANALYSIS OF CADMIUM.*

By A. GRÜNWALD,
Professor of Mathematics in the Imp. Roy. German Polytechnic University at Prague.

(Concluded from p. 19).

Conclusion.

(1.) I have hitherto principally used the water spectrum as comparison spectrum, because it is now known with great accuracy and to a large extent.

The probable errors of its wave-lengths, measured by Liveing and Dewar, may ordinarily amount (according to the observers) to from 0·2 to 0·3; but in very weak and also in diffuse or broad lines the errors may be greater, and the most part of the nebulous lines may be in reality only representatives of double or even more lines. A similar thing may be the case with regard to the wave-lengths of the ultra violet rays of the so-called elements measured by Hartley and Adeney, and by Liveing and Dewar. (It would be, however, very desirable for the sake of control, that these excellent observers and other observers equally qualified, should repeat all these measurements with the aid of Rowland's method by concave gratings, which is evidently simpler and less liable to errors than that hitherto employed, as it substitutes linear for angular measurements, and secures therewith the greatest possible exactness).

As the lines of the water spectrum lie close together, the doubt arises whether the coincidences or close agreements between the lines calculated and the corresponding lines of the water-spectrum may not be perhaps only accidental and not real. For the closer set the lines of a comparison spectrum (for instance of the solar spectrum, or as here of the water spectrum), the easier it can happen that some wave-lengths written (or lines delineated) at random may agree with more or less accuracy with wave-lengths or lines of the compared spectrum, and that the conclusions founded upon such comparisons may lose their demonstrating power and prove nothing.

If this doubt, which I have already apprehended and kept in view from the beginning of my researches, were to be admitted without any restriction, if there were no means or criteria proper to distinguish pretended or accidental from well-founded and real coincidences, or close agreements—

(α.) Between one set of rays observed and other observed rays.

(β.) Between calculated and observed wave-lengths.

(γ.) Between two sets of wave-lengths derived by calculation from two distinct sets of directly observed wave-lengths.

If that be so, the trouble and care applied to the accurate measurements of certain spectra, such as the solar spectrum or the water spectrum, would be truly foolish, or at least superfluous, as no one could make use of the result for anything. Nay, what is more, if we keep in view that even the spectra of such elements as seem to emit only few and often far distant rays, may be probably merely incomplete representatives of the true spectra which may (at least in certain regions) consist of close set but very faint and, therefore, ordinarily not visible lines, it would have to be conceded that almost the whole

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* A Paper read before the Royal Society, December 13, 1888.

use of spectrum analysis, so much praised, would be an illusion.

Fortunately this is not the case, and even my researches furnish already, and will supply in future, still more remedies (criteria), proper to remove the doubt above mentioned, and to distinguish real agreements (even of few lines) with great probability from others only accidental.

As the evidence of laws in physics rests upon the testimony of coincidences or close agreements, either (α) between two series of direct measurements or observed images (for instance, of spectral lines), or (β) between numbers calculated from one series of observations and a series of direct measurements, or, finally (γ), between two series of numbers derived by calculation according to certain rules from two different series of direct measurements, it is plain that the reality or probability of a given series of such agreements can be proved by other series of agreements connected with the former by laws established and ascertained beforehand. The more such series of coincidences or agreements ("criteria") co-ordinated to the series of agreements to be tested are satisfied, the greater is the probability that the series tested is not an accidental one, but consists rather of real agreements.

When such series (co-ordinated by certain laws as criteria to a series under examination) are not known, as is, for instance, the case in the first examination of agreements, which are themselves to be used as criteria for others, and when numerous series of agreements of a similar kind are possible, the evidence that no better series of agreements of the same kind exists, may in the first instance warrant sufficiently the probability of the series under examination. Particularly striking, however, would the evidence become if the close agreements under examination could be transformed into complete coincidences by minimum corrections applied to the compared numbers within the limits of possible errors, and if the values thus corrected should be confirmed by later and more accurate measurements, *experimentum crucis!* (crucial proof!)

Finally, the calculus of probabilities may also afford us its assistance in the case when the series under examination consists of numerous single agreements, and may convince us, upon the ground of the known observations, of the degree of probability for the real and not accidental character of the examined agreements. Especially may the graphical method be used with advantage, given by E. F. J. Love (now Lecturer in the University of Melbourne, Australia). (See the interesting paper of Love "On a Method of Discriminating Real from Accidental Coincidences between the Lines of different Spectra, with some Applications;" communicated to the Physical Society—read November 26th, 1887—in the *Philosophical Magazine*, 1888, pp. 1—6).

(2.) In order to determine the rational numbers occurring in the criteria used, I was compelled to multiply the simple wave-lengths of the rays of hydrogen and oxygen with the rational numbers $\frac{1}{2}$, $\frac{2}{3}$, $\frac{3}{4}$, $\frac{2}{5}$, $\frac{3}{5}$, $\frac{4}{5}$, &c., and to compare the results with the wave-lengths of the water spectrum with one another I searched at once by chain division for rational rhythmical relations between the wave-lengths of the compared spectra, and tried then the rational numbers thus found on other wave-lengths to prove if they were or were not reduction factors for certain groups of the latter.

In so far as only a few rational reduction factors were the outcome of a great number of such mathematical experiments, in spite of the nearness to one another of the lines due to the water spectrum, and in so far as the above-mentioned calculations, originally performed with a very incomplete water spectrum,—were later brilliantly confirmed and amplified by the later new and more accurate measurements, communicated to me by Mr. G. D. Liveing, all possible security was given at first that the few found rational numbers were not accidental, but rather characteristic or typical of the relations between the compared spectra. Their internal meanings result from theoretical reflections which belong to the first elements of new chemical mechanics, and will form the last, but perhaps not the least interesting, part of my spectral analytical communications.

As soon as the criteria that characterise the condensation forms of the primary bodies occurring in hydrogen, oxygen, and in aqueous vapour were established and ascertained, the possibility was afforded of admitting and ultimately recognising the correspondence of certain rays in the spectra of given elements with certain condensation forms of the primary elements, or of making such relations at least very probable. For suppose the agreements corresponding to a single criterion to be for some rays only accidental, there would be little probability that the same rays would satisfy simultaneously also a second criterion, and much less probability that they would answer to a third or even to a fourth criterion with the same accuracy. The greatest difference admissible between two compared numbers whose probable errors may be numerically δ and δ' respectively, is δ and δ' (numerically); this will be 0·4 to 0·6, if the errors δ and δ' amount to 0·2 to 0·3, as may be the case for a great part of my comparisons.

Hence there is, I believe, sufficient security given for the exactness of the spectrum analyses performed in such a manner, if not in all single cases, at least for the result as a whole; a security which could only be augmented by new and more accurate measurements, in so far as these would produce better agreements between the compared numbers.

(3.) The rhythmical relations which exist between the wave-lengths, due to the condensation forms of the primary bodies and between the hydrogen or the oxygen spectrum, can be used at present only in a few cases as criteria. In the remaining cases they give rise to wave-lengths still unknown, due to such condensation forms of the primary elements, such as occur in hydrogen or in oxygen, and in peculiar physical modifications also in other secondary elements. The wave-lengths thus obtained form not only important supplements to the wave lengths of the same kind hitherto observed, but supply also at once handles for the experimental investigation of my theory, in so far as the corresponding rays can really be found partly in the spectra of hydrogen or of oxygen, partly in the spectra of such bodies as contain the condensation forms referred to in proper physical modifications. (See the Introduction, sub. III.)

The statement, however, that rays due to a special condensation form of a primary element which in a certain physical modification disappear on account of their extremely low or vanishing intensity, may be seen (or made visible by the photographic plate) in another physical modification of the same chemical condensation form, and *vice versâ*, is by no means an hypothesis, but rather the expression of a mechanical necessity.

(4.) The experimental and theoretical spectrum analysis in the largest sense is a field in which chemistry, physics, and astronomy (astrophysics) touch one another intimately. As such it forms a central or nodal point of the whole field of our perception and knowledge.

This position leads naturally to the conclusion that as every important progress upon that ground results from the co-operation of the sciences above mentioned, so every new discovery upon that field reacts simultaneously upon chemistry, physics, and astronomy.

For mathematics, which has for its object to penetrate natural philosophy, especially in the more concrete form of mechanics, acquires on that ground the office of disposing of the almost overwhelming abundance of important physical and chemical constants (principally wave-lengths), which experimental investigations supply in order to search for and to find the secret relations hidden in that ocean of numbers, and to discover the internal mechanical meaning of the latter.

Here is the foundation upon which I base my researches: to this belong the mathematical experiments, the troublesome calculation by which I, at first groping about entirely in the dark, then seeing more and more clearly, have brought to light a small part of the numerical relations concealed in the large amount of material of measured wave-lengths: to this the dynamical researches by which I have tried to open up, with the aid of a minimum of most probable hypotheses, the path to the gradual understanding of their internal meanings.

Whatever may be the final fate of my results in this matter, whether they be or be not accepted by the chemists of our days, they merit at least to be regarded with attention and to be examined without prejudice. I am, for my part, thoroughly convinced that my results in that field, and especially the chief result of all my relative researches, "that many, perhaps all, bodies hitherto considered as elements are compounds composed of condensation forms of the primary elements '*a*' and '*b*' of hydrogen $H = ba_4$ in various physical modifications," will be finally acknowledged and received as true or at least as most probable.

UNIFORM METHODS FOR THE ANALYSIS OF FERTILISERS, CATTLE FOODS, DAIRY PRODUCTS, SUGAR, AND FERMENTED LIQUORS.*

(Continued from p. 23).

Criticism of Wollny's Methods.

Goldmann criticises Wollny's original method chiefly because it gives only a part of the volatile acid present and takes no account of the whole. It has never been claimed, however, for the Reichert process that it gave anything more than a portion of the volatile acid present, but the percentage of the total volatile acids obtained is approximately constant, and therefore the results are comparable among themselves.

Goldmann proposes to remove the last traces of alcohol after saponification by distillation in a current of steam. Before the distillation of any part of the alcohol, however, the solution is heated with a reflux condenser for half an hour so that any ethers which have been formed may be re-combined by the excess of alkali present. The apparatus for the removal of the last traces of alcohol is illustrated in the *Chemiker Zeitung*, No. 14, 1888, p. 216.

Goldmann's paper is so long that for all details I can only refer to the original. The method finally adopted by him is as follows:—5 grms. of the melted butter fat are weighed in a flask of 300 c.c. capacity, the neck of which is 12 c.m. long and 2 c.m. wide. Add 10 c.c. alcohol, 96 per cent, and 2 c.c. of a 50 per cent aqueous soda lye made and preserved out of contact with carbonic acid. The flask, furnished with a reflux condenser, is heated for twenty minutes with a small flame. The condenser is turned to an angle of 55°, and 6 c.c. of the alcohol distilled off. The flame is then extinguished, the apparatus connected with the flask delivering steam, and the whole of the alcohol driven off by a slow current of steam.

Full directions for the conduct of this part of the work are given by Goldmann.

After the alcohol is driven off the soap is decomposed by the addition of 5 c.c. of sulphuric acid containing 200 c.c. of strong acid to the litre. The volatile acids are distilled off in a current of steam and 600 c.c. of distillate taken, which is titrated with one-tenth normal solution of barium hydrate.—(Abstract from *Chemiker Zeitung*, 1888, No. 12, p. 183; No. 14, p. 216; No. 20, p. 317).

Application of the Reichert-Meissl-Wollny Method to Italian Butters.

Besana has made an extended examination of 114 samples of butter, and from the study of them draws the following conclusions:—

One hundred and fourteen samples of butter examined belong to 30 provinces. These show a melting-point from a minimum of 33° C. to a maximum of 37·7°, not including one sample which seems to be essentially different in constitution. No positive relation has been established between the point of fusion and the quantity of volatile acids; therefore the knowledge of the first offers no special utility.

The percentage of volatile acids, or the quantity of the same expressed in c.c. of deci-normal alkaline solutions, shows a variation from a minimum of 21·83 to a maximum of 30·19. The classification of the 114 samples of butter, according to their quality or condition, would be as follows:—

Volatile acids from		No. of Samples.
29	to 30·19	23
28	to 29	25
27	to 28	49
26	to 27	9
25	to 26	3
24	to 25	2
23	to 24	1
21·80	to 22	2
		114

The variation in the quantity of the volatile acids, in the different butters, already recognised by various experimenters in Germany and Sweden, is confirmed by these researches also in the Italian butters. Even the butters of the same dairy may present quite different qualities, although made within a very few days of each other. Upon the cause of this variability I have not ventured, up to the present time, to present any theory, and I have not even sufficient data for the support or contradiction of the theories of others. I hold the causes to be biological, and I would like the researches tending to their discovery to be made by following very closely the chemistry of nutrition and of the lacteal secretions or the transformation of aliment into milk, keeping note of the quantity and quality of the food, the stage of lactation, the condition of health in the animal, &c.; but such researches, in my opinion, should be followed upon individual cases, instead of upon a group of milch cows.—(Prof. Carlo Besana, extract from the journal *Le Stazioni Sperimentali Agrarie Italiane*, 1888, vol. xiv).

In regard to the cost of the lactocrite, I would say that I recently secured one for the West Virginia Experiment Station for 125 dollars from the De Laval Separator Company, of Philadelphia.

It is arranged in such a way that it can be set in the place of the drum of the separator, and run by the power that runs the latter. The construction is very simple, and for the rapid testing of milk it appears to be the most satisfactory method yet devised.

There is likewise an apparatus provided by the same company which is intended to mix artificial fats with the skimmed milk. It is arranged so that the liquid fat and the skimmed milk are violently whipped together, the fat being delivered in a finely divided condition.

I have been suspicious for a considerable time that much of the cream now in the market is cream manufactured in this or some similar manner, and, as we have ordered one of these machines for the experiment station, we propose in the near future to see to what extent we can mix fat of cotton, pig, or cow, with skimmed milk to supply the gastronomic needs of our national capital.

Mr. Richards spoke of Swedish machines for taking out cream and putting back cotton-seed oil, illustrated in the London *Engineering*

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[*] Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

The Secretary then read the following communication from Professor G. E. Patrick, of Iowa:—

NOTES ON THE METHOD FOR SOLUBLE AND INSOLUBLE FAT ACIDS.

In the determination of soluble and insoluble fat acids I have recently found it convenient, as well as economical of time and material, to change slightly the mode of procedure as laid down in the method (originally Muter's) adopted by this Association at its last meeting (1887), and published in *Bulletin* No. 16 from the Department of Agriculture, Chemical Division, pp. 70 and 71.

The purpose of the modification is to avoid the use of a separate saponifying bottle, and the consequent transfer of the soap solution to an Erlenmeyer flask, and evaporation of the alcohol added in this transfer.

This end is accomplished by saponifying directly in the Erlenmeyer, the latter (with stopper tied down) being inclosed in a "conversion" jar with tight cover, and containing absolute alcohol (50 c.c.), the vapour of which gives an outside pressure on the Erlenmeyer equal to that within. The jar is made with vertical sides, and is only a little larger than the flask it is to inclose; its cover is held down by a screw-clamp in the usual way, a disc or washer of rubber making the union tight.

Breakage by contact of the flask with the walls of the jar while agitating is prevented by a ring of corks strung upon a wire. Thus arranged, *with a tight jar*, there is no danger of breaking the Erlenmeyer if the work is executed with ordinary care. Fifty c.c. of absolute alcohol in the jar will suffice for many analyses.

Two styles of jar have been tried, one of heavy glass, iron bound (made by Eimer Amend), the other of heavy sheet copper, made (excepting the clamp) by an ordinary tinsmith; the cover of each is a thick ground-glass plate, with a metal disc to receive the pressure of the screw. The glass one, allowing a view of the interior during saponification, is the more convenient.

The saponification is conducted in a steam or air oven at a few degrees below 100 c.m. Neither style of jar can be heated directly on the water or steam *bath* with safety to the contents. This needs further trial.

Another slight deviation from the method of last year, which I find convenient, is to retain the cake of insoluble acids in the Erlenmeyer for weighing, using alcohol merely to dissolve into the flask whatever fat acids are on the dried filter. This small amount of alcohol is quickly removed, first on the water-bath and then in the oven, with a current of dry air or hydrogen.

By these two changes in the method the entire determination of insoluble acids is effected without any transfer of material from first to last. At the start the filtered, still liquid, and well-shaken fat is weighed into the tared Erlenmeyer; at the end, after the insoluble acids are weighed, they are removed, and the flask is dried and tared again to insure against error from "nicking" or corrosion during the operation. However, in the few trials thus far made, the first and last weights of the flask have been practically identical.

REPORT OF THE COMMITTEE ON PHOSPHORIC ACID.

As required by the constitution of the Association, the Committee on Phosphoric Acid herewith presents its report. The report presents: 1, brief notices of new analytical methods for determining phosphoric acid proposed during the year; 2, results of work done by the committee and members of the Association; 3, recommendations for the next year.

C. Mohr (*Chem. Zeit.*, 11, 417—418; Abs. *J. Chem. Soc.*, 1887, p. 884) proposes the following volumetric method for phosphoric acid:—Two grms. of the phosphatic substance is treated with successive small quantities of 2 per cent sulphuric acid in a mortar. The residue is added to the extracts, and the whole made up to 100 c.c. and allowed to digest for one hour; 10 c.c. of the filtered solution, corresponding to 0·2 grm., are then treated with potassium ferrocyanide so long as iron is precipitated. After the addition of sodium acetate, the phosphoric acid is titrated in the usual way with a standard solution of uranium acetate. It is stated that the end reaction is not influenced either by an excess of potassium ferrocyanide or by the presence of Prussian blue.

G. Kennepohl (*Chem. Zeit.*, 11, 1089-1091; Abs. *J. Chem. Soc.*, 1888, 321; *J. Soc. Chem. Ind.*, 6, 680) confirms the opinion expressed by Klein (*Chem. Zeit.*, 10, 721; *J. Chem. Soc.*, 1886, 835) as to the practical non-occurrence of iron phosphide in normal Thomas slag. The phosphoric acid may be accurately determined in the following manner: Ten grms. of the finely powdered slag are introduced into a 500 c.c. flask, moistened with alcohol to prevent adhesion, and heated in a water bath for at least half an hour with 40 c.c. of HCl (1·12 sp. gr.) and 40 c.c. of water. After cooling the flask is filled to the graduation mark and the solution filtered. An aliquot part is mixed with ammonium nitrate and molybdic solution without previous removal of the silica. The solution, after heating at about 80° for fifteen minutes, is filtered, and the precipitate washed with water containing 3 per cent of nitric acid, re-dissolved in 2½ per cent ammonia, and then precipitated with magnesia mixture. The presence of silica does not interfere, owing to the ready solubility of ammonium silico-molybdate in the washing water.

If the presence of ferrous salts should tend to cause the separation of molybdic oxide, which dissolves but slowly in ammonia, an addition of nitric acid or bromine, before adding the molybdic solution, will insure the production of a precipitate instantaneously soluble in the ammonia.

Isbert and Stutzer (*Zeit. Anal. Chem.*, 26, 583-587; Abs. *J. Chem. Soc.*, 1888, 194; Chem. News, 57, 211; *J. Soc. Chem. Ind.*, 7, 44; *J. Anal. Chem.*, 2, 193). The method based on the determination of the ammonia in the phospho-molybdate precipitate (*Chem. Zeit.*, 11, 223) is confirmed. A further simplification consists in washing the yellow precipitate with cold water, instead of with ammonium nitrate solution. The ammonium silico-molybdate is soluble in pure cold water, although insoluble in ammonium nitrate solution. On the other hand, the phospho-molybdate requires 10,000 parts of cold water for its solution.

The analysis is conducted as follows:—

Five grms. of the phosphate are dissolved in hydrochloric acid or aqua-regia, diluted to 500 c.c. and filtered. Fifty centimetres of the filtrate are mixed with an excess of ammonia, acidulated with nitric acid, and the phosphoric acid precipitated with ammonium molybdate. The precipitate is allowed to settle at 60° to 70° C. for fifteen minutes, and then filtered, the supernatant liquid being first passed through the filter, the precipitate repeatedly washed by decantation, then placed upon the filter and washed with water until the wash water amounts to about 250 c.c. The precipitate is transferred, filter and all, to a ¾-litre Erlenmeyer flask, sodium hydroxide added in excess, and the ammonia distilled off into a solution of standard acid, which is then titrated back with baryta water, using rosolic acid as the indicator.

One part of nitrogen in the precipitate corresponds with 1·654 parts of phosphoric acid.

Test analyses with known quantities of phosphate, with and without silicic acid, and comparative tests of phosphatic manures by the above and gravimetric process, show that for commercial purposes the method is sufficiently accurate.

Ch. Malot (*Monit. Scient.*, 1887, 487; *J. Pharm.*, 16, 157-159; *J. Chem. Soc.*, 1887, 1063; *J. Soc. Chem. Ind.*, 6, 563) describes a new volumetric method for P_2O_5 by uranium nitrate. Oxide of uranium gives a green lake with cochineal, which property is utilised for the determination of phosphoric acid.

The phosphate is treated according to Joulie's method, *i.e.*, dissolved in HCl, the phosphoric acid precipitated with citro-magnesium mixture, and the precipitate dissolved in dilute nitric acid. A few drops of tincture of cochineal are added, then ammonia until the violet colouration just appears, and this in its turn is made to disappear with one or two drops of nitric acid. The solution is now heated to 100° C., 5 c.c. of sodium acetate solution added, and mixture titrated with uranium nitrate. Each drop of the latter causes a greenish-blue zone, which, on agitation, disappears again. As soon as precipitation is complete, the solution assumes a lasting greenish-blue colour, remaining unchanged by excess of the uranium solution. The end reaction is most distinct. By employing a very dilute solution of uranium nitrate, the determination is rendered very exact. The author uses solutions, 1 c.c. of which represents 0·002 grm. of phosphoric acid.

A. Emmerling (*Zeits. Anal. Chem.*, 26, 244, Abs. Chem. News, 57, 15; *J. Anal. Chem.*, 2, 228) describes a new method for the determination of soluble phosphoric acid in superphosphates.

The solution of superphosphates, mixed with calcium chloride, is allowed to flow into a standardised solution of caustic soda, to which some phenolphthalein has been added. The following solutions are required :—

(1) Sodium hydrate, of which 1 c.c. represents about 0·005 P_2O_5.

(2) Calcium chloride solution, made by dissolving 200 grms. $CaCl_2$ in one litre of water.

(3) Penolphthalein, 1 grm. in 500 c.c. of alcohol.

(4) Methyl orange in aqueous solution.

The execution of an analysis is carried on as follows :—

Two hundred c.c. of the solution of the sample prepared in the ordinary manner are well mixed with 50 c.c. solution of calcium chloride. One burette is filled with this mixed solution and a second with the soda solution. Of this latter 20, 10, or 5 c.c. (according to the strength of the superphosphate) are measured into a beaker; 2 c.c. of the phenolphthalein solution are added, and some water, and the superphosphate solution is then run rather rapidly. As soon as the colour begins to grow faint the superphosphate liquor is added more gradually, and at last drop by drop, until the redness has entirely disappeared.

The author next measures off again the same number of the c.c. of the mixed solution of superphosphate and calcium chloride as used above, dilutes with a little water, and mixes with 4 to 6 drops of the methyl orange solution. The liquid is titrated cautiously with the soda solution, finally drop by drop until the reddish colour changes to a yellow or orange yellow.

The smaller number of c.c. of soda solution, as consumed in the titration with methyl-orange, is deducted. from the number obtained in titrating with phenolphthalein. If we have dissolved 20 grms. superphosphate in 1000 c.c. of water, and make up 200 to 250 c.c. by the addition of 50 c.c. of the calcium chloride solution, and if a is the measured quantity of soda, b the solution of superphosphate and calcium chloride consumed, c the soda used for neutralising the free acid, and t the standard of the soda expressed as P_2O_5, the percentage of soluble phosphoric acid in the sample is equal to

$$a - c \times t \times \frac{250 \times 1000 \times 100}{200 \times 6{\cdot}20}$$

This method is applicable to ferriginous superphosphates.

J. Ruffle (*J. Soc. Chem. Ind*, 6, 327—333; Abs. *J. Chem. Soc.*, 1888, p. 87; *J. Anal. Chem.*, 1, p. 455) has contributed an interesting paper on moisture and free acids in superphosphate. The loss of moisture, dried to constant weight, at various temperatures varied in one sample from 12·92 per cent at 38° to 50° C., to 17·93 per cent at 150° C. Drying at the same temperature, 100° C., for different periods, showed a variation of from 9·97 per cent for thirty minutes, to 17·15 per cent for seven hours. The fertiliser dried in its natural state, at 100° C., showed a much greater loss of moisture than when previously rubbed to a fine paste in a mortar.

It is also shown that the soluble phosphoric acid existing in superphosphates is not entirely present as mono-calcium phosphate, and that the exposure of 100° C. drives off more than the true moisture, that is, the adhering uncombined water. It is recommended to determine the moisture in the following manner:—Weigh out 2 to 5 grms. of the phosphate in its natural state on a double watch-glass, place under an air-pump over dry calcium chloride, exhaust, then leave for eighteen to twenty-four hours and weigh.

John Clark (*J. Soc. Chem. Ind.*, vii., 311—312) describes a modification of Perrot's (*Compt. Rend.*, xciii., 495) for the estimation of phosphoric acid as phosphate of silver.

The objections to Perrot's process, when applied to manures and natural phosphates, are—

1. The chlorides which may be present will be estimated as phosphates.

2. The method of separating the phosphates of iron and alumina from the phosphates of lime and magnesia is inaccurate, as it is practically impossible to dissolve out the whole of the phosphate of lime in the manner indicated.

The modifications which the author recommends are—

1. The solution of the phosphate of silver precipitate in nitric acid, and the titration of the silver with sulphocyanide.

2. The neutralisation of the acid solution with caustic soda instead of ammonia to avoid the presence of an excessive quantity of ammoniacal salt, which affects the results.

3. The previous precipitation of the iron and alumina as phosphate with acetate of soda containing free acetic acid.

The following is an outline of the process :—The phosphate is dissolved either in water, nitric acid, or sulphuric acid, the greater portion of the free acid neutralised with caustic soda, and to the cold solution acetate of soda containing free acetic acid is added in excess. If the addition of the acetate of soda produces a precipitate, this must be filtered off, re-dissolved, and re-precipitated with acetate of soda, as before. The filtrate and washings are added to the previous filtrate, then excess of nitrate of silver, which will give an immediate precipitate of phosphate of silver, Ag_3PO_4, and the free acetic acid is neutralised with caustic soda till there is only a faint acid reaction to litmus-paper.

The slightest excess of caustic soda will cause a brown precipitate of oxide of silver, but this oxide of silver dissolves easily on the addition of a few drops of dilute acetic acid.

The precipitate of phosphate of silver, which will contain any chloride which may have been present, is thrown on a filter, thoroughly washed with water, then dissolved off the filter with hot dilute nitric acid, mixed with a little ferric sulphate, and the silver titrated with sulphocyanide, as described by Volhard, and calculated to phosphoric acid.

The precipitate of phosphate of iron and alumina is dried, ignited, and weighed, then dissolved in acid, the iron determined volumetrically, calculated to phosphate of iron, and the balance assumed to be phosphate of alumina; or the oxide of iron may be separated with caustic soda and the alumina in the filtrate weighed as phosphate of alumina, using the precautions recommended by Thomson (*J. Soc. Chem. Ind.*, vol. v.).

Comparative tests on a variety of materials show a close agreement with the molybdic method.

Dircks and Werenskiold (*Landw. Versuchs. Stat.*, 1887, 425—453; Abs. *J. Chem. Soc.*, 1888, 628) have tested the various processes employed for the estimation and separation of tri-calcium from mono- and di-calcium phosphate, namely, the various modifications of the ammonium citrate method. They find that although none of the methods give a really satisfactory and exact result, Petermann's process is perhaps the most trustworthy.

C. Schindler (*Zeit. Anal. Chem.*, xxvii., 142—146; *J. Chem. Soc.*, 1888, 753; *J. Soc. Chem. Ind.*, vii., 455) describes a volumetric method for the determination of phosphoric acid, based upon the formation of a compound of phospho-molybdate of ammonia of definite composition. The following solutions are requisite:—

1. *Molybdic Solution.*—To a litre of molybdic acid solution, prepared in the usual manner, 30 c.c. of a solution of citric acid containing 500 grms. to the litre are added.

2. Concentrated ammonium nitrate solution containing 750 grms. to the litre.

3. Dilute ammonium nitrate solution containing 100 grms. to the litre and 10 c.c. nitric acid.

4. Magnesia mixture prepared in the usual manner.

5. Lead solution, 1 c.c. of which corresponds to 0·04 grms. P_2O_5. This is obtained by dissolving 55 grms. lead acetate in one litre of water and a little acetic acid.

6. Molybdate of ammonium solution, 1 c.c. of which corresponds to 1 c.c. lead solution; 25 grms. ammonium molybdate are dissolved in one litre and standardised against the lead solution.

7. Tannin solution; 1 grm. tannin is dissolved in 20 to 30 c.c. of water.

The analysis is conducted as follows:—50 c.c. of the nitric acid solution of the phosphate (0·5 grm. of substance) is mixed with so much of the concentrated solution of ammonium nitrate that after the addition of the molybdic acid solution the mixture shall contain 25 grms. ammonium nitrate per 100 c.c. Then, for each 0·1 grm. of P_2O_5, 100 c.c. of the molybdic acid solution is added, and the mixture heated in a water-bath to about 58° C. The precipitate is allowed to settle for ten minutes, and the liquid decanted and passed through a filter. The precipitate is washed with 50 c.c. dilute ammonium nitrate solution by decantation, and dissolved in 3 per cent ammonia solution. The solution, together with that dissolved off the filter, is brought into a quarter-litre flask, 10 to 20 c.c. magnesia mixture added; after shaking it is made up to 250 c.c. and filtered. 50 c.c. of the filtrate are taken, acidified with acetic acid, and the liquid made up with boiling water to 300 c.c. Lead solution is now added from a burette until a small excess of lead goes into solution, and is titrated back with ammonium molybdate solution, using the tannin solution as an indicator. A drop of tannin solution gives a red colouration with ammonium molybdate, which is visible in a solution of 1 in 400,000, whereas lead molybdate gives no colouration, and lead acetate only a greenish colouration.

Comparative determinations on a variety of materials show a close agreement with the magnesia method.

At a meeting of the directors of the Belgian experiment stations, the following method for the estimation of the phosporic acid soluble in water and in citrate of ammonia was adopted:—

Two grms. of ordinary superphosphate (or 1 grm. of a rich simple, say over 20 per cent) are triturated in a mortar with water and thrown upon a filter. The filter is washed with water until about 200 c.c. have passed through; to the filtrate is added 1 c.c. of nitric acid, and the volume of the solution is made up to 250 c.c. The filter, and the insoluble matter contained in it, is now introduced into a 250 c.c. flask with 50 c.c. of Petermann's alkaline citrate of ammonia solution, and allowed to digest for one hour on the water-bath at a temperature of 38° to 48° C. After rapidly cooling the flask is filled up the mark with water. Of the above filtered liquid (the citrate of ammonia solution), take 50 c.c. and mix it with 50 c.c. of the aqueous solution, acidify with nitric acid, and precipitate with molybdic acid solution. The remainder of the operations remain as for the ordinary estimation of phosphoric acid.

Petermann's alkaline citrate of ammonia is prepared by dissolving 500 grms. of citric acid crystals in water and mixing with 700 c.c. of ammonia of 0·920 specific gravity. Bring the concentration of the liquid to 1·09 specific gravity at 15° C., and add to each litre 50 c.c. ammonia of 0·920 specific gravity.

The report being open for discussion, the President called attention to the dependence of amount of soluble phosphoric acid on the size of filters used during its extraction, and thought it would be well for the committee to recommend a definite size of nine centimetres.

Professor Frear spoke of differences due to variations in moisture in different laboratories.

Mr. Gascoyne said the variations in moisture was not proportional to the variations in phosphoric acid, and that such differences as 12 and 19 per cent could not be due to anything but carlessness, the highest determinations of moisture being accompanied by highest percentages of phosphoric acid.

Professor Lupton, on examining the results, said he could see no way to harmonise variations.

The President thought the publication of these results would be most beneficial to the Association, and that results another year would be sent in with greater care.

The President then introduced the subject of the use of pumps for extracting soluble phosphoric acid, considering it an advantage where much work was to be done.

Mr. Gascoyne spoke of quick work with molybdate and magnesia solutions, allowing them to stand but five to ten minutes for the yellow precipitate, and not more than fifteen for magnesia precipitate.

Mr. Gaines's and Mr. Richardson's experiences confirmed his observations.

(To be continued).

NOTICES OF BOOKS.

A Text-Book of Elementary Metallurgy for the Use of Students. By Arthur H. Hiorns, Principal, School of Metallurgy, Birmingham, and Midland Institute. London: Macmillan and Co.

This little work is strongly "examinational," the author being probably of opinion that the system will "last his time." To 172 pages of the actual text, the instructive portion of the book, there are superadded not fewer than 64 pages of examination questions set by the Science and Art Department during the last twenty years. This section of the work is doubtless intended for the convenience of students, or rather of young men preparing for examination, and of "coaches." But the list makes no mention of the time when the various questions were set, nor of the periods of their recurrence, and thus it does not show either the "coach" or his pupil what subjects must be especially "got up," or what may be safely overlooked.

Among these questions we notice one which is decidedly unfair, namely, "What is a metal?" Here eminent chemists differ widely among themselves, not only, *e.g.*, arsenic and silicon, but even tin, being by some authorities held to be metals, and by others to be non-metallic elements. Here, therefore, the student may easily commit himself, except he knows the peculiar views of the examiner. Another question is, "What is meant by the term 'autogenous soldering?'" We have always known this term to be applied to the Richemont process where two sheets of lead are united at their edges by letting one overlap the other, and then running, by means of a flexible tube, the flame of an oxy-hydrogen blowpipe along the junction, as it is always done in fitting up the lead chambers at sulphuric acid works. Professor Hiorn, however, tells us that "sheets of lead and tin can be rolled into one compact sheet called autogenous soldering." We submit that if *two* metals are present the process is not autogenous, and that the presence of tin would be fatal in the lead chambers. Now, if Prof. Hiorn's definition of autogenous soldering is not the one recognised at South Kensington, woe be to his students.

The body of the work has few blemishes. But, in our opinion, the examination-questions had better have been omitted, and their place occupied by more useful matter. A more copious index would have been an improvement.

The Blowpipe in Chemistry, Mineralogy, and Geology; containing all Methods of Anhydrous Analysis, many Working Examples, and Instructions for Making Apparatus. By Lieut.-Colonel W. A. Ross, R.A., F.G.S., &c. Second Edition, Revised and Enlarged. London: Crosby Lockwood and Son.

The fact that a second edition of this book has been found necessary proves that an increasing interest must be felt in blowpipe analysis. This fact may serve as a set-off to the circumstance, mentioned in a foot-note, that "the City and Guilds of London Institute have, quite recently, by the advice of an irresponsible chemist, cut out blowpipe analysis from their curriculum. It is still untaught at the Royal School of *Mines!*" If there is here no mistake, this is a fact much to be regretted. It is to be hoped that in these days of "technical education" such a state of things cannot long be suffered to continue.

The author differs from many authorities in considering that the use of blowers, worked by foot or hand, is not merely permissible, but in some cases preferable to the mouth-blower, as affording, if duly proportioned to the bulk of the flame, a "greater and a more localised heat." He takes an independent standing also in recommending a gas-flame as the source of heat, always excepting cases where the operator is testing for sulphur and its compounds.

He recommends his students to use a "hot-gas lamp," worked by a foot-blower, whenever procurable. We do not at all question the dictum of Col. Ross when saying that he has worked twelve years with oil-lamps and twelve years with gas, and has found no *great* difference in the results. Still we can scarcely see that the use of gas can be indifferent in all the cases where sulphur reacts strongly upon the substances under examination.

The aluminium plate as a support, first devised by Col. Ross, has approved itself in practice, and now seems to have been generally adopted, except at Freiberg, and at the "J. C. Green School of Science" in New Jersey.

A very commendable feature in the work, or we may rather say in the author's system, is the endeavour to dispense with costly and cumbersome articles of apparatus wherever possible. In this undertaking he has been very successful.

The additional matter first appearing in the edition consists of exercises in the determination of minerals by the blowpipe alone, with the solutions by a correspondent of the paper in which they were first published.

That Col. Ross has done good service in promoting, improving, and facilitating blowpipe analysis is beyond all question.

The Introductory Address to the Eighth Lecture Course at the Albany College of Pharmacy. Delivered October 1st, 1888. By Willis G. Tucker, M.D., Ph.D., Professor of Chemistry. Published by the Class, Albany, N.Y.

Sound, earnest advice, not specially applicable to pharmacists, but deserving to be marked, learned, and inwardly digested by students in every science! Nay much of what we here find may be taken to heart by numbers who are never seeking to become *savants*. The speaker insists, first and foremost, upon exactitude. He suggests that young men should make a thorough study of some one of the natural sciences, and acquire in the laboratory or museum "the habit of exact observation and precise measurement and statement, in such way that it will stick to them for life."

The reader is next reminded that science is painstaking, laborious, patient. He is referred to the lives of Agassiz and Darwin to learn what diligence is.

The scientific worker, further, is governed by a judicial spirit. Here we find reference to certain "paper philosophers" who criticise theories which they are unable to comprehend. It is admitted with regret "that clever partisans with their specious and fallacious reasonings, their rhetorical vapourings and heated arguments, carry the multitude along with them."

True scientific work also is not inspired by a love of gain. In developing this part of his theme Dr. Tucker might have added that the highest results in every science are necessarily unremunerative. He speaks of a "class of middlemen, a kind of rear-guard science, ever on the alert to seize upon those ideas which can be turned to practical account, and this class secures the profit and often much of the credit of discovery." We do not know whether this class, instead of being called a rear-guard, might not better be designated as camp-followers eager to plunder the wounded.

Perhaps the lessons here enforced are not novel. But until they are apprehended by the public at large, they cannot be too often or too emphatically reiterated. Dr. Tucker, therefore, has spoken well and wisely.

CORRESPONDENCE.

THE USE OF PEROXIDE OF HYDROGEN FOR THE DETERMINATION OF THE METALS OF THE IRON GROUP.

To the Editor of the Chemical News.

Sir,—I see from the paper under the above heading copied from the *Comptes Rendus*, vol. cvii., p. 997, into the Chemical News (vol. lix., p. 15), that its author, M. Adolph Carnot, recommends the volumetric estimation of manganese by means of hydrogen peroxide and ammonia, the solution of the manganous salt to be precipitated by these reagents, excess of the oxidant expelled by boiling, and the manganic hydroxide to be treated by any well-known procedure.

If M. Carnot quantitatively examines his method he will find that manganic hydroxide obtained as he proposes approximates in composition to Mn_7O_{13}, and varies in composition, so that as a basis for the volumetric estimation of manganese, the results may differ six per cent.—I am, &c.,

Norman McCulloch.

Laboratory of Clyde Iron Works,
(by Tollcross), Glasgow,
January 14, 1889.

ELECTRIC SUGAR.

To the Editor of the Chemical News.

Sir,—The questions put by Mr. G. A. Keyworth, in the last number of the Chemical News (vol. lix., p. 24), as to "electric sugar," have been, to a great extent, already answered in an article written by ourselves, and which appeared in the November number of the new journal *Sugar*. Referring to a trial of the so-called "electric process," we then stated that "from examination of the sugar produced in this experiment, it is evident that it had, at one period of its existence, assumed the form of loaf sugar, or cubes, and from this state, possibly by means of the granulators alluded to in the report, after being damped, it had been reduced to small pieces, which were subsequently separated by sieves of various sizes, thereby forming samples of comparatively even grade. This explanation of the *modus operandi* is corroborated by the fact that pieces of hard sugar, of considerable size, passed out of the apparatus during the progress of the trial, owing doubtless to the unfortunate break-down which is said to have taken place. As a matter of fact, granulated sugars of an exactly similar appearance may be readily obtained by breaking up loaf sugar, or cubes, and sifting the rough powder through a set of sieves so as to separate the sugar into various grades."

We may add that the so-called "electric sugar" is no purer than the usual run of loaf sugar and cubes which contain only a very minute amount of impurity. The trace of glucose present in some samples of "electric sugar" is due to the sugar having been kept for some time in a moist state previous to being manipulated in the way already described.—We are, &c.,

Newlands Bros.

Laboratory, 27, Mincing Lane, E.C.,
January 15, 1889.

SCIENCE AND ART DEPARTMENT.

To the Editor of the Chemical News.

Sir,—With regard to the strictures of Mr. Bloxam on my answer to "Student," I may say that I did not think it necessary to inform a student of organic chemistry how to prepare a solution containing inorganic bases for the detection of organic acids. I certainly did not mean "separation of the inorganic bases as usual" to imply what Mr. Bloxam understands by it, viz., removal of the metals, group by group, by the ordinary methods of inorganic analysis, but rather treatment, as Mr. Bloxam says, with Na_2CO_3, and further—which Mr. Bloxam does not say—treatment with H_2S in the presence of such metals as As, Sn, or Sb soluble in alkaline solutions. I may also remark that I doubt whether "Student" will be able to detect the organic acids mentioned decisively, when *mixtures* of them or their salts are heated with dilute or concentrated H_2SO_4.—I am, &c.,

W. E. Youle.

25, Deptford Lower Road,
January 14, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Bulletin de la Société Chimique de Paris. Vol. 1., No. 11.

Rapid Method for the Analysis of Industrial Waters, with a View to their Chemical Purification.—Leo Vignon.—The author's method comprises two distinct operations. He first determines by saturation with a standard solution of calcium hydroxide the carbonic acid other than that existing in natural carbonates, using phenolphthalein as indicator. He then measures, by means of a standard solution of sodium carbonate, the proportion of that salt necessary to precipitate as carbonates all the soluble salts of calcium and magnesium, using the same indicator. In both cases the phenolphthalein does not take and retain its characteristic rose colour until the lime or the sodium carbonate is in excess in the liquid.

Action of Hypophosphorous Acid upon Benzoic Aldehyd; Formation of Dioxyphosphinic Acid.—J. Ville.—Hypophosphorous acid is capable of combining with benzoic aldehyd, so as to yield a triatomic monobasic acid, the dioxyphosphinic acid, which might otherwise be called dioxybenzylphosphinic acid.

On "Adjacent" Metaxylidine and its Identity with the Orthoxylidine of Wroblewsky.—E. Noelting and B. Pick.—The metaxylidine in question is distinguished from all its isomers by the great solubility of its sulphate, by its resistance to acetylisation, its high fusion-point, and the great stability of its acetylic derivative. It is present in small quantity only in commercial xylidine, so that a large quantity of material must be taken for its isolation.

On the Azoxylenes, the Diamido-dixylenes, and the Colouring-matters derived from the latter.—E. Noelting and B. Strecker.—The authors give a table of the shades obtained by diazotising all the bases which they have obtained, and conjugating them with naphthionic acid, α-naphthol-α-sulphonic acid, and naphthol-disulphonic acid, R.

On the Sulphonic Acid of the Methylic Ether of Phenyl-carbaminic Acid.—E. Noelting.—The amido-sulphobenzoic acid of Hentschel should apparently be considered as a phenylcarbamine-sulphonic acid, and the direct introduction of carboxyl into aniline by means of chlorocarbonic ether becomes in general very problematic.

On a New Franceine derived from Tetrachlorised Benzene.—MM. Georgesco and Mincou.—This franceine, $C_{16}H_4O_6Cl_3$, differs absolutely from that obtained from the chloro-derivative. In fragments it is of a greenish black colour, with a metallic lustre and a conchoidal fracture. When finely-powdered it is black. It is very soluble in alkalies. The neutral potash or soda solution has a blackish red colour. In this state it may serve as an ink or for painting in water-colours. In this state it gives an earthy-red colour. It is but sparingly soluble in alcohol; the yellowish red colouration is not dichroic, nor is the rose-coloured solution in glycerin.

The Determination of Sugar by Fehling's Liquor.—H. Causse.—This determination is interfered with by the precipitation of cuprous oxide, which, towards the end of the process, occasions bumping, so that it is necessary to operate at a point below ebullition. The author avoids this difficulty by adding to the cupro-potassic liquid a solution of potassium ferrocyanide.

On Anagyrine.—E. Hardy and N. Gallon.—Anagyrine, $C_{14}H_{18}N_2O_2$, is the essential principle of *Anagyris fœtida*, a leguminous plant growing around the basin of the Mediterranean.

Transformation of Methyl-valeryl-acetylene into Hexyl-acetylene.—A. Béhal.—Sodium, by mere action of presence, converts a substituted acetylenic carbide into a true acetylenic carbide.

Action of Phosphorus Perchloride upon Malonic Acid.—A. Béhal and V. Auger.—The authors obtain by this reaction a mixture of phosphorus oxychloride and of malonyl chloride.

Action of Phosphorus Perchloride upon Acetophenone.—A. Béhal.—This paper is not adapted for useful abstraction.

Homopterocarpine and Pterocarpine from Santal Wood.—P. Cazeneuve and L. Hugounenq.—Homopterocarpine is probably a kind of methylated polyorcine, comparable to the polyglucosides. Pterocarpine is probably an inferior homologue containing the same fundamental nucleus, and differing only in its substitution radicles.

On Manganese Oxalate.—J. Castelhaz.—Oils prepared with manganese oxalate may be advantageously substituted for drying oils in all their applications by reason of beauty and other properties. From 2 to 5 per cent of manganese is sufficient for boiling oils. The manganese salt is first ground up with 1 or 2 parts of the oil to be boiled, and this mixture is added very gradually to the bulk of the oil, stirring well. The oil is heated very gradually at first, but after the escape of the gases it may be boiled in the ordinary manner.

No. 12, December 20, 1888.

The Presence of Benzene Vapour in Lighting-Gas and its Determination.—M. Berthelot.—In 1876 the author found that the gas of Paris owes much of its illuminating power to the vapour of benzene. He estimated its proportion by weighing the crude nitrobenzene, obtained by passing the gas through fuming nitric acid.

Preparation of Concentrated Formic Acid.—M. Maquenne.—By two successive distillations over sulphuric acid, the ordinary acid of commerce is easily converted into a product containing 98 per cent of real acid. The crude yield is about 55 per cent.

Researches on Rhodium.—E. Leidie.—The author first examines former processes employed for preparing rhodium sesquichloride; he describes his method for preparing the anhydrous sesquichloride, the corresponding hydrate; the double chlorides of rhodium and potassium, rhodium and sodium, and rhodium and ammonium. He then describes rhodium sesquioxide, sesquisulphide; the neutral and basic rhodium sulphates and the double oxalates. The author considers that although rhodium is distinguished from such metals as aluminium, iron, and chromium, by its inability—as far as we can judge at present—of forming alums, it approaches them, nevertheless, by certain common characters, such as the formation of a sesquichloride and double chlorides, a sesquioxide with a series of salts, a sesquisulphide and double sulphides, a regular series of double oxalates, and lastly a chloramidide and its derivatives which approximate it, especially to chrome. We may therefore consider it as the analogue of chrome among those metals known as the platinum group.

Conditions of the Formation of Durol and Production of Mono-benzyl-durol by the Aluminium Chloride Method.— M. Beaurepaire.—The author obtains this compound by heating together in a very dry flask, fitted with a reflux cohobator, 10 parts purified durol, 7 parts dry benzyl chloride, 50 dry carbon disulphide, with traces of aluminium chloride.

MISCELLANEOUS.

The Sanitary Institute.—At a meeting of the Council of this Institute, held 9th January, G. J. Symons, F.R.S., in the chair, it was decided to hold two courses of twelve lectures for Sanitary Officers, the first course to commence in March and the second in October. 64 Members and Associates were added to the Register, and 20 applications read for election at the next meeting.

City and Guilds of London Institute.—Technical College, Finsbury.—A course of six Evening Lectures on the "Science of Brewing" will be delivered by Dr. E. R. Moritz, F.I.C., F.C.S., commencing January 23rd.

Central Institution, Exhibition Road.—During the Spring Term, Professor Armstrong will give about ten lectures on "Some of the More Important Current Problems in Chemistry" on Mondays at 4.30 p.m., commencing Monday, January 21st. The following subjects will be dealt with as far as time permits:—The nature of chemical change; the interdependence of chemical change and electrolysis; the molecular composition of gases, liquids, and solids; the nature of solutions; physical constants; laws of substitution and isomeric change as bearing on the problem of the nature of chemical change; valency; geometrical isomerism and allo-isomerism.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose o giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Arborescent Crystals.—Will any of your readers kindly inform me if any arborescent forms of crystals have been observed other than the so-called lead and zinc tins? I have made some with salts of copper, cobalt, &c., and before communicating my results I should like to know if they are original.—H. O. H.

MEETINGS FOR THE WEEK

Monday, 21st.—Medical, 8.30.
—— Society of Arts, 8. Cantor Lectures. Lecture I.
Tuesday, 22nd.—Institute of Civil Engineers, 8.
—— Society of Arts, 8. "Some Recent Movements in relation to the Applied Arts," by Sir James D. Linton, P.R.I.
—— Royal Institution, 3. "Before and After Darwin —II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Royal Medical and Chirurgical, 8.30.
Wednesday, 23rd.—Society of Arts, 8. "Electric Meters for Central Stations," by Prof. George Forbes, F.R.S.E.
—— Geological, 8.
Thursday, 24th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "The Metamorphoses of Minerals," by Prof. J. W. Judd.
Friday, 25th.—Quekett Club.
—— Society of Arts, 8. "The Asiatic Colonization of East Africa," by H. H. Johnston, F.R.G.S.
—— Royal Institution, 9. "Meteorites and the History of Stellar Systems," by Prof. G. H. Darwin, F.R.S.
Saturday, 26th.—Royal Institution, 3. "The Character of the Great Composers and the Characteristics of their Works," by Prof. E. Pauer.
—— Physical, 3. "Notes on Polarised Light; on the Structure of Natural Diffraction Gratings of Quartz; on Ahrens's Modification of Delezenne's Polariser; and on the Use of Two Quarter-wave Plates in combination with a Stationary Polariser," and "Note on a Relation between Magnetisation and Speed in the Dynamo Machine," by Prof. S. P. Thompson, D.Sc. "On the Divergence of Electro-motive Forces from Thermo-chemical Data," by Prof. E. F Herroun.

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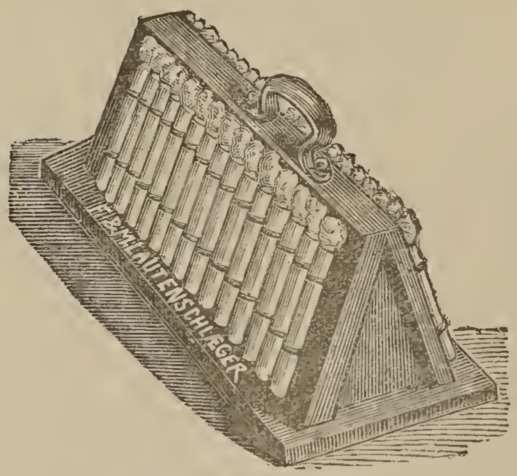

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THE CHEMICAL NEWS.

Vol. LIX. No. 1522.

DECOMPOSITION OF NICKEL AND COBALT.

Though we have not yet obtained the original paper laid before the Chemical Society of Munich by Dr. Krüss, we lay before our readers such further particulars as have come under our notice. It does not now appear, as we had supposed from the first announcement of the discovery, that cobalt and nickel have been entirely split up into three hitherto unknown compounds, one common to both the metals whilst each of the other two was found only in one of them. On the contrary, as we understand the most recent intelligence, Dr. Krüss has found in each of these metals an unknown substance to the extent of 2—3 per cent. After this new body is eliminated, cobalt or nickel—as the case may be—still remains, though with modified properties. The salts of pure cobalt, or new cobalt, are said to be of a violet colour, and those of pure nickel of a dark green. Dr. Krüss was occupied with re-determining the atomic weights of cobalt and nickel; to this end he treated carefully weighed portions of cobalt or of nickel with a neutral solution of gold chloride, and weighed the gold which was eliminated. The results of these operations were not constant, and after various other attempts to detect any possible source of error the gold deposited was closely examined. It was found that after having been dissolved in nitro-hydrochloric acid and reduced with sulphur dioxide there was a loss of weight, and that the washing-waters had a green colour. On concentration these washings gave a colourless liquid, which turned green on the addition of hydrochloric acid, and gave a white deposit on the addition of caustic soda or ammonia, insoluble in the former.

As these reactions could not belong to cobalt or nickel Dr. Krüss sought to procure a larger quantity of the unknown material. He ignited freshly precipitated cobalt or nickel oxide with caustic alkali, extracted the melt with water, and obtained a solution possessing the characters above mentioned, though the pure nickel oxide or cobalt oxide was left undissolved. The solution on treatment with ammonia gave a bulky precipitate of hydroxide. On ignition this yielded a white oxide, giving a brown malleable metallic powder by reduction with charcoal. From the solution ammonium sulphide threw down a deep brown sulphide, soluble in acids. From these reactions the presence of a new metal was inferred. Dr. Krüss is engaged with a further investigation of this substance as well as with a re-determination of the atomic weights of nickel and cobalt.

We lay before our readers the following portion of a letter which has been kindly forwarded us by Professor Krüss:—

"I have in fact succeeded in splitting up nickel and cobalt each into two parts, and both these metals have one component in common. In concert with my colleague, I sent a brief notice on this subject to the *Berichte*, which will appear in Berlin on Monday next (21st inst.). The matter communicated in this short memoir has been intentionally kept very scanty, and I gave as little room as possible to speculation for fear of being led to assertions which I might perhaps soon have to withdraw. Meantime, I have fully confirmed our first observations, and we have now about ten different methods by which we can resolve these bodies, hitherto regarded as elementary, each into two parts. We shall soon give a full report on our results, but in the meantime I may inform you, as a curious fact, that we have succeeded in obtaining *green* so-called nickel salts from *red* cobalt salts and the *colourless* salts of the substance which accompanies both metals, and further, in transforming some green nickel salts into red cobalt salts and other components. This may perhaps sound alchemical, but it cannot be denied. As for the spectra of the three components of cobalt and nickel, we have not yet, with the ordinary experimental arrangements, observed any characteristic lines. This is doubtless the reason why hitherto no spectral lines have been found common to pure cobalt and nickel.

VICTOR MEYER'S VAPOUR DENSITY METHOD MODIFIED FOR USE UNDER DIMINISHED PRESSURE.

By THEO. W. RICHARDS.

The many researches which have recently been published upon the vapour densities of substances which are easily decomposed, suggested to the writer the great desirability of some good method of determination which could be used under reduced pressure. The only methods as yet used for this purpose are: first, the method of Hofmann, which is open to the great objection of the necessity of measuring the vapour over mercury, which makes it impossible to use a temperature much above 200° C.; and second, the application of Dumas's method, used by Friedel and Crafts* for the determination of the density of iron chloride, which is open to all the objections to Dumas's method, and is at the same time complicated in execution.

For the application of Victor Meyer's method to reduced pressures, it is only necessary that we have in the whole interior of our apparatus an artificial atmosphere, of constant low tension, which not only pervades the vapour density bulb itself, but also is in connection with both surfaces of the water over which the displaced air is collected.

The apparatus used may be divided into three parts: first, the vapour density bulb itself, which is exactly like that described by Grünwald and V. Meyer†; second, the apparatus for receiving the displaced air; and third, the arrangement to secure a constant reduced pressure.

The apparatus for receiving the replaced air is an upright U-tube, having an internal diameter of about 1·3 c.m. and a height of 50 c.m., the end of each arm being drawn out to allow of rubber connections. A small tube is melted into each side near the bend, and through one of these the displaced air from the Meyer apparatus enters and replaces the water, which rises in the other arm, and may be drawn out or let in through the other side tube by means of an arrangement of tubes, nipper taps, and a flask, to preserve constant level.

As before said, in one arm of the U-tube the air is collected as it comes from the Meyer apparatus, and from this arm it is driven out at the top after the vapourisation is ended, and measured in an ordinary eudiometer at the atmospheric pressure and temperature. The other arm of the U-tube is connected with the constant pressure arrangement, which must now be described.

In seeking after material for such an apparatus mercury was of course first decided upon, and an arrangement somewhat like Mariotte's flask was set up, but it was found that with heavy mercury columns it was impossible to secure constant pressure. If was evident that if mercury was to be used it must be in a small column. Accordingly, the following apparatus, consisting of two parts, was arranged:—

The tube leading from the U-tube is led through the stopper of a wide barometer tube, 17 m.m. in diameter, which we may call the regulator, and ends at a height of 520 m.m. above the free surface of mercury, in which the

---

* *Comptes Rendus*, cvii., 301.

† *Berichte d. Deutsch. Chem. Ges.*, xxi. (1888), 683.

lower end of the latter is immersed. Another tube, just penetrating this same stopper, is led to the depth of 200 m.m. in mercury contained in a closed vessel, which is connected with the water-pump. Let us now suppose that the pump is set in motion, and that the barometer stands at 740 m.m., the available pressure of the pump being then about 730 m.m. Mercury of course then rises in the regulator to the height of 730 − 200 m.m. = 530 m.m., or 10 m.m. above the end of the tube connected with the first part of the apparatus. It is evident that this extra 10 m.m. *can have no effect on the tension of the air in the U-tube* and Meyer bulb; this tension is influenced only by the distance between the end of the tube and the free surface of the mercury in the dish below. As this distance is constant the tension must be constant, no matter how the pump varies in action or what changes there may be in the atmospheric pressure, provided always that the mercury does not fall below the end of the tube above mentioned. Of course any addition of volume in the Meyer bulb merely causes air to quietly bubble up through the small layer of mercury, and a barometer tube interposed between the regulator and the U-tube showed that the compensation was as nearly perfect as could be desired. Of course, by altering the lengths of the tubes and the heights of the mercury columns any desired pressure may be secured; but it is always better to have the column in the regulator stand at a height of about 10 m.m. above the end of the small tube inside.

The exact manner of working the apparatus cannot possibly be explained without an illustration, which is now being made, and which will appear later in a more complete description of the whole apparatus.

Two determinations have already been made by this method, and the results show that the apparatus is thoroughly practical. No difficulty was found in making the joints tight, and the pressure remained completely constant for an indefinite length of time. The time occupied by an experiment is not much longer than that occupied by an ordinary Meyer determination, as the pressure very soon reaches constancy.

The substance used was pure toluol, boiling at 110°; it was weighed out in a small sealed tube, the end of which was broken off just before introduction into the apparatus. The temperature used for vapourisation was 100° C. (steam), and the tension used in each case was 220 m.m.—the difference between the atmospheric pressure and the height of the mercury in the barometer connected with the apparatus. The vapourisation was very rapid and the conclusion of the experiment perfectly definite. Of course, in the calculation allowance was made for the tension of aqueous vapour, and through the whole course of the experiments all possible precautions were taken to procure trustworthy results. Below are the data of the two experiments which have thus far been made:—

I.

Weight of toluol taken	0·0247 grm.
Vol. of air at 738 m.m. and 12° C..	6·8 c.c.
Tension	220 m.m.
Temperature of bath	100°
Result = vapour density of toluol ..	3·06

II.

Weight of toluol taken	0·0338 grm.
Vol. of air at 738 m.m. and 12° C..	9·05 c.c.
Tension	220 m.m.
Temperature of bath	100°
Result = vapour density of toluol ..	3·15

The volume of the air while yet in the apparatus under diminished pressure was about 25 c.c. to 35 c.c. The two results average 3·10, the theoretical density of toluol with reference to air being 3·18. The results, then, are as good as those by Meyer's method at ordinary atmospheric pressure.

It is possible that the same end might be accomplished by a much simpler piece of apparatus, substituting for the two mercury pressure regulators and the pump merely a large glass globe, which has been previously exhausted. If the globe were large enough the very small volume of vapour evolved in the Meyer bulb would have a scarcely perceptible effect on the tension of this confined artificial atmosphere, and any slight error might be easily corrected by careful application of the pump. Experiments with this simplified apparatus will be tried in the near future.

The object of the method was to determine with greater certainty the density of several substances which have recently been investigated in this laboratory; among others, iron and aluminium chlorides; but the method is a very general one, and will prove useful not only for those substances which decompose, but also because it will often do away with the necessity of using high temperature baths and consequent complications.

In conclusion the writer would express his heartiest thanks to his friends Messrs. W. P. Bradley and H. E. L. Horton, whose encouragement, advice, and assistance helped very materially in the carrying out of the idea; and also to Prof. Dr. Geh.-Req.-Rath Victor Meyer for his kindly permitting the use of the excellent advantages of his magnificent new laboratory.

Göttingen, Jan. 12, 1889.

NOTE ON THE DETERMINATION OF THE FREE CAUSTIC ALKALI IN SOAP.

By J. A. WILSON.

Soap, made by the so-called cold process, may contain both the caustic alkali and free oil or fat. When such soaps are dissolved in alcohol, to estimate the free alkali by titration with N/10 acid and phenolphthaleine, the free alkali immediately saponifies the free glycerides in the usual manner. Hence, a soap which by a qualitative test showed free caustic alkali, would not do so after treatment with spirit. The author therefore prefers to estimate the alkali in total by titration with normal acid and methyl orange; and in another portion, the alkali needed to neutralise the fatty acids isolated from the soap. Any silicate, carbonate, or borate in the soap would, of course, vitiate the results; but these can be accurately estimated, if necessary, by other means.

The Laboratory, Tottington Mill,
Jan. 16, 1889.

ACTION OF THE HALOGENS ON RUFIGALLOL DICHLORHEXHYDROXY-ANTHTRAQUINONE.

By C. S. S. WEBSTER and L. G. HUNT.

By the action of chlorine upon rufigallol in acetic acid solution of 60 per cent, it is converted into a substance crystallising in nodules composed of microscopic prisms of a brilliant red colour.

The anhydrous substance on analysis was found to contain 18·96 chlorine and (calculated for $C_{14}Cl_2H_6O_8$) 19·2 per cent chlorine.

That the reaction is one of simple substitution we conclude from its being unattended with any evidence of decomposition, as well as from the properties of the compound in question. The derivative is, therefore, dichlorhexhydroxy-anthraquinone.

By the action of bromine upon rufigallol in acetic acid solution at 80° C. we obtain a derivative crystallising from absolute alcohol in microscopic needles of a light red colour.

We intend shortly to publish an account of these researches in detail.

ON THE

VOLUMETRIC DETERMINATION OF SULPHUR BY MEANS OF BARIC CHLORIDE.

By C. and J. J. BERINGER.

The titration of sulphates by means of baric chloride in the presence of hydrochloric acid has the well-known disadvantage of requiring an excess of baric chloride, leaving, towards the end, a solution which is precipitated equally by baric chloride and sulphuric acid. In addition, the interference of nitric acid and nitrates excludes the use of nitre for the oxidation of the sulphides—and fusion with this reagent is in many cases the quickest and most convenient method of bringing the sulphur into solution.

The effect of nitric and hydrochloric acids on the titration is shown by the following experiments. A standard solution of barium chloride (100 c.c. = 1 grm. of sulphur) was used and tested against a solution of sulphuric acid of equivalent strength. The assay solution had a volume of 500 c.c. in each experiment, and was titrated boiling. The finishing point was determined by withdrawing portions of 5 c.c. and testing after filtration with dilute sulphuric acid. The first indication of a precipitate was taken as the finishing-point.* 20 c.c. of the sulphuric acid were used with varying quantities of the acids, and the results on titrating were:—

	C.c.	C.c.	C.c.	C.c.
Hydrochloric acid present .	0	1	2	5
Baric chloride required ..	20·0	20·0	19·7	12·5
Nitric acid present	0	1	2	5
Baric chloride required ..	20·0	19·5	18·0	10·0

In gravimetric work this interference may be overcome by using an excess of baric chloride, but it is evident that for volumetric work the removal of such a disturbing agent will be an advantage. With this object we tried a series of experiments.

Effect of Acetic and Citric Acids and of Sodium Acetate.—Experiments similar to the last, to compare the effect of these with the other acids, were made, using 20 c.c. of the sulphuric acid under the same conditions as before. The results were:—

Acetic acid present .	0 c.c.	5 c.c.	50 c.c.	100 c.c.
Baric chloride reqrd.	20·0 c.c.	20·0 c.c.	20·0 c.c.	20·0 c.c.

Citric acid present	0 grm.	1 grm.	5 grms.
Baric chloride required ..	20·0 c.c.	20·0 c.c.	20·0 c.c.

These results being sufficiently satisfactory, and acetic acid being more convenient for use, we tried the effect of varying quantities of sodic acetate in the presence of 5 c.c. of acetic acid.

Sodium acetate added	0 grm.	1 grm.	10 grms.	50 grms.
Barium chloride reqrd.	20·0 c.c.	20·0 c.c.	20·0 c.c.	20·0 c.c.

It next remained to determine the quantity of baric chloride solution required in 500 c.c. of water, and in the presence of these substances to give an indication when 5 c.c. were withdrawn and tested with sulphuric acid. The results were:—

Conditions of the assay solution.	Baric chloride required.
Water only	0·05 c.c.
With 10 grms. of sodium acetate and 5 c.c. of acetic acid	0·05
The same with 5 grms. of nitre ..	0·10
The same with 5 grms. of sodium chloride	0·10

To determine whether the same finishing point would be obtained on testing the filtered portions with baric chloride as is got on testing with sulphuric acid, a titration was made with 20 c.c. of the sulphuric acid, 5 c.c. of acetic acid, and 10 grms. of sodium acetate, and the usual volume of 500 c.c. In testing, two portions of 2 c.c. each were filtered into two test-tubes after each addition of the standard. One series was tested with sulphuric acid and the other with dilute baric chloride. The finishing point in each series was the same. We, however, in finishing, adopt the sulphuric acid test, since it is better to look for the appearance of a precipitate in the test-tube than to watch for its disappearance, except when the quantity of standard solution required is not approximately known, in which case we add barium chloride in testing, so as to get, by the appearance of the precipitate an indication of an approach to the finish.

Effect of Varying Sulphur.—The conditions in these and the following experiments were, except it is otherwise stated, 500 "c.c." bulk with 10 c.c. of acetic acid and 10 grms. of sodic acetate.

	C.c.	C.c.	C.c.	C.c.	C.c.
Sulphuric acid added ..	5	10	20	50	100
Baric chloride required ..	5·0	10·0	20·0	50·0	100·0

Effect of Varying Temperature.—With 5 c.c. of the sulphuric acid titrated at 15° C., 5 c.c. of baric chloride were required; but with larger quantities the results when titrated cold were altogether unsatisfactory.

Effect of Foreign Salts.—In these experiments 20 c.c. of the sulphuric acid were used with varying amonnts of the salt whose effect we desired to determine. The other conditions of the titration were as before.

Sodic chloride added ..	0 grm.	5 grms.	10 grms.	
Baric chloride required ..	20·0 c.c.	20·0 c.c.	19·7 c.c.	
Ammonic chloride added	0 grm.	5 grms.	10 grms.	
Baric chloride required ..	20·0 c.c.	20·0 c.c.	19·5 c.c.	
Calcic chloride added	0 grm.	1 grm.	2 grms.	5 grms.
Baric chloride reqrd.	20 0 c.c.	20·0 c.c.	19·2 c.c.	19·0 c.c.
Zinc chloride added	0 grm.	1 grm.	3 grms.	5 grms.
Baric chloride reqrd.	20·0 c.c.	20·0 c.c.	20 0 c.c.	20·0 c.c.
Ferrous chloride add.	0 grm.	1 grm.	3 grms.	5 grms.
Baric chloride reqrd.	20·0 c.c.	19·7 c.c.	19·5 c.c.	19·0 c.c.
Ferric chloride added	0 grm.	1 grm.	3 grms.	5 grms.
Baric chloride reqrd.	20·0 c.c.	20·0 c.c.	20·0 c.c.	20·0 c.c.
Copper chloride add.	0 grm.	1 grm.	3 grms.	5 grms.
Baric chloride reqrd.	20·0 c.c.	20·0 c.c.	20·0 c.c.	20·0 c.c.
Potassic nitrate add.	0 grm.	1 grm.	5 grms.	10 grms.
Baric chloride reqrd.	20·0 c.c.	20.0 c.c.	20·0 c.c.	19·0 c.c.
Potassic nitrite added ..	0 grm.	1 grm.	5 grms.	
Baric chloride required ..	20·0 c.c.	20·0 c.c.	20·0 c.c.	
Sodic phosphate added	0 grm.	1 grm.		
Baric chloride required	20·0 c.c.	22·5 c.c.		
Sodic arsenate added	0 grm.	1 grm.		
Baric chloride required	20·0 c.c.	20·5 c.c.		

Phosphates and arsenates interfere counting as sulphur, but can be thrown out by the addition of ferric chloride to the assay solution before boiling. The ferric precipitate need not be removed before titration; its presence will be an advantage rather than otherwise, as it helps to give a clearer filtrate for testing.

The non-interference of as much as 5 grms. of nitre allows of the use of this reagent for oxidising the ore by fusion.

Mode of Working.—Those substances, such as pyrites, the sulphur of which can be got into solution as sulphate by treatment with nitric acid without any separation of globules of sulphur, are treated with this acid, evaporated, taken up with hydrochloric acid, and again evaporated to a small bulk, diluted with water, and transferred to a large

---

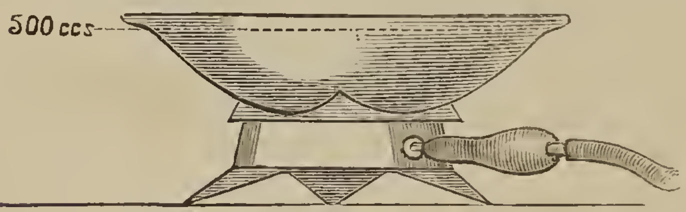
* The quantity of sulphur thus withdrawn did not in any case amount to 0·5 m.grm

evaporating dish. Ten grms. of sodic acetate and 5 c.c. of acetic acid are then added, and the solution diluted to half a litre and boiled.

With grey copper and similar substances which are not easily oxidised with nitric acid, 1 grm. of the substance is ground in a small mortar with 5 grms. of nitre and transposed to a porcelain or platinum dish. The mixture is fused for a quarter of an hour at a low temperature over a bunsen, and when cold placed in the large evaporating dish. Extract with hot water, add sodic acetate and acetic acid, and dilute to half a litre. The dish used for fusion should be removed, but there is no necessity for filtering.

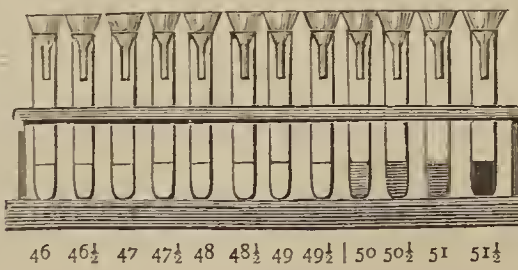
With insoluble sulphates such as barytes, 1 or 2 grms. of the substance is fused with 5 grms. of fusion mixture, the melt extracted with water, filtered into the dish, acidulated with acetic acid, and diluted to half a litre.

The solution before titration must contain no free mineral acid, but 5 or 10 c.c. of acetic acid should be present. It must contain 10 grms. of sodium acetate or sufficient to convert any free mineral acid into its corresponding sodic salt, and if chlorides, nitrates, or sulphates of the metals are present, sufficient to decompose them. If a precipitation occurs, as is the case with ferric salts, &c., the solution is titrated with the precipitate in it. Ferrous salts may with advantage be previously oxidised.



Porcelain dish and round burner.

In titrating the solution is kept steadily boiling by means of a round burner; an ordinary Bunsen would cause bumping. The baric chloride solution is run in, in quantity known to be insufficient, and 3 or 4 c.c. of the assay withdrawn with a pipette and filtered through a fine filter-paper into a test-tube. Add a drop or two of baric chloride, and judge from the appearance of the precipitate how much more of the standard solution may be safely run in. Towards the finish add half a c.c. at a time to the assay, and filter off a portion after each addition. It is best to have the test-tubes arranged in order on a stand and to continue the addition of the standard until half a dozen portions for testing have been drawn off. These are tested with dilute sulphuric acid, and that tube which shows the first appearance of a precipitate marks the point at which the titration is complete. With a little practice one can judge whether a quarter c.c. should be deducted from this reading. There is no chance of accepting a false finishing point if the titration is overdone and read back.[*]



Finishing point, 49¾.

The following are a few examples of determinations made in this way, mainly on crystallised minerals :—

	Sulphur found.	Theoretical.
Pyrites, dissolved in acids	52·9%	53·33%
Chalcopyrite, fused with nitre ..	34·7	34·91
Chalcocite, ,, ,, ..	20·6	20·17
Mispickel, dissolved in acids ..	18·7	19·63
Barytes fused with fusion mixture,	13·6	13·73

The following are of crystallised salts :—

Copper sulphate	12·8%	12·83%
Magnesium sulphate	13·0	13·01
Zinc sulphate	11·2	11·15
Ferrous sulphate	11·6	11·51

The following are some determinations on burnt ore, comparing results got by this method with gravimetric work :—

Percentage of Sulphur.

Volumetric.	Gravimetric.
2·52	2·45
5·98	5·84
3·62	3·53
4·40	4·43

In these for the volumetric determination 5 grms. of the ore were fused with 5 grms. of nitre.

These experiments were carried out in the first instance with the objects of saving labour and getting at a satisfactory method of treating mineral sulphides. The separation of globules of sulphur during solution, the interference of nitric acid and nitrates, and the nicely drawn conditions required for getting a pure precipitate of baric sulphate have made the gravimetric determination troublesome. With this process the determination of sulphur in any sulphide may be made in an hour, and the conditions of the assay allow of considerable variation without affecting the results. It yields not merely proportional but theoretical results, since the standard of the baric chloride solution may be calculated from the quantity of the crystallised salt weighed up.

In conclusion, we have to thank Messrs. Seth Clarke and Bailey, and more especially Mr. J. H. Grant, for their care in performing the greater number of the experiments.

Camborne, January 11, 1889.

UNIFORM METHODS FOR THE ANALYSIS OF FERTILISERS, CATTLE FOODS, DAIRY PRODUCTS, SUGAR, AND FERMENTED LIQUORS.[*]

(Continued from p. 34).

The discussion of the Report of the Committee on Phosphoric Acid being in order, it was directed that the method for the coming year provide for the use of Schleicher and Schüll No. 589 filters, 9 c.m. in diameter, in the determination of soluble phosphoric acid, and that the preliminary washing be by decantation from a beaker, using small quantities of water, as described by Messrs. Gascoyne and Voorhees, who considered the use of the pestle only necessary with the very high grade phosphates in New England.

After some argument the use of a pump in determining soluble phosphoric acid was left to the judgment of the analyst.

Dr. Gascoyne then called attention to the method of Isbert and Stutzer for the estimation of phosphoric acid, and gave the following determinations comparing it with the official method. The method was carefully followed,

---

[*] If the first test shows the assay to be already overdone a measured portion of a standard solution of a sulphate may be added (and subsequently deducted) and the titration continued.

[*] Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

except that half normal sulphuric acid and caustic soda were used, and cochineal as the indicator.

	Association method.	Isbert and Stutzer's method.
Acid phosphate	16·10	16·03
South Carolina phosphate	26·43	26·58
Tankage	11·16	11·19
Steamed bone..	30·15	30·07
Ammoniated superphosphate ..	10·72	10·68
Acid phosphate, total	15·77	15·74
Acid phosphate, soluble	9·63	9·57
Acid phosphate, insoluble	2·26	2·20

He also called attention to the time required for the complete precipitation of the molybdic acid and magnesia precipitates.

The following table is the result of some experiments on this subject. The phosphate was dissolved in the usual manner, filtered, ammonia added in slight excess, acidified with nitric acid, heated to about 80° or 85° C., the molybdic acid solution added, and the solution well stirred. In the first set of experiments the molybdic precipitate was allowed to stand for five minutes, filtered magnesia mixture added, and allowed to stand two hours. In the second set the molybdic precipitate was filtered in ten minutes. In the third set the molybdic precipitate was allowed to stand one hour, and the magnesia precipitate for fifteen minutes. In the fourth set the magnesia precipitate was allowed to stand thirty minutes. In the fifth set the molybdic acid precipitate stood five minutes, and the magnesia precipitate fifteen to twenty minutes.

(Acid phosphate containing 15·82 by the official method).

Molybdic precipitate five minutes, magnesia precipitate two hours	15·78
Molybdic precipitate ten minutes, magnesia precipitate two hours	15·80
Molybdic precipitate one hour, magnesia precipitate fifteen minutes	15·80
Molybdic precipitate one hour, magnesia precipitate thirty minutes	15·82
Molybdic precipitate five minutes, magnesia precipitate fifteen to twenty minutes..	15·79

	Official method.	Molybdic precipitate five minutes, magnesia precipitate 15 to 20 minutes.
Acid phosphate, total	16·10	16·07
,, soluble . ..	10·22	10·24
,, insoluble ..	2·12	2·08
Ground bone	22·14	22·17
Tankage	9·93	9·90

The report was then adopted and the committee directed to insert the modifications in the method.

REFRACTIVE INDEX OF BUTTER FAT.

By H. W. WILEY.

Heretofore very little attention has been given to the refractive index of butter fat in studying the properties of that substance. Having had occasion this year to examine the refractive index of various fats and oils used in the adulteration thereof, I extended the examination to twelve samples of butter fat from butter bought in the open market. The object of the investigation was twofold: First, to determine the mean refractive index; and second, the rate of variation of the refractive index for rise or fall of temperature. It is, of course, obvious that the refractive index of butter cannot be read after it solidifies, and therefore the minimum temperature at which the refractive index can be determined is not much below 30°, although the butter fat may be kept some time even at 25° without solidification. A very warm room where the temperature was reasonably constant was selected in the determination of the refractive index at the lower temperature. For the higher temperature the hot room of a Turkish-bath establishment was used. The temperatures at which the reading was made and the observed index of refraction, the rate of variation for each degree for each sample, and the mean rate of variation for each degree of the twelve samples are given in the following table:—

Number.	To.	Index.	Rate for each degree.
1	32 54·6	1·4535 1·4497	0·000169
2	31·9 56 2	1·4535 1·4495	0·000165
3	31·8 55·0	1·4530 1·4485	0·000194
4	30·8 54·8	1·4530 1·4495	0·000146
5	32·3 55·8	1·4530 1·4495	0·000153
6	33·2 55·4	1·4535 1·4888	0·000203
7	32·2 56·6	1·4540 1·4495	0·000186
8	32·4 54·8	1·4540 1·4505	0·000157
9	32·2 55·0	1·4536 1·4500	0·000158
10	31·8 56·2	1·4530 1·4490	0·000164
11	31·6 56·8	1·4540 1·4493	0·000186
12	31·8 56·2	1·4528 1·4485	0·000171

The reading of the instrument with distilled water at 18° = 1·3305. Having determined the rate of variation for butter fats in order to reduce the reading to any standard temperature, it is simply necessary to use the mean factor and add or subtract the result of the multiplication as the case may be. For instance, take the case of the first sample. The refractive index at 32° is 1·4535; suppose it is wished to reduce this to a temperature of 25°; the difference in temperature between 32° and 25° is 7°, the mean rate of variation for each degree is 0·000171, for 7° it would be 0·001197. Since the index of refraction would be higher at 25° than at 30° we add this number to the number obtained above. Then 1·4535 + 0·001197 = 1·4547 = index of refraction of that sample at 25°. The index of refraction of butter fat is distinctly lower than that of cotton-seed oil, lard oil, olive oil, and linseed oil. The rate of variation for change of temperature is also less for that of butter fat than the substances mentioned.

Dr. Farrington called attention to the fact that water was as suitable for washing the yellow molybdate precipitate as ammonic nitrate.

Isbert and Stützer had observed this, and Dr. Gascoyne said that his experience confirmed it.

On motion, the committee on phosphoric acid was directed to insert this as an alternative in the methods.

Dr. Crampton, in the absence of the chairman, Professor Rising, presented the report of the committee on fermented liquors, as contained in the following letter:—

OFFICE OF STATE ANALYST,
Berkeley, July 18, 1888.

Dear Sir,—I hope you will not think that I have intentionally been wanting in respect to the other members of the committee on "fermented liquids" because I have till now failed to communicate with you. Early in the year we began some original work upon artificial colours, &c., and it was my expectation to have had some results that I could have submitted to you for your approval before the close of the year, but our work was interrupted by other analyses, and at the last moment the results were not sufficiently satisfactory to offer to the public. However, I believe we are on the right track, and that we may yet be able to recognise many of these artificial colours in a very short time. I had until a few weeks ago fully expected to have been present at the August meeting of the asssociation. I had planned to have spent a few weeks in your laboratory before the annual meeting, and then and there we could have made up our report. This was my plan, but at the last moment I find myself unable to carry it out, and now am unable to make any suggestion. If the association would grant us another year I would promise to be on hand, and I think I could also promise to spend some time in your laboratory, when we could perfect our report. However, if you can make a report I would not in the least hamper you, but wish you to feel at liberty to do so. I have written Professor Wiley and Mr. Clifford Richardson my views, which are intended as an explanation to the association for the failure on my part to do my duty in the matter.

We have proved beyond all question, as I think, the presence of boracic acid in many unadulterated California wines. In addition to the test with turmeric paper we have obtained the flame-test so decided that there can be no doubt. I have just received a new spectroscope, and I shall hope by its aid to settle this point beyond all question. Our method of work is as follows:—50 c.c. to 100 c.c. of wine are evaporated in a platinum dish, ignited, and burned to ash. Part of this ash is transferred to a platinum spoon; such a one as is used for blowpipe work answers very well. A few drops of the strongest H_2SO_4 (I have used a 96—98 per cent acid), then alcohol is added, and then lighted and immediately blown out, and re-lighted and again extinguished. The first flash will show the acid very distinctly if it is present.

The adulterations that we have had to look for have been easily detected. The wine in all cases was taken direct from the wine-maker. It was taken upon its sale to the wine-dealer, who had required a certificate of purity before accepting it. Naturally, only pure wine or wine that was believed to be pure would be offered. The only kind of adulteration believed to have been practised by wine-makers is, first, the use of antiseptics, salicylic acid, sulphurous acid, and boracic acid, colouring matters, alkalies (K_2CO_3) to neutralise excess of acid, &c. The watering of wine (stretching) belongs to the dealer's art, &c. We have not had occasion to investigate this branch of the subject. We examine for plaster, bases added, antiseptics, artificial colours, copper, lead, zinc salts, alcohol, free acid (volatile and non-volatile), solid residue, ash (soluble and insoluble), alkalinity of the soluble portions, sugar, glucose, glycerin, &c., tannic acid, cream of tartar, &c. Some samples of eastern wine were clearly "manufactured."

I have been obliged to go into the country on account of my family, and am now in the midst of the Napa Valley wine region and am making the acquaintance of the wine men here, and hope to gain their confidence so that they will consult me in regard to their troubles, &c. There is a strong sentiment among the wine-makers against the use of any agent that could be called an adulterant, and I find them very anxious to maintain the reputation they already have for purity. The wine-dealer is the man we have to fear; he is ready to do almost anything and to get ahead of the chemist if he can. The Viticultural Commission has sent a special agent to Paris. They have instructed him to go about and get as many of the practices of wine-makers and dealers as possible. I find great difficulty in getting a set of samples of wine-colouring substances. They are only sold in original packages, &c., under various names. I shall hope through our special agent to get a pretty complete set, and then if I can identify them and give them their true scientific names, we will have a surer base to stand upon.

I regret that I cannot attend the meeting this year. If the convention will continue the committee I think we can get to work very early the coming year, and present to the next convention a valuable contribution to the subject. May I ask you to present my apology to Professor Fellows. I do not know his address, nor can I get it till I return to Berkeley.—Very truly yours,

W. B. Rising.

Report of the Committee on Potash.

The committee on the determination of potash would respectfully submit: That since the last meeting of this association little has appeared in chemical literature relating to the determination of potash, so far as we know, which calls for notice here. The method of Lindo as modified by Gladding appears to give universal satisfaction. The New Jersey Agricultural Experiment Station (Report for 1887, p. 175) has determined the potash in forty-eight mixed fertilisers by this method, with certain slight modifications, and also by the Stohmann method. The greatest difference in the results in any case was 0·27 per cent; the average difference 0·08 per cent. In two-thirds of the determinations the differences were not over 0·10 per cent, and in only one case was the difference over 0·15 per cent. Stohmann's method gave on the average slightly higher results than the other. The modified Lindo-Gladding method used at the New Jersey station is as follows:—

"The solutions were made as described in the (official method), but previous to the addition of ammonium hydrate 1 c.c. of ammonium oxalate was added; the solution was then filled to the mark, thoroughly mixed, and filtered; an aliquot part was transferred to a porcelain dish of approximately 60 c.c. capacity. From this dish the material was not removed until the double salt of potassio-platinic chloride was ready to be brought upon the Gooch filter. After the determination was removed from the bath the precipitate was moistened with water, and then washed with 80 per cent alcohol till all traces of platinic chloride were removed. It was then washed with the saturated ammonium chloride solution recommended. It was found in this laboratory that better results could be secured by adding this solution to the precipitate in the porcelain dish, and washing by decantation until all salts other than the potassio-platinic chloride were removed. Since a relatively small amount only of the potassio-platinic chloride is necessary to saturate the ammonium chloride solution, these washings were all rejected, the time saved and the greater accuracy secured compensating for the loss of larger amounts of the solution.

"After this washing has been completed, the double salt was transferred to the Gooch filter, washed with pure alcohol, dried, and weighed. The salt was then dissolved in hot water, and the final weight of the potassio-platinic chloride secured by difference."

The Report being open to discussion, Dr. Gascoyne called attention to the recent experiments of Lindo contained in Chemical News, lvi., 103, approving the Association's methods.

Professor Scovell said he had some difficulties, and Mr. Richardson spoke of the presence at times, in the case of superphosphates, of sulphate of lime in the final double salt

Mr. Voorhees then described the modification practised at the New Jersey Agricultural Experiment Station, as given in the Eighth Annual Report, p. 175, and said that they found the Lindo-Gladding method most desirable when a little oxalate of ammonia was used to remove lime, and the evaporation was not carried too low, and referred to the large series of results which he had published in the Report referred to.

If the evaporation were carried too far, solids might form which would be insoluble in alcohol, in which case a small quantity of water should first be added, and then the strong alcohol. The greatest error in inexperienced hands lies in this point.

Mr. Chazal said he had also found error in not evaporating low enough.

Mr. Voorhees called attention to the fact that the presence of ammonia in the air of the laboratory produced no effect with the Lindo method, as the ammonia double salt would afterwards be dissolved out by the wash, and then moved the addition to the Association method of the use of oxalate with the ammonia and evaporation to dryness with HCl, taking up with water, repeated evaporation, and taking up with alcohol.

Report of the Committee on Nitrogen.

Your Committee on Nitrogen have the honour to present the following Report of the work which has been accomplished during the year:—

Abstract of Articles which have Appeared during the Year on the Determination of Nitrogen in Fertilisers.

(Compiled, by request, by Dr. E. H. Jenkins, Connecticut Agricultural Experiment Station, and A. M. Peter, Kentucky Agricultural Experiment Station.)

The Kjeldahl Method.

Lenz (*Fres. Zeitschr. Analyt. Chem.*, xxvi., p. 590) has tested the effects of omitting oxidation with potassium permanganate after boiling the substance to be analysed with sulphuric acid. He used a flask of 100 c.c. capacity, 0·2 to 0·7 grm. of substance, 10 c.c. oil of vitriol, and 5 grms. metallic mercury. The boiling was continued until the substance was clear and colourless. In one series of determinations no permanganate was added; in another it was added as recommended by Kjeldahl. In all cases higher results were obtained when permanganate was used; generally the differences were small, but in some cases amounted to 0·33 per cent.

Ulsch (*Zeitschr. für das Gesammte Brauwesen*, 1887, p. 3; *Fres. Zeitschr.*, xxvii., 73) calls attention to the fact that if platinum chloride is added to hasten oxidation when the substance is boiled with oil of vitriol, as recommended by him in a previous paper, an excess must be avoided. Too much platinum chloride retards, instead of hastening oxidation, and if the boiling is continued too long, platinum may destroy ammonia by "catalytic action," and so cause loss of nitrogen. He also recommends the use of iron sulphate to destroy mercuro-ammonium compounds formed when mercury is used to hasten oxidation. It has the advantage over potassium sulphide that it can be added to the acid before neutralising it, thus avoiding danger of losing nitrogen.

Dafert (*Landwirtschaft. Versuchs-St.*, xxxiv., 311; also *Fres. Zeitschr. für Analyt. Chem.*, xxvii., 222) has studied the chemical reactions involved in the method, and the question how generally applicable the original method of Kjeldahl is, and whether it can be so modified as to make it available for determining nitrogen in all classes of compounds. His conclusions are briefly as follows:—

(1). Sulphuric acid withdraws from the nitrogenous organic matter the elements of water and of ammonia, and from them forms ammonia.

(2). The sulphurous acid which is evolved regularly reduces the nitrogenous compounds; but this effect is insignificant compared with that mentioned above.

(3). The addition of organic compounds (sugar, &c.) to nitrogeneous matters delays the formation of ammonia, except in cases where it changes a nitrogenous substance, which is volatile or easily decomposed, into one which is less easily attacked by sulphuric acid.

(4). Potassium permanganate, when brought into the hot mixture, destroys the organic compounds still remaining. A part or all of the nitrogen in such compounds forms ammonia. In quantitative work, when the previous digestion with acid has been carried far enough, and the permanganate is added carefully, all the nitrogen is thus converted into ammonia.

(5). His study of the effect of adding metals or metallic oxides leads to the conclusion that the addition of a metal to a substance which is easily oxidised, or is easily decomposed by sulphuric acid, may cause loss of nitrogen by a too rapid oxidation during the formation of ammonia, and in this way the process is shortened by sacrificing accuracy. Only in special cases, where the substance is very stable, is it safe to use platinum chloride to hasten oxidation, as recommended by Ulsch.

(6). He finds that nitrogen can be accurately determined by the original Kjeldahl method in all amides and ammonium bases, pyridin and chinolin bodies, alkaloids, bitter principles, albumenoids, and allied substances; also, most likely, in the indol derivatives.

In the following substances nitrogen can not be determined satisfactorily by Kjeldahl's original method.

All nitro-, nitroso-, azo-, diazo-, hydrazo-, and amidoazo- bodies, compounds of nitric and nitrous acids, the hydrazines, and probably cyan-compounds.

For the determination of nitrogen in these classes of compounds probably no general rule can be given, but the peculiarities of each group must be studied as Jodlbauer has studied the special modifications required by nitrates.

E. Waller and H. C. Bowen (*Jour. Analy. Chem.*, xi., 293) give a sketch of the history of the method, and mention modifications which they have adopted, containing nothing essentially new, except that they evaporate off most of the sulphuric acid used in the oxidation of the substance, and heat some time after adding the permanganate, an operation which seems hazardous. To the paper is appended a list of the papers which have been published on the Kjeldahl method.

The New Jersey Agricultural Experiment Station (*Report N. J. Expt. Sta.*, 1887, p. 169) has compared, in the case of nineteen fertilisers, the results obtained by the modification of Kjeldahl's method as described by Scovell with those obtained by the absolute method as described in the "Report of the Connecticut Experiment Station" for 1879. The results showed very satisfactory agreement. The largest difference was 0·14 per cent; the average difference, 0·06 per cent; in eight cases the absolute method gave on the average 0·05 per cent more nitrogen; in eleven cases the modified Kjeldahl method gave on the average 0·06 per cent more nitrogen.

E. H. Farrington (*Report Conn. Expt. Sta.*, 1887, p. 126) reports comparative determinations of nitrogen in thirty-four samples of mixed fertilisers containing nitrates by the Jodlbauer-Kjeldahl method and the absolute method as described in the reports of the same station for 1878 and 1879. His conclusions are as follows:—

"An inspection of these results shows that in 68 per cent of the cases the difference between the two methods was not over 0·1 per cent, and in 88 per cent of the cases not over 0·15 per cent. The greatest difference was 0·21 per cent."

"The plus differences are 14 in number, the minus differences 20. The average of the former is 0·066, of the latter 0·085. It is evident, then, that the two methods are about equally accurate."

Otto Shönherr (*Chem. Zeit.*, xii., 217) applies the azotometer to the Kjeldahl determination. The digestion flasks are graduated by a mark on the neck to a convenient volume (150 c.c.), and after the oxidation has been effected in the usual way the contents of the flask are diluted, neutralised approximately, made up to the mark, and mixed, and an aliquot part (50 c.c.) decomposed in the azotometer with 50 c.c. hypobromite solution. Results accurate.

R. Meldola and E. R. Moritz (*Jour. Soc. Chem. Ind.*, vii., 63) purify sulphuric acid from ammonium sulphate by adding about 0·05 grm. potassium nitrate per 10 c.c. to the acid and heating about two hours.

(To be continued).

Experiments on the Action of Various Phosphates in the Cultivation of Cereals.—J. Raulin.—The author concludes that, at least under the conditions of his experiments, insoluble native phosphates may be utilised, like superphosphates and precipitated phosphates, provided they are employed in the first year in a proportion five to six times larger.—*Comptes Rendus*, cviii., No. 1.

OBITUARY.

PROFESSOR BRAZIER.

Mr. James S. Brazier, F.C.S., Emeritus-Professor of Chemistry in Aberdeen University, died at his residence, 17, Bon Accord Square, on the afternoon of the 14th inst., heart disease being the immediate cause of death. It was the rapid development of this ailment that led to his retirement from office last year, and since that time he has more or loss suffered. In June last he had, under the care of his medical adviser, Dr. Angus Frazer (one of his old students and assistants), to be removed from Alford, whither he had gone for change of air, and he has not since been able to leave the house. His death, therefore, which occurred at five o'clock on Monday, January 14, was not unexpected, and the end came peacefully.

Mr. Brazier's connection with the Medical School of Aberdeen commenced thirty-six years ago, when, in 1852, he was appointed assistant and substitute to Dr. Clark, Professor of Chemistry in Marischal College. He was a native of Rye, Sussex, was educated in King William's College, Isle of Man, and, in 1847, entered the laboratory of the Royal College of Chemistry, London, where he soon attracted the special attention of Professor Hofmann by the perseverance and earnestness with which he prosecuted his studies. His remarkable skill and dexterity in the performance of experiments rapidly carried him through the Course, and in time he rose to be Senior Assistant in the College. After this he accepted an offer made to him by Professor Andrews to become Chemical Assistant in the laboratory of Queen's College at Belfast, from which town he came to Aberdeen, as has been said, in 1852, succeeding Dr. John Smith, who had been appointed to the Chair of Chemistry in Sydney, for which appointment Mr. Brazier too had been an applicant. He continued as Dr. Clark's substitute till the union of the Colleges in 1860, when that gentleman retired. Professor Fyfe, of King's College, then succeeded to the Professorship in the University, but, as that gentleman never lectured, Mr. Brazier discharged the duties of the chair. On Dr. Fyfe's death in 1862 Mr. Brazier received the well-merited promotion, and he resigned the Fordyce Lectureship, which he had held since 1853.

The promise of professional distinction given by Mr. Brazier in his earlier days was amply fulfilled. Though not a medical man he was a brilliant chemist. As a lecturer it has been said of him that perhaps he was not quite so clear as a beginner would like, sometimes overrating the power of his students to follow him into the intricacies. But as an experimenter he could hardly have been surpassed—one authority saying that in this department "he was so felicitous as to be unrivalled," and another that the "class of practical chemistry was one of the best Courses in the University." The Professor's method of letting each student do the testing required for himself is said to be a special feature of this school. It was well for the University in those days that it had a man of such talent on its staff. Whoever else may claim credit, none will deny, as Principal Geddes said of him when his retirement was announced, that he exerted a powerful influence on the development of the Medical School, whose high reputation it was ever his aim to maintain. With colleagues and students alike Mr. Brazier was a great favourite. In their weekly journal, *Alma Mater*, the latter, in an appreciative article, truly characterised him as "a popular professor," and at the close of last summer session, when the intelligence of his retirement was announced, the students presented him with an address of sympathy. The secret of his popularity with them was said by their organ to lie in this—

"That he is a gentleman in every sense of the word, and consequently he treats his students as gentlemen. There is not a word, not an act, of his which can be recalled, that clashes with this description, and, among the many pleasant memories we will carry with us through the world of Aberdeen and Aberdeen University, one of the most pleasing will certainly be the hearty ringing laugh of Professor Brazier."

Apart from his duties as a teacher, Mr. Brazier did other important work for the University. For many years he acted as Secretary to the Medical Faculty and for the examinations for the Degree, and he succeeded to the office of Dean on the retirement of Dr. Ogston. His promptitude, accuracy, and courtesy in all matters of business were on many occasions acknowledged by his colleagues. With affairs outside the University he did not take much concern, but for many years he held the office of gas analyst to the Corporation of Aberdeen, and was for a time Chairman of the Laundry Company. The labours of his Chair prevented him from contributing to the literature of his profession, but in his earlier days he published, as the result of his own researches, several papers, the most important of which were an "Analysis of the Mineral Constituents of the Flax Plant, and of the Soils on which the Plants had been Grown," an "Analysis of Plate Glass," and the results of a series of experiments on two organic acids.

Mr. Brazier, who was in his 63rd year, married his cousin, Miss Russell, by whom he is survived, as also by their family, which consists of three sons and two daughters. All the sons are in the Customs service of the Chinese Government, and the eldest is at home at present on furlough. Deceased was connected with St. Paul's Episcopal Church, of which he was a manager.—*Aberdeen Journal.*

NOTICES OF BOOKS.

Water Analysis: A Practical Treatise on the Examination of Potable Water. By J. Alfred Wanklyn and Ernest Theophron Chapman. Seventh Edition; by J. Alfred Wanklyn, M.R.C.S., Corresponding Member of the Royal Bavarian Academy of Sciences, &c. London: Trübner and Co.

The treatise before us is not a simple re-issue of the last edition, but contains some important additions. Part I., describing the "ammonia" process for water analysis, together with the ordinary accessory determinations required in the examination of drinking-waters, has undergone no alterations. We find an account of the "moist combustion process"—the method for the determination of the organic matter in water, which was patented by the author some time ago. We do not intend to re-open the discussion on this unusual step. But it might, we think, have been a convenience if an account had been given of the permanganate process as now practised and recommended by Dr. Tidy, so that the chemist might the more conveniently satisfy himself whether the strictures on the top of p. 54 are justified. It would be interesting, further, to see Mr. Wanklyn's estimate of the Girardin process, which turns not upon a determination of the oxygen required to burn up all the organic matter present, but of that remaining dissolved in the water and supposed to decrease progressively with the readily oxidisable impurities. This process, however, is more applicable to polluted streams and the effluents from the treatment of sewage than to drinking-waters, properly so-called.

Under the heading "Poisonous Metals" we are glad to see instructions for detecting traces of chromium. The soluble compounds of this metal are at once so formidable and so extensively used in the arts that their absence in the drinking-waters of the manufacturing districts ought to be fully ascertained. At the end of this chapter the author makes the very justifiable remark that London has, perhaps, had a most fortunate escape in the collapse of the great scheme for bringing water to it from the Lake District of Cumberland. We may here add "or from any metalliferous region."

It is an important question in how far the new water supply of Manchester, obtained from Thirlmere, is blameless in this important respect. We have never heard the present water supplied to the cotton metropolis, derived from the Woodhead Valley, impeached on this score. At the same time we know that in making the Woodhead railway-tunnel very important deposits of galena were found, which were practically ignored because their working would have interfered with the traffic on the line.

The author has a favourable opinion of filtration, on the large scale, as a means of dealing with organic pollutions.

The second part of the work treats of the specific gravity of natural waters and the precautions to be taken in its determination; of the carbonic acid present; of the residues, soluble and insoluble, left on the evaporation of the water; on hardness, the general quantitative analysis of residues, and on gases and vapours held in solution. Carbonic acid appears, in some waters at least, to form a considerable item. In the water supplied by the West Middlesex Company it amounts to no less than 11·9 grains per gallon. Mr. Wanklyn does not consider that the nitrates and nitrites furnish a trustworthy measure of the defilement of water. The question of phosphates is noticed in this edition. The author considers that "much nonsense has been talked about phosphates in drinking-water, and the fact has been overlooked that, except as infinitesimal traces, they cannot exist along with carbonate of lime in a clear water." This contention can scarcely be disputed. But in practice the analyst may meet with waters containing no carbonate of lime, and in such the proportion of phosphates may throw a useful light on the degree of animal pollution.

Under "Purification of Waters" Mr. Wanklyn discusses distillation, filtration, and precipitation by lime. His opinion on filtration, if properly conducted, is very favourable. The Clark process he decidedly recommends as removing not mere hardness, but to a considerable extent organic matter. Precipitation by means of alum is mentioned as having been used by the Chinese in the case of the river Peiho. In reality it has been used by that nation for time immemorial in all cases of foul—rather than hard—waters.

For the examination of sewage, industrial waters, and sewage-effluents no particular directions are given. This is also, perhaps, the proper place to remark that we find no reference to the use of the microscope in the examination of waters. Mr. Wanklyn's opinion would here, doubtless, have been of value.

The third part of the treatise contains examples of complete mineral analyses, notices of the water supply of London, and of other important towns, and an appendix, largely controversial, which the author thinks may serve "for the encouragement of all such as are suffering persecution for the sake of truth."

Mr. Wanklyn is by no means disposed to join in a crusade against the London Water Companies. He considers that even Thames water, as taken at places above the metropolis, may be, and actually is, purified by filtration to such an extent as to compare not unfavourably with municipal water supplies drawn from purer sources. On the other hand, he considers it a fortunate circumstance that London is not largely supplied with hard waters, rich in calcium and magnesium sulphates, like that furnished by the Kent Company. We believe that in districts supplied with such water the death-rate from diarrhœa has been found to be on the average higher than in parts using, *e.g.*, filtered Thames water.

We do not suppose that any chemist who practises water analysis will omit to add this new edition to his library.

CORRESPONDENCE.

BLOWPIPE ANALYSIS.

To the Editor of the Chemical News.

Sir,—In the review of Colonel Ross's book on the blowpipe it is stated that blowpipe analysis is still untaught at the Royal School of Mines; and then the remark is made "if there is here no mistake this is a fact much to be regretted."

May I be permitted to say that as long as I was connected with the School of Mines as much blowpipe work was done by students commencing chemistry as the limited time of the chemistry course for Associate Students allowed. We were not able to take the ordinary run of students through such a complete course of instruction in the blowpipe as that indicated in Colonel Ross's comprehensive book; but, in a good many cases, where a student had more than the usual short time at disposal, or was interested in mining or mineralogy, or likely to take up mining as a profession, much attention was given to blowpipe work; and, I believe, in some cases, even Colonel Ross's book was consulted and worked by.

I have not heard that instruction in the use of the blowpipe has been cut out of the chemical course since I left the school.—I am, &c.,

W. R. Hodgkinson.

Royal Artillery College, Woolwich.

DETECTION OF BLOOD.

To the Editor of the Chemical News.

Sir,—A sample of human blood, taken from the heart of a victim of "fuel gas" poisoning, still shows, after an interval of two years, all the characteristics noted at the time of the autopsy. The bottle in which it is contained has been frequently opened for purposes of examination.

Odour of decomposition has developed, of course, but the vivid redness, lack of coagula, and absorption bands peculiar to carbon-monoxide poisoning, still remain.—I am, &c.,

W. P. Mason.

Rensselaer Polytechnic Institute,
Troy, Jan. 9, 1889.

SOLUBILITY OF BRASS.

To the Editor of the Chemical News.

Sir,—In this month's number of the *Journal of the Chemical Society* is a paper by Mr. S. U. Pickering on "The Principles of Thermo-chemistry," in which (p. 17) he mentions incidentally, as an illustration of his argument on a thermo-chemical point, that brass dissolves in weak sulphuric acid.

Having been hitherto unaware that this was the case, and having been unable to find reference to it in such books as I have consulted, I should feel obliged if Mr. Pickering would say whether the statement is based on the result of his own observation, or has been recorded as a fact by others, and in the latter event indicate where it is to be found.

Bertram Blount.

Laboratory, Broadway, Westminster,
Jan. 22, 1889.

INDIAN INK.

To the Editor of the Chemical News.

Sir,—I find that a colour apparently identical to Indian ink can be produced by the action of sulphuric acid on camphor.

An excess of camphor should remain some twenty-four hours in strong sulphuric acid; it then results in a gelatinous mass of a slighly reddish colour. This, when heated, effervesces, gives off fumes of sulphurous acid, and turns intensely black. By evaporation the superfluous sulphuric acid and camphor (for there remains an excess of both, the weakened acid not acting on the camphor), can be driven off. The remainder when applied to paper as a paint appears, to my unartistic eye, to be Indian ink.

When dissolved in water it remains an indefinite time without precipitating. It appears to be dissolved, not held in suspension.—I am, &c.,

B. Piffard.

Hill House, Hemelhempsted,
Jan. 11, 1889.

SEXTON'S INORGANIC CHEMISTRY.

To the Editor of the Chemical News.

Sir,—A few days ago I received from the publishers (Blackie and Son), a copy of a new text-book on Inorganic Chemistry, by Professor A. Humboldt Sexton, F.R.S.E., F.I.C., F.C.S. Uhder the heading "Nitric Oxide" the following statements occur:—

"*Composition.*—The composition of the gas may be determined by exactly the same method as described for nitrous oxide."

"*Difference from* O *and* N_2O.—Leaves half its own volume of N on explosion with H."

On turning to "Nitrous Oxide" I find the methods given for the determination of its composition are:—

(1). "By burning Na in a measured quantity of the gas."

(2). "A quantity of the gas is measured in a eudiometer over mercury, excess of H is added, and an electric spark is passed."

It is, of course, easy enough to distinguish nitric oxide from oxygen, or nitrous oxide; but Professor Sexton, by saying how he would burn sodium in nitric oxide, or explode that gas with an excess of hydrogen, would, perhaps, confer a favour on others of your readers, besides

A Benighted Teacher.

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. cvii., No. 27, December 31, 1888.

Action of Sulphuretted Hydrogen upon Zinc Sulphate in a Neutral or Acid Solution.—H. Baubigny.—This paper will be inserted in full.

The Determination of Manganese by Means of Hydrogen Peroxide.—Ad. Carnot.—A correction to the author's last paper on this subject. The salt of manganese employed in his experiments is not the dioxide, but the saline compound, $5MnO_2,MnO$.

Preparation and Properties of Ferric Orthose.—P. Hautefeuille and A. Perrey. — This paper is rather of mineralogical than of chemical interest.

Preparation and Properties of Methyl Fluoride and of Isobutyl Fluoride.—H. Moissan and H. Meslans.—The reaction of silver fluoride upon the methyl, ethyl, propyl, and butyl fluoride easily yields fluoric ethers, which have not hitherto been studied. They possess a great stability, and are less readily saponified than the corresponding chlorine compounds. As far as the butyl fluoride they are gaseous; fluorine, when substituted for chlorine in the molecule, greatly lowers the boiling-point.

New Method for the Assay of Alcohol Founded on the Action of the Amines upon the Aldehyds.—Ch. Girard and X. Rocques.—If a mixture of aldehyd and of metaphenylene-diamine hydrochlorate are heated together in an alcoholic solution the liquid takes an orange-red colour, which increases on agitation, and a splendid green fluorescence is developed. On adding ammonia the colour turns to a yellow and the fluorescence disappears. The authors proceed as follows:—They dissolve in 200 c.c. of alcohol at 50 per cent, 3 grms. of metaphenylene-diamine hydrochlorate, and boil for half an hour with a reflux condenser. The liquid takes a light yellow tint. It is let cool for half an hour and agitated a little towards the end of this time. The colour of the liquid darkens, and if aldehyd is present it takes a fine green fluorescence. It is then distilled rapidly, and 125 c.c. of the distillate is collected, which marks 75°. To this Savalle's test is applied, and the tints obtained are compared with those given by typical solutions of pure amylic alcohol in (ethylic) alcohol of 75°. If the amylic alcohol is present in small quantities (from 1 to 0·1 per cent) it passes over entirely in the 125 c.c. Savalle's test, which is inaccurate except aldehyd is previously removed, depends on the brown colour produced on heating alcoholic solutions of amylic alcohol with an equal volume of pure undiluted sulphuric acid.

Combination of Sodium Glycol-alcoholate with Glycol.—M. de Forcrand.—A thermo-chemical paper.

The Active Crystalline Principle Extracted from the Seeds of Strophantus glabrus, of the Gaboon.—M. Arnaud.—This highly poisonous principle, which is non-nitrogenous, and ranks not among the alkaloids but the glucosides, has received the name ouabaine, and scarcely differs from the principle extracted from the *Acokanthera.* The formula assigned to both is $C_{30}H_{16}O_{12},H_2O$.

Study of the Combustion-heats of the Terpilenols of Terpine Hydrate and of Anhydrous Terpine.—W. Louguinine.—Not susceptible of useful abstraction.

Vol. cviii., No. 1, January 7, 1889.

Reactions of Oxygenated Water with Chromic Acid.—M. Berthelot.—The author proposes a thermochemical explanation of the reactions recently pointed out by Ad. Carnot. He observes that the two opposite determinations of hydrogen peroxide by chromic acid and of chromic acid by hydrogen peroxide are not reciprocal. We cannot, without the risk of error, overstep the limits of the reaction and then return by means of an excess of the antagonistic reagent, as it can be done with permanganate. The use of a notable quantity of one of the two reagents added at once in a proportion sufficient for the complete reaction is admissible in very dilute liquids on account of the slowness of the reactions. But in strong solutions this method of operating might occasion at certain points the presence of a momentary excess of the reagent and change the character of the reaction.

Butylic Ethers, Mixed, and properly so-called.—E. Reboul.—This memoir does not admit of useful abridgment.

A Contribution to the Study of the Ptomaines.—Oechsner de Coninck.—The author has converted the ptomaine $C_8H_{11}N$ into pyridin, and the intermediate product, carbono-pyridin, presents the principal characters of nicotianic acid.

The Determination of Organic Nitrogen by Kjeldahl's Method.—L. L'Hote.—The author considers it unnecessary to insist upon the accuracy of the soda-lime process. Analysts know that its results are irreproachable if we take care not to heat too strongly, so as to avoid the dissociation of the ammonia, and if the soda-lime in fine powder is intimately mixed with the substance under examination. His researches show that, contrary to what has been asserted, the figures yielded by the Kjeldahl process are lower than those furnished by soda-lime. All the organic nitrogen does not reappear in the sulphuric acid in the state of ammoniacal nitrogen.

The Forage Legumens on Acid Soils.—Paul de Mondesir.—The author does not question the beneficial action of limestone on leguminous forage plants. But he concludes from his experiments that if these plants find in the soil phosphates and potash they can content themselves, as far as lime is concerned, with the proportion existing in combination with the humic matters.

MEETINGS FOR THE WEEK

Monday, 28th.—Medical, 8.30.
— Society of Arts, 8. Cantor Lectures. "Egyptian Tapestry and Textiles," by Alan S. Cole.
Tuesday, 29th.—Institute of Civil Engineers, 8.
— Society of Arts, 8. "Gold and Silver Mining in Colorado," by Thomas W. Goad.
— Royal Institution, 3. "Before and After Darwin —II. Evolution," by Prof. G. J. Romanes, F.R.S.
Wednesday, 30th.—Society of Arts, 8. "The Construction of Photographic Lenses," by Conrad Beck.
Thursday, 31st.—Royal, 4.30.
— Royal Institution, 3. "The Metamorphoses of Minerals," by Prof. J. W. Judd.
Friday, Feb. 1st.—Geologists' Association, 8. (Anniversary).
— Royal Institution, 9. "The Life-History of a Marine Food-Fish," by Prof. W. C. McIntosh, F.R.S.
Saturday, 2nd.—Royal Institution, 3. "The Character of the Great Composers and the Characteristics of their Works," by Prof. E. Pauer.

THE LONDON GEOLOGICAL FIELD-CLASS LECTURES on the "Thames Valley," by PROFESSOR H. G. SEELEY, F.R.S., in Holborn Town Hall, Gray's-Inn Road, every Wednesday Evening from February 6th to the 27th, at 8 o'clock. Tickets, 5s. each for the Course, may be had from W. Wesley and Son, 28, Essex Street, Strand, W.C.

TO MANUFACTURING CHEMISTS AND OTHERS.

THE METROPOLITAN BOARD OF WORKS will meet at the office of the Board, Spring Gardens, S.W., on Friday, the 8th day of February, 1889, at 12 o'clock at noon precisely, and will then be prepared to open TENDERS by parties who may be willing to CONTRACT for the SUPPLY of 1000 tons of MANGANATE OF SODA, to be delivered at the rate of 100 tons per week, from the 18th of March next. Parties desirous to submit tenders may obtain a copy of the specification, form of tender, and information as to places of delivery on application to the Chemist of the Board, at the office, Spring Gardens, between the hours of 9 a.m. and 4 p.m. (on Saturdays between the hours of 9 a.m. and 2 p.m.), until Thursday, the 7th day of February, 1889. The tenders, which must be on the form supplied from this office, and addressed to the Clerk of the Board, are to be delivered at the office before 4 o'clock on the last-mentioned day, and no tender will be received after that hour. The parties tendering must be in attendance at the Board at 12 o'clock on the day appointed for opening tenders, and any tender which is not fully filled up in every particular will be rejected. The Board do not bind themselves to accept the lowest or any tender.

J. E. WAKEFIELD, Clerk of the Board.
Spring Gardens, S.W., 18th January, 1889.

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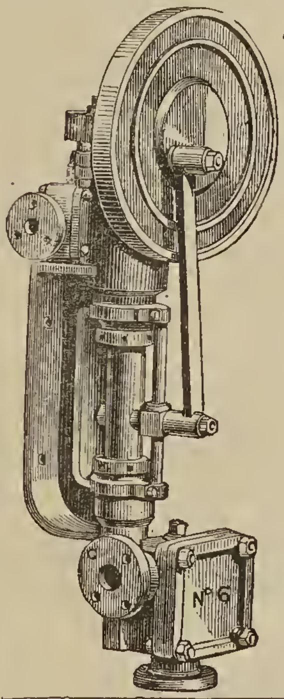

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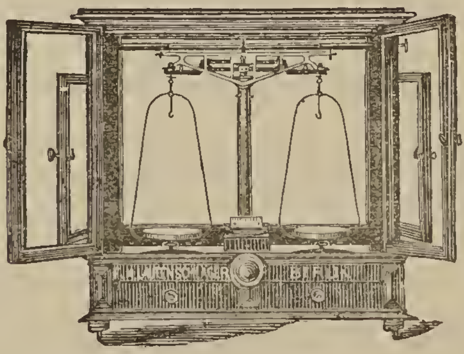

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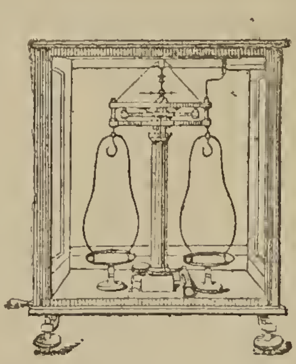

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THE CHEMICAL NEWS.

Vol. LIX. No. 1523.

THE VOLUMETRIC ESTIMATION OF COBALT IN PRESENCE OF NICKEL, MANGANESE, AND OTHER METALS.

By NORMAN McCULLOCH.

In the writer's inquiry on the more likely methods hitherto suggested for the volumetric estimation of cobalt in the presence of nickel (Chemical News, vol. lvi., p. 27) it was shown that the processes were inherently valueless, and justifying the so far exclusive use of gravimetric methods for accurate work. The inquiry, in fact, constituted in part a corroboration of Bayley's analyses of the higher oxides of nickel and cobalt (Chemical News, vol. xxxix., p. 81), and in so demonstrating the unstable and indefinite character of cobaltic hydroxide as ordinarily obtained precluded the idea of accepting the "available" oxygen of this compound as a means to the exact estimation of cobalt.

But, the writer now finds, peroxide of cobalt in cyanide solution, so to speak, is of stable and definite composition, and in the determination of the oxygen necessary to convert cobalt*o*cyanide to cobalt*i*cyanide, there is a ready means to the exact estimation of cobalt in presence of nickel, manganese, and other metals.

Cobaltocyanide exhibits, in its affinity for oxygen, powerful reducing properties, determining the complete or partial reduction of many metallic oxides, and, in the case of chromic acid, robbing it of one half of its oxygen, so:—

$$6CoCN_2+24KCN+2CrO_3+3H_2O= \\ =3Co_6(CN)_{12}Co_2+Cr_2O_3+6KHO.$$

Further, the above reducing effect of a metallic cyanide or chromic acid is peculiar to the cobalt compound, and not materially exhibited by other cyanides. It follows, then, from the foregoing, that the reduction of chromic acid in cyanide solutions is an indication of the presence of cobaltocyanide, and, by the indirect estimation of the reduced chromate with standard ferrous salt, quantitatively applicable to the estimation of cobalt.

Thus indicating the process to be described, the necessary apparatus and standard reagents are sufficiently familiar, and it will suffice to touch on the following:—

Standard Normal Bichrome (49·17 grains in 10,000 grains H_2O) should be delivered from a burette graduated to fifths of a division (1 div. = 10 grains) 1 div. = 0·059 grain cobalt.

Standard Ferrous Salt—($FeSO_4NH_42SO_4+6H_2O$).—This reagent is standardised with bichrome in the usual way, and best on such quantity as is used in the estimation.

Potassium Cyanide Solution of any convenient strength, and, in the author's case, a five per cent solution of very pure cyanide (95 per cent), and of this solution, 12·5 divs. theoretically sufficed for one grain of cobalt. The cyanide solution may be standardised by delivering into a hot aqueous solution of 3 grains pure sulphate of nickel until the precipitate first formed is re-dissolved, and considering the quantity so consumed *plus* one half more, as equivalent to 1·14 grains of cobalt in the process.

Apparatus.—An arrangement is required for effecting the reaction of the cobaltocyanide with the chromate in absence of air and at the boiling-point; and it may consist simply of a 12 oz. flask fitted in the neck with a double holed cork, one hole for reception of thistle funnel, the other for escape of vapour. The tail end of the funnel should dip beneath the surface of the liquid in flask, and its mouth be somewhat constricted.

The Estimation.—The standard bichrome and cyanide solutions are conveyed in their proper quantities to the flask above described, a few drops of ammonium hydrate added for subsequent neutralisation of any free acid in solution to be tested, and the whole diluted, if necessary, to a convenient bulk with water.

The amount of bichrome taken need not *greatly* exceed the theoretical requirement for the greatest probable quantity of cobalt to be estimated, but, with the cyanide, an allowance is made also for the conversion to soluble double cyanides of such other metals as may be present.

The cork and thistle-funnel are now placed in position, and the solution boiled to expel air from the flask. The hot solution to be tested, of convenient bulk and not too acid, and free, of course, from oxidising or reducing constituents, is now added, and the ensuing reaction is instantaneously complete.

After this stage the continued use of the cork and thistle-funnel is necessary only in presence of manganese.

The contents of the flask are now cautiously treated with excess of a moderately warm concentrated solution of ammonium chloride, and the ebullition sustained for about ten minutes longer to expel volatile cyanide (an operation conducted in acid chamber or in a draught of air to carry off poisonous fumes).

In digression, the stronger acids may not substitute the ammonium salt, as tending to reduce chromic acid in presence of hydrocyanic acid, and particularly *insoluble* cyanide.

It is now left, preceding the estimation of non-reduced chromic acid with ferrous salt, to throw down soluble cobaltocyanide and decompose potassium-nickel cyanide by the addition of nickel sulphate. This is to prevent the subsequent formation of ferrous cobaltocyanide and double cyanide of iron and nickel respectively—compounds difficultly soluble in dilute acid—and, consequently, low results. To effect the above precipitation, a weight of nickel is required at least equal to that of the nickel and cobalt existing in the contents of the flask, but if such acids as arsenic and phosphoric are present more is needed, as their precipitation is involved. Simply, the solution of nickel is added until no further precipitate is formed, or until the precipitate settles in a peculiar manner to be known by experience; great excess of nickel is thus avoided, which would tend to interfere with the ferricyanide reaction in the subsequent operation.

It now only remains to pour the contents of the flask into excess of a hot aqueous solution of standard ferrous salt contained in a basin, acidify with a few drops of hydrochloric acid, and titrate with bichrome in usual way in order to complete the estimation.

The cobalt is calculated by multiplying the difference between the number of divisions bichrome taken at the outset of the estimation and that found at the completion by 0·059 grain and correcting this by a slight allowance for reducing action of the potassium cyanide and its impurities on the chromate. In the author's case this correction has been taken from the experiments of Table I., and it has been deemed sufficiently near to accept the reducing action of the cyanide as simply proportionate to the quantity of this reagent used in the estimation, although it is not altogether independent of the proportion and amount of the bichrome, the degree of dilution, length of time of boiling, &c. The subjoined table shows that 100 divs. of the bichrome boiled for a few minutes with its own bulk of the cyanide, and then for about ten minutes more with addition of excess ammonium chloride, loses in value to the extent of about one division. One division, then, has been deducted from the amount of bichrome reduced by the cobaltocyanide in such estimations, using the above bulk of cyanide, a fifth of this for 25 or 30 divs., and so on. It is, of course, advisable, where the highest accuracy is desired, to determine the necessary correction by a blank experiment, and duplicating also the approximate quantity of cobalt.

TABLE I.

Divs. std. $K_2Cr_2O_7$ taken.	Divs. KCN solution used.	Grains std. ferrous salt used.	Divs. std. $K_2Cr_2O_7$ consumed.
100	—	40	1·0
100	—	40	1·2
100	100	40	1·9
100	100	40	1·8
100	100	40	2·2
100	10	40	1·4
10	100	5	3·6

Table II. shows results of volumetric estimations of cobalt alone, and in presence of nickel, manganese, lead, phosphorus, and arsenic respectively. The figures of the fourth column have been submitted to correction on basis already described.

TABLE II.

Grains of cobalt and other substances taken.	Divs. std. $K_2Cr_2O_7$ used.	Divs. KCN solution used.	Divs. std. $K_2Cr_2O_7$ reduced.	Grains CO found.
3·62 Co	70·0	80·0	60·8	3·59
1·14 ,,	25·4	25·4	19·2	1·13
1·14 ,,	25·4	25·4	19·3	1·13
0·07 Co+3·80 Ni	3·0	50·0	1·3	0·07
1·14 ,, +2·28 ,,	25·0	50·0	19·1	1·12
0·03 ,, +2·28 ,,	2·0	25·0	0·4	0·02
0·73 ,, +2·28 ,,	16·0	40·0	12·5	0·73
5·42 ,, +1·14 ,,	98·0	120·0	91·5	5·40
1·08 Co+6·80 Mn	25·0	30·0	18·4	1·08
0·36 ,, +1·36 ,,	10·0	10·0	5·9	0·34
0·36 ,, +1·36 ,,	10·0	15·0	6·1	0·36
1·08 ,, +2·27 ,,	25·0	30·0	18·3	1·08
1·08 Co+1·65 Pb	25·0	20·0	18·5	1·09
0·91 Co+0·57 P	25·0	20·0	15·5	0·91
1·08 Co+5·13 As	25·0	30·0	18·2	1·07
1·08 ,, +1·54 ,,	25·0	30·0	18·4	1·08

Estimations have been made in presence also of aluminium, zinc, antimony, molybdenum, and uranium with perfectly satisfactory results. The process, though, is not applicable in presence of copper. Cuprous cyanide is formed, and cyanogen liberated, which converts its equivalent of cobaltocyanide to cobalticyanide, and the cuprous cyanide is not completely oxidised by the ferric chloride in the final operation of the process. Consequently the results are too low (*vide* Table III.), and copper must not be present in any solution in which it is proposed to determine cobalt by the volumetric process described in this Paper.

TABLE III.

Grains of cobalt and other substances taken.	Divs. std. $K_2Cr_2O_7$ used.	Divs. KCN solution used.	Divs. std. $K_2Cr_2O_7$ reduced.	Grains CO found.
1·08 Co+0·05 Ca	25·0	25·0	17·8	1·05
1·08 ,, +0·10 ,,	25·0	25·0	17·3	1·02
1·08 ,, +0·05 ,,	25·0	25·0	17·8	1·05

The experiments of Table IV. have been devoted to studying the influence of iron.

TABLE IV.

Grains of cobalt and other substances taken.	Divs. std. $K_2Cr_2O_7$ used.	Divs. KCN solution used.	Divs. std. $K_2Cr_2O_7$ reduced.	Grains Co found
1·08 Co+0·45 Fe	25·0	30·0	18·1	1·06
1·08 ,, +0·45 ,,	25·0	40·0	17·5	1·03
1·08 ,, +0·90 ,,	25·0	40·0	17·9	1·05
1·08 ,, +0·90 ,,	40·0	25·0	18·1	1·06
1·08 ,, +0·90 ,,	50·0	25·0	18·0	1·06
1·08 ,, +0·90 ,,	50·0	50·0	18·2	1·07
2·17 ,, +0·90 ,,	50·0	50·0	35·4	2·08
0·10 ,, +0·15 ,,	3·0	8·0	1·0	0·06
2·17 ,, +0·15 ,,	50·0	50·0	36·1	2·13
2·17 ,, +0·90 ,,	70·0	50·0	36·2	2·13
3·62 ,, +0·15 ,,	90·0	70·0	62·0	3·65

Ferric hydroxide readily oxidises cobaltocyanide in presence of excess cyanide to cobalticyanide, and is itself converted to ferrocyanide. A soluble chromate checks this action as being the more ready oxygen furnisher, but, nevertheless, the tendency of the results is to come out beneath the truth.

It will doubtless be best to separate iron as well as copper, and in the case of a cobalt ore the author would dissolve the sample in aqua-regia, and evaporate to dryness. The nitric acid would then be destroyed by twice or thrice evaporation to dryness with hydrochloric acid, and the copper precipitated from the solution of the residue by sulphuretted hydrogen. In the filtrate from sulphide the iron would be separated by the acetate of *soda* method, and the iron precipitate re-dissolved and re-precipitated in a similar way to separate any small portion of cobalt. The combined filtrates from the acetate precipitates would be evaporated to convenient bulk, and the excess of acid neutralised by caustic or carbonated soda. The solution so obtained would then be added to suitable amounts of bichrome and cyanide in a manner that will now be understood, and the estimation completed volumetrically. Thus, in the author's opinion, may cobalt be determined in its ores, &c., with an accuracy to be surpassed and a convenience to be approached by no other known analytical procedure.

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ON SOME NEW TESTS FOR TANNIC AND GALLIC ACIDS.

By S. G. RAWSON, B.Sc.

THE ordinary reagents which are used in detecting these acids are ferric chloride, which gives its well-known reaction with both, and a solution of gelatin which reacts only with tannic acid. In the case, however, of a dilute solution of tannic acid no precipitate is obtained with gelatin; and hence considerable difficulty arises in distinguishing between the two acids. Young's test for these acids, viz., potassic cyanide, I found to work well, giving a reddish colour with gallic acid and none with tannic acid.

If a solution of tannic acid be treated with ammonium chloride alone a precipitate falls, but only with extreme slowness; whereas on the addition of ammonia a beautiful white precipitate instantly appears, but this, probably by oxidation, becomes rapidly of a reddish brown colour. With gallic acid no precipitate falls in either a strong or a weak solution, but the liquid becomes of a red colour. In a solution of tannic acid containing one part of tannic acid in 5000 of water a precipitate falls, but slowly, and with more dilute solutions, therefore, it is better to drop the mixture of ammonic hydrate and chloride very cautiously on to the top of the tannic acid solution. Where the two liquids come in contact with one another the white precipitate makes its appearance at once in a well-marked line. This white line is distinctly visible in a solution of tannic acid containing 1 part in 20,000 of water. If, however, a piece of black paper be held behind the tube the delicacy of the test is increased and 1 part in 50,000 parts of water may be now detected. There is no advantage in substituting other ammonium salts such as the phosphate, carbonate, or oxalate for ammonium chloride.

With gallic acid, as previously mentioned, no precipitate is formed; but a ring, usually of a greenish colour on its lower surface, is produced, this being recognisable in solutions containing 1 part of gallic acid in 100,000 of water.

Some few experiments were tried, in the case of tannic acid, with a view to using the method as a quantitative one; but owing to the unstable nature of the precipitate in alkaline solutions, this attempt was, as I anticipated, a failure.

Another delicate test for both gallic and tannic acids is to add to the solution containing one of them chlorine water and then ammonia, a beautiful red colour being at once produced. With tannic acid the colour is very well marked and distinct, but is not quite so noticeable with gallic acid, for with this acid, as is known, ammonia alone gives a red colour. With a mixture of potassic ferricyanide and ammonia both acids also give a dark red coloured solution. In the case of tannic acid 1 part in 10,000 of water gives a distinct red colour to the whole of the solution. In a weaker solution, say 1 part in 30,000 of water, the red colour is best seen by looking down the test-tube through the whole column of the liquid. In still more dilute solutions, containing only 1 part tannic acid in 100,000, of water it is better to compare the tint, which is now more of a yellowish brown, with the tint of a blank experiment, *i.e.*, one containing the same amount of ammonia and of potassic ferricyanide in the same volume of water, but with no tannic acid present. Under these conditions the change in colour will be perfectly apparent, and the delicacy or the reaction may be carried considerably further. The red colouring matter can be salted out, and I am at present engaged on some further investigations into its composition and properties.

University College, Liverpool.

ACTION OF SULPHURETTED HYDROGEN UPON ZINC SULPHATE IN NEUTRAL OR ACID SOLUTIONS.

By H. BAUBIGNY.

If we pass a current of sulphuretted hydrogen through a saturated solution of zinc, says Berzelius in his celebrated treatise, a part of the metal is precipitated, but when the liquid becomes acid up to a certain point the action ceases.

Thus expressed the fact is exact. But on generalising it for all cases, as it has been subsequently done, we have formulated a law which is false, and is entirely at issue with experience, especially if the liquids are dilute.

In principle every solution of zinc sulphate or chloride (taken in the state of neutral salts), made in the proportion of 0·3 grm. of the salt to 100 c.c. of water, no longer contains zinc if, after being treated with a current of sulphuretted hydrogen at the ordinary temperature (20°), it is left for some hours in a closed vessel.

If the weight of zinc is doubled for the same volume of liquid the precipitation seems at first less perfect. Still, after the lapse of five hours, the liquid contains merely 0·004 to 0·006 grm. of the salt used, and if the action is prolonged, not filtering off the sulphide until the expiry of three days, the mother-liquor does not contain more than 0·001 grm.

In the simplest case, that of a neutral liquid, the reaction is produced similarly with the chloride and the sulphate. Hence, as it is the more easily procured and weighed in a state of purity, the author has exclusively employed it in his experiments.

In a liquid acidified with sulphuric acid, in the case of zinc sulphate, the phenomenon preserves its general course; zinc sulphide is not formed at first, but, after a certain time, the shorter the less free acid is present, the liquid becomes turbid, small traces of sulphide are formed, and the precipitate increases gradually.

Zinc sulphate in an acid solution behaves like neutral nickel and cobalt sulphates (*Comptes Rendus*, xciv., pp. 1183 and 1251 and cv., pp. 751 and 806). With 0·3 grm. of the salt to 100 c.c. of the liquid it was necessary to add sulphuric acid to the extent of about thirty times the acid present in the salt in order that in such a solution saturated at 0° with sulphuretted hydrogen no action shall ensue on leaving it in a closed vessel at the ordinary temperature. But if we apply heat the rise of temperature diminishes the solubility of the sulphuretted hydrogen, and consequently increases its tension so that a decomposition of the zinc salt takes place, and there is a formation of sulphide, the weight of which increases progressively. The case is very distinct at 100°. At this temperature the action of the zinc salt is annulled only if we add a weight of free acid 90 or 100 times greater than the acid existing in combination with the salt.

The multiplicity of the conditions which intervene in the transformation of zinc sulphate into sulphide gives for every case a different result, varying with these conditions.

Thus experience confirms that the weight of free acid to be added to a given and constant weight of zinc sulphate to annul the action of sulphuretted hydrogen decreases with the volume of water in which the salt is dissolved. Inversely, in a given acid liquid (*e.g.*, 7·5 grms. SO_3 in 100 c.c.) and saturated with sulphuretted hydrogen at 0°, nothing will be produced if the weight of the dissolved sulphate is 0·150 grm., even if we heat to 100° in a closed vessel; whilst the conversion of the sulphate into sulphide will take place gradually, even at the common perature, if the weight of the salt is increased to 1·500 grms.: and this transformation will reach such a limit that the weight of the sulphate remaining undecomposed will be decidedly lower than 0·150 grm.

Thus, the results vary with the conditions of the experiment, and for the decomposition of zinc sulphate by hydrogen sulphide there can be no question, properly speaking, of a limit depending on the degree of acidity of the liquid, since the decomposition is a function not merely of the original proportion of the free sulphuric acid at the outset and of the water which serves as a solvent, but further of that of the acid and the metal present in the state of a salt, soluble or insoluble, the sulphide intervening, as the author has already shown in the case of nickel and that of cobalt.

These facts being thus established, M. Baubigny proposes to draw from them conclusions bearing on the solution of a number of analytical questions.—*Comptes Rendus*, vol. cvii., p. 1148.

UNIFORM METHODS FOR THE ANALYSIS OF FERTILISERS, CATTLE FOODS, DAIRY PRODUCTS, SUGAR, AND FERMENTED LIQUORS.*

(Concluded from p. 45).

Report of the Committee on Nitrogen (continued).

Other Methods.

Houzeau (*Pharm. Centr.*, xxviii., 627, 628, also *Jour. Analyt. Chem.*, ii., 354) proposes a mixture to be used in determining nitrogen for the conversion of nitrogen in any combined form into ammonia. Equal weights of sodium acetate and thiosulphate are melted in their water of crystallisation and allowed to solidify. The mixture is powdered and kept in well-stopped bottles. The combustion is made as follows:—In the posterior end of the combustion tube are placed two grms. of the above mixture and two grms. of coarsely-pulverised soda-lime, and then a layer of soda-lime a few c.m. long.

The finely-powdered substance to be analysed (0·5 grm. if rich in nitrogen, 10—25 if a soil) is well mixed with 10 grms. of the salt mixture and 10 grms. of soda-lime, and filled into the tube, followed by soda-lime and an asbestos or glass-wool plug. The combustion is made as usual

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* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

and the mixture at the rear end of the tube is used at the close of the operation for aspirating. The ammonia is absorbed and titrated in the usual way.

The New Jersey Agricultural Experiment Station (*Rep. N. J. Expt. Sta.*, 1887, p. 169) has determined the nitrogen in 140 samples of complete fertilisers, 22 samples of nitrogenous matter of high grade, and 19 samples of ground bone, both by the soda-lime method and the Kjeldahl method. The latter gave on the average 0·04 per cent more nitrogen in complete fertilisers, 0·05 per cent more in high-grade nitrogenous matter, and 0·10 per cent in bone.

Reference should also be made to an elaborate series of experiments and observations on the soda-lime method made in the laboratory of the Wesleyan University by or under the direction of Prof. W. O. Atwater (*Am. Chem. Jour.*, ix., 311; x., 111, 113, 197, 262). A complete abstract of these papers is not deemed necessary here. Prof. Atwater says in closing his paper: "The perfection to which Kjeldahl's method has lately been brought, and its accuracy, convenience, and inexpensiveness have led us to its use in this as in many other laboratories. Our experience leads us to decidedly prefer it to the soda-lime method, though we find it advantageous to use both, making one check the other. But the danger of incomplete ammonification of some classes of compounds, *e.g.*, alkaloids, makes us feel it necessary to control both by the absolute method for all classes of substances except those for which they have been most thoroughly tested."

Recommendations.

Your committee would recommend the continuance of the five methods adopted last year, viz:—

(1). The absolute method.
(2). The Kjeldahl method.
(3). The Kjeldahl method modified for nitrates.
(4). The Ruffle method.
(5). The soda-lime method.

But after a careful consideration of the results obtained above, they would recommend:

(1). That the soda-lime method be given more in detail in the hopes of obtaining more concordant results.

(2). That detail changes be made in the Kjeldahl methods.

(3). That attention be called to the use of zinc-dust in the Kjeldahl modified method. Prof. H. A. Weber calls attention to the fact that unless the zinc-dust be in an impalpable powder and well mixed into the solution, the nascent hydrogen fails to come in contact with all the nitro-compounds, and therefore reduction is incomplete.

Discussion of the report being in order, Messrs. Frear, Gascoyne, and Voorhees stated that they had found trouble with zinc-dust, blanks showing some nitrogen.

Dr. Voorhees stated that at the New Jersey Station they always made blanks for error, and questioned whether commercial chemists did so.

Professor Scovell said he had found that sulphuric acid often contained nitrogen, but the strictly C. P. from Aimer and Amend was quite free.

Dr. Voorhees then gave an account of the experiments at his station with the Scovell modification of the Kjeldahl method, as published in their last annual report, and described a convenient form of iron gas-pipe condenser. Of the soda-lime method, Dr. Gascoyne said that the necessity for absence of a channel, as shown by Atwater, was an important factor.

Dr. Voorhees pointed to the necessity of fine division of the substance to at least 60 mesh, while coarse samples could be used with the Kjeldahl method.

Professor Scovell called attention to the generally bad results on cotton-seed and blood with soda-lime in the tables given in his report, and a general opinion that a careful understanding of the details of working this method were very necessary, and without this results would easily fall too low.

With the Scovell modification of the Kjeldahl method general satisfaction was expressed by those who had tried it carefully.

Professor Stubbs then presented the Report of the Committee on Sugar, as follows:—

REPORT OF THE COMMITTEE ON SUGAR.

The increasing interest in sugar-growing in this country is manifested by the large governmental aid recently given to the manufacture of sugar from sorghum and sugar-cane. This interest has created a demand for chemical information relative to all sugar matters, from the raw juice to the manufactured articles, and to meet this demand is one of the increasing duties of this association. "A Manual of Sugar Analysis," by J. H. Tucker, published by D. Van Nostrand, New York, in 1881, contains all of the approved methods of analyses up to that date, many of which are still used without modifications in the laboratories of the world. Others have been slightly modified, while a few have been discarded as totally without merit.

In all sugars and sugar products, including raw juices, the following determinations are needed for industrial work:—

(1). Total solids.
(2). Percentage of sucrose.
(3). Percentage of invert sugars.
(4). Ash.

In raw juices.—(1). Syrups and molasses: The total solids may be obtained in the following manner:—

(1). By accurately graduated spindles, preferably Baix.
(2). By taking specific gravity.
(3). By evaporating to dryness a weighed quantity mixed with ignited sand in a tared dish.
(4). A method (Wiley's) of trying and weighing a piece of filter paper, say 12 by 2 inches, saturating with juice or with molasses (easily disseminated over the paper by means of a few drops of alcohol), drying and re-weighing.

Of the above methods only the third is absolutely correct. The fourth in our hands gives results slightly low, while the second and first are only approximate. However, the first method, when accurately graduated spindles are used, corrections made for temperature are sufficiently approximate for industrial work. A sufficient time should elapse between the pressing of the cane and the reading of the spindle to permit all the air bubbles to escape; half an hour is time enough.

TABLE I.

Analyses of Varieties of Sorghum from Experimental Plats of Sugar Experiment Station in Louisiana, made July 12 and 13; all immature.

Number of variety from experimental plats.	Total solids by Bux.	Per cent sucrose, polarisation.		Per cent glucose.
		Single.	Double.	
1	6·8	1·0	1·81	3·40
2	7·0	2·0	2·96	1·90
3	9·8	4·8	5·78	1·59
4	6·5	0·4	2·00	3·29
5	10·9	5·4	6·90	1·82
6	9·0	2·3	3·95	2·12
7	11·7	6·0	7·50	2·13
8	10·6	4·8	6·67	2·68
9	13·3	6·9	8·81	4·25
10	8·5	2·0	4·18	3·40
11	11·1	6·2	8·89	1·70
12	8·9	0·0	1·53	6·34
14	13·2	7·0	7·78	3·71
15	13·6	8·4	9·20	2·75
16	13·3	8·3	8·95	2·85
17	11·8	4·0	5·12	3·40
18	11·5	5·2	6·22	3·30
19	9·8	2·2	3·22	2·95

No.	Where from—plantation.	Beaumé.	Sp. gr.	Total solids.	Per cent sucrose by double polariscope.	Per cent glucose.	Other solids.	Per cent sucrose by Fehling.	Total sugar as glucose.
1	Belle Chasee	41·4	1·4039	78·2	39·59	24·32	15·03	39·65	65·06
2	John Crossly & Sons	41·8	1·4092	79·0	41·68	22·69	14·44	40·61	65·44
3	Joseph Garr	40·6	1·3933	76·6	34·91	29·19	9·05	32·25	63·14
4	Boujere	40·7	1·3940	76·7	37·62	24·77	15·32	37·53	64·28
5	Belle-Terre	41·6	1·4065	78·6	42·57	22·78	14·63	41·30	66·26
6	Woodlawn	42·3	1·4165	80·1	33·42	33·75	14·49	32·79	68·22
7	Crescent	42·3	1·4165	80·1	36·44	28·42	14·92	37·67	67·08
8	Mary	42·3	1·4165	80·1	38·82	26·86	16·72	39·08	67·84
9	Perseverance	43·2	1·4287	81·9	40·31	20·00	22·93	43·54	65·84
10	David	42·3	1·4165	80·1	37·62	26·92	16·72	36·97	65·84
11	Orange Grove	42·4	1·4179	80·3	42·25	26·73	13·05	39·94	68·78
12	Palo Alto	42·6	1·4205	80·7	38·14	25·96	16·43	40·28	68·36
13	Hester	42·5	1·4192	80·5	34·72	30·17	18·52	33·14	65·06

Sucrose.—For sugars, raw juices, and syrups sucrose is best determined by a simple polariscopic test with the following precautions.

(1). Proper sampling of substance.

(2). Careful weighing of sample.

(3). Avoid excess of sub-acetate of lead.

(4). Dissipate bubbles, which prevent accurate gauging by a drop or two of ether.

(5). Perfect filling of polariscope tube.

(6). Careful reading of polariscope.

(7). Making all tests in duplicate.

(8). Testing the accuracy of polariscope daily. Instead of direct weighing of substance the Ventzke's process may be used. Following the above (see Tucker, pages 261 and 262), all ripe sorghum juices, all sugars, and syrups of above grade give accurate results. With immature sorghum juices double polarisations show increased results. (See Table I.).

With molasses of all kinds, at least from Louisiana cane, simple polarisation gives results always too low, especially if during the process of manufacture much sugar has been inverted. Double polarisation by Clerget's method of inversion is then usually used for determining the sucrose in these bodies, and when invert sugar is the only optically active body, is approximately accurate. When optically active bodies other than invert sugar are present, recourse must be had to inversion and estimations by Fehling's or Violette's methods. Tuchsmidt has confirmed the accuracy of Clerget's process, and Reichardt and Bellman have perfected it, giving us what is now known to us as Clerget's method.

Creydt, on the other hand, has corrected the constant 144 of Clerget, and substituted therefore 142. He further prescribes HCl of 1·1888 specific gravity, equal to 38 per cent of acid, and washes with this acid the bone charcoal used for filter, dries, and pulverises it. Herzfeld thinks the exact truth as to this constant is not yet known on account of the difficulties; first, of maintaining the temperature of observation; second, the nature of the so-called "pure sugar" used. Landolt recently adds other errors, among others, 1° Ventzke (white light) $=0·34455$ circular degrees (sodium light) is too high, and that diverse active substances give numbers sensibly different. He has found with Dr. Rallyan for 1° Ventzke (white light). Sucrose $=0·3465$, dextrose $=0·3448$, invert sugar $=0·3433$ circular degrees. Landolt finds the constant of Clerget to be 142·4, an expression believed to-day to be the most exact. Herzfeld gives a perfected Clerget method which has the following differences:—Water of local temperature surrounds the tube, which cools the solution, at once permitting accurate reading of temperature. The use of washed and dried bone-black after Reichardt and Bellman, and calculation of results according to the formula of Clerget, modified by Landolt, viz:—

$$R=\frac{100\,S}{142·4-\frac{1}{2}T}.$$

The table of work (see above), carefully done by my assistant, Prof. W. L. Hutchinson, with molasses from different plantations in Louisiana, shows results by double polarisation and inversion and estimation with Fehling's solution.

While the concurrence of results in the main are satisfactory, there are some which could not be made to agree, suggesting strongly either a fault in the method or other optically active bodies than invert sugar, perhaps both; and while for the present we recommend Clerget's method we earnestly request an investigation of Herzfeld's modification of Clerget's method during the coming year by all sugar chemists.

Invert Sugar.

The exact estimation of invert sugar in sugar matters has been recently ably investigated and discussed. Heretofore invert sugar has been determined by a simple titration with the cupric tartrate liquor of Fehling, Violette, &c. The formulæ for the preparation of these solutions are numerous. They all contain sulphate of copper, rochelle salts, and caustic alkali, and present little real difference. Meissl and Herzfeld have described a process based upon the weight of copper reduced from the Fehling solution when accompanied by particular conditions. In spite of its great precision it has found only limited application, especially in France, where its numerous difficulties have prevented its use on an extensive scale. Beggart employs Fehling's solution, which he keeps in bottles (bouchées á l'èmeri), and which are placed in a dark place. To titrate this liquid they dissolve 0·95 grm. of pure sugar in a little water with 2 c.c. of hydrochloric acid, and after adding 500 c.c. of water it is gently heated for ten minutes at 70° C. This solution is cooled and saturated with bicarbonate of soda and raised to one litre; 0·25 c.c. of this liquid will reduce 5 c.c. of Fehling's solution, the end reaction being determined as usual by means of ferrocyanide of potash and acetic acid, using Wiley's tubes.

To preserve a standard solution of invert sugar he prepares a 15 per cent solution and made strongly alkaline. In this way it will be preserved many months. With this solution he daily tests his Fehling's solution. This constitutes the only merit of this process, a merit which should be observed in every process using the cupric tartrate process.

Patterson's process is based upon another principle. To 100 c.c. of Fehling's solution he adds a quantity of sugar insufficient to precipitate all the copper, and determines excess of copper by a titration with a normal invert sugar solution containing 0·002 grm. per c.c. Herzfeld rightly condemns the process, since no correct conclusions from the use of the cupric tartrate solution can be drawn without considering the strength of ebullition and influence of crystallisable sugar upon the reducing power of invert sugar.

All the copper liquids so far proposed, although different in composition, have one common property, viz., they all contain a salt of copper, a double tartrate of potash and soda, and caustic or carbonated alkali. They are all reduced not only by invert sugar but also by dextrine and sometimes even by sucrose. After a certain time they undergo alteration, deposit the oxide of copper, especially if exposed to light.

Soldaini's solution does not possess these objectionable qualities, at least so says Degener, who has studied carefully its properties.

This liquid is prepared, according to Degener, in the following manner:—(1) 40 grms. of sulphate of copper is dissolved in water, and, in another vessel, 40 grms. of carbonate of soda is also dissolved in water. The two solutions are mixed and the copper precipitated in the state of hydrobasic carbonate according to following equation:—

$$2CuSO_4+2Na_2CO_3+H_2O= \\ =CuCO_3CuOH_2O+CO_2+2Na_2SO_4.$$

The precipitate is washed with cold water and dried. This precipitate (15 grms.) is added to a very concentrated and boiling solution of bicarbonate of potash (about 415 grms.) and agitated until the whole is completely, or nearly so, dissolved, water is added to form a volume of 1400 c.c., and the whole mass heated for two hours upon a water-bath. The insoluble matter is filtered, and the filtrate, after cooling, is of a deep blue colour, and has a density of about 22·5° (Baumé (1·185). The sensibility of this liquid is so great that it gives a decided reaction with 0·0014 grm. of invert sugar. The presence of sucrose in the solution increases still this sensibility. Ammoniacal salts are not hurtful to the reaction, but they do sometimes retain in solution a slight quantity of copper.

It is then indispensable to boil the solution for five minutes at least in order to drive off ammonia. The quantitative test for sugar is made in the following manner:—Fifty c.c. of Soldaini's solution is boiled for five minutes upon a water-bath, and 15 c.c. of the sugar liquid (containing 100 grms. of matter in 100 c.c. of water) added, and boiled again for five minutes. After a rapid cooling the liquid is thrown upon a Swedish filter and washed with water until every trace of a blue colour disappears. Then the paper is removed and the precipitate examined, which should be of a clear red colour.

Bodenbaender and Schiller (*Zeitschrift des Vereins fur Rubenzucker-Industrie*, 1887, p. 138) have determined the following quantitative process with this liquid:—100 to 150 c.c. of Soldaini's solution is placed in an Erlenmeyer flask and heated for five minutes over a gas jet. A solution containing 10 grms. of sugar (clarified with subacetate of lead if necessary) is added, and heated again for five minutes, always over a direct flame. This precipitates all the copper, to which is added 100 c.c. of distilled water, in order to cool the mass very quickly. The troubled liquid is filtered (preferably through a Sohxlet or Herzfeld filter) and washed with distilled water. This oxide of copper is reduced in a current of hydrogen, and the copper is weighed in a metallic form, and this weight multiplied by 0·3546 gives the weight of invert sugar. By this method 0·01 per cent of invert sugar can be accurately determined.

Sidersky has recently offered a new volumetric method, based upon the use of Soldaini's solution. With sugars the same method as is now in use with Fehling's solution can easily be followed, watching the disappearance of the blue colour, and testing the end with ferrocyanide of potash and acetic acid. This process offers no serious objections common to Fehling's solution, but is inapplicable to coloured sugar solutions, such as molasses, &c. For the last the following is recommended:—25 grms. of molasses are disssolved in 100 c.c. of water and subacetate of lead added in sufficient quantities to precipitate the impurities, and the volume raised to 200 c.c. and filtered. To 100 c.c. of the filtrate are added 25 c.c. of concentrated solution of carbonate of soda, agitated, and filtered again. 100 c.c. of the second filtrate with excess of lead removed is taken for analysis. On the other hand, 100 c.c. of Soldaini's solution is added to a flask of Bohemian glass and heated five minutes over an open flame. The sugar solution is now added little by little, and the heating continued for five minutes. Finally, the heat is withdrawn and cooled by turning in 100 c.c. of cold water, and filtered through a Swedish filter, washed with hot water, letting each washing run off before another addition. Three or four washings will generally remove completely the alkaline reaction. The precipitate is then washed through a hole in the filter into a flask, removing the last trace of copper. 25 c.c. of normal sulphuric acid is added with two or three crystals of chlorate of potash, and the whole gently heated to dissolve completely the oxide of copper, which is transformed into copper sulphate, according to equation—

$$3Cu_2O+6H_2SO_4+KClO_3=6CuSO_4+6H_2O+KCl.$$

The excess of sulphuric acid is determined by a standard ammonia solution (semi-normal), of which the best indicator is the sulphate of copper itself. When the deep blue colour gives place to a greenish tinge the titration is completed. The method of titration is performed as follows:—Having cooled the contents of the flask, a quantity of ammonia equivalent to 25 c.c. of normal sulphuric acid is added. From a burette graduated into one-tenth c.c. standard sulphuric acid is dropped in drop by drop, agitating after each addition. The blue colour disappears with each addition to reappear after shaking. When the last trace of ammonia is saturated the titration is complete, which is known by a very feeble greenish tinge. The number of c.c. is read from the burette, which is equivalent to the copper precipitated. The equivalent of copper is 31·7, and the normal acid equivalent is 0·0317 of copper. Multiplying the copper found by 3546 we have the invert sugar. A blank titration is needed to accurately determine the slight excess which gives the pale green tinge. This process is to be highly recommended if experiments show it to be as accurate in our hands as it has in France.

(4) *Ash.*—For the determination of ash, Scheibler's process of ignition with H_2SO_4 and deducting one-tenth is recommended. For details, see Tucker's "Manual," p. 226.

Your Committee, in conclusion, recommends that for technical work the following is admissible:—

(1) Taking the total solids with an accurately graduating Brix spindle and correcting for temperature.

(2) A polariscopic test for raw juices, low syrups, and sugars, using the precautions mentioned in this Report.

(3) For heavy syrups, molasses, and tank bottoms, double polarisation with Clerget's tables.

(4) For invert sugar use Fehling's or Violette's solutions, preferably the last, using as an end reaction ferrocyanide of potash and acetic acid; best accomplished by use of Wiley's tubes.

(5) Ignition with sulphuric acid at a low red heat and deducting one-tenth for ash.

For laboratory work the above may be substituted by some of the more accurate methods given above.

REMARKS ON PROFESSOR STUBBS'S REPORT.

By H. W. Wiley.

In connection with the Report of Professor Stubbs on sugar analysis, wuich has just been presented to the Association, I beg leave to call the attention of the members to a standard polariscope which I have had constructed by Schmidt and Haensch in Berlin. This instrument is the double compensating apparatus manufactured by that firm, which has already gained great favour among chemists. The apparatus which I show you was specially constructed for the use of this Department, and is capable of receiving an observation tube 600 m.m. in length.

By means of the double compensating apparatus any error which may be due to an inaccuracy in the quartz wedge is reduced to a minimum. The apparatus has the advantage of using ordinary lamp-light, which is of great importance when outside-station work is to be considered, where the difficulty of securing a monochromatic flame is great. This instrument has lately been examined by Professor Andrews, the expert employed by the United States Treasury to investigate the methods of sugar analysis employed in the United States custom-houses. He proved it to be as nearly exact as any instrument can be made. It is not necessary to mention that for general purposes of research a rotation instrument like the large model Laurent is preferable to any form of compensating apparatus; but in sugar work, where an arbitrary scale is used, I think an instrument of this kind would be found superior to anything now in use.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 17th, 1889.

Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. Arthur G. Bloxam, T. O. Sandell, and Walter Tate were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John William Clayton, Blackburn; Philip Norman Evans, Nash Mills, Hemel Hempstead; Robert Ferguson, M.A., Burgh School, Linlithgow, N.B.; John Joseph Hickey, Beech Mount, Harpurley; William Hall Jowett, Blackburn; William Eggleston Lauer, Chemisches Laboratorium, Georgen Strasse 35, Berlin; George McAlman, 246, Bath Street, Glasgow; Harry East Miller, 1264, 14th street, Oakland, California, U.S.; Arthur Frederick Morgan, 21, Rumford Street, Manchester; George Arthur Pingstone, Yew Bank, Brook Road, Heaton Chapel; Harry Holliss Robins, 11, Mecklenburgh Street, W.C.; James Speakman, 4, Craigisbank Terrace, Dundee; Stanley Southam, 7, Ritson Road, Dalston, N.; Thomas B. Stilleman, 358, Bloomfield, Street, Hoboken, New Jersey, U.S.A.

The following were duly elected Fellows of the Society:—Messrs. Charles Lightfoot Barnes, Percy Carter Bell, Albert Cooper, William Hepworth Dixon, Dr. Carl Duisberg, Frederick Charles Garrett, B.Sc., B. S. Gott, B.A., Robert J. Gow, Edward Gudeman, Ph.B., Allan Twistleton Hall, John A. Hall, Cecil Leigh, Lionel Remond Lenox, Ph.B., George Lloyd, Arthur Lloyd Mackeroy, M.A., James Muir, Robert Hodgson Parker, Charles W. Priestley, B.Sc., Frank R. Peace, John Percival, B.A., John Provis, Edgar Richards, Percy Andrew Ellis Richards, Siegfried Ruhemann, Ph.D., M.A., Walter Venis.

The following papers were read:—

1. "*A Cubical Form of Bismuthous Oxide.*" By M. M. Pattison Muir and Arthur Hutchinson.

A puce-coloured precipitate is produced by adding excess of potassium cyanide to a boiling solution of bismuth nitrate in dilute nitric acid. Boedeker (*Annalen*, cxxiii., 61) gave the formula $Bi_2O_5 \cdot 2H_2O$ to this substance; according to C. Hoffmann (*Annalen*, ccxxiii., 110), however, the precipitate is Bi_2S_3, the sulphur being derived from impurity in the cyanide; and one of the authors has described it as an oxycyanide of bismuth (*Proc. Roy. Soc. Edin.*, xi., 557). Further experiments show that the precipitate is a compound of Bi, C, N, and O. When this precipitate, without being washed, is repeatedly treated with boiling concentrated potash solution, 2—3 per cent of the bismuth in the precipitate goes into solution with practically the whole of the carbon and nitrogen, and tetrahedral crystals of bismuthous oxide remain. It is almost impossible to free these crystals from an adhering film of the puce-coloured compound by treatment with potash; very long-continued action of boiling potash—so concentrated that it solidifies on cooling—does, it is true, remove the last trace of the carbon and nitrogen compound, but the crystals are much corroded by this action. To obtain the cubical form of bismuthous oxide free from the puce-coloured compound, it is better to remove the last traces of this substance by heating for a short time to full redness in air. Cubical bismuthous oxide has the density 8·838 at 25° relatively to water at the same temperature; the relative density of the ordinary rhombic bismuthous oxide is 8·3.

2. "*Cupric Iodide and the Interaction of Iodides with Cupric Salts.*" By D. J. Carnegie, B.A.

By digesting cuprous iodide with iodine and water in a tightly closed bottle at 80° for a few minutes, the author has obtained solutions of cupric iodide containing as much as 0·82 grm. per 100 c.c., but has been unable to obtain cupric iodide in the solid state, either from such solutions or by other means. A well-defined basic periodide, $[CuI_2 2CuO \cdot 4H_2O]$, was obtained by digesting copper with barium iodide. The author attempts an explanation of the fact that concentrated solutions of cupric iodide are not obtainable from the interaction of soluble iodides and cupric salts, or of iodhydric acid and cupric hydroxide, in terms of (1) the affinity which iodhydric acid and iodides generally possess for iodine; and (2) the disturbance of equilibrium which the separation of solid iodine causes in a medium which holds cupric iodide in solution. He regards the usual reason given for the non-existence of cupric iodide, viz., its intrinsic instability, as probably inadequate.

3. "*Periodates.*" Part II. By C. W. Kimmins.

The following salts are described:—

Lead Salts.—The interaction of lead nitrate and $K_4I_2O_9$ or $Na_2H_3IO_6$ results in the production of $Pb_3H_2(IO_6)_2$. When the salt was dissolved in nitric acid, and the solution was concentrated, $Pb_3(IO_5)_2$ was formed. By boiling the first salt with concentrated nitric acid, $Pb(IO_4)_2$ was produced. The salt $Pb_3(IO_5)_2$ is formed by heating $Pb_3H_4(IO_6)_2$ to 275° for four hours. These lead periodates are more or less soluble in nitric acid; the more insoluble salts are lighter in colour than the others; the more soluble salts show a tendency to take up moisture.

Iron Salts.—On treating $Na_2H_3IO_6$ or $K_4I_2O_9$ with ferric chloride, a light brown precipitate was obtained, which on drying at 100° formed a red powder, $FeHI_2O_9$; when this was boiled with nitric acid, the salt $Fe(IO_4)_3$ was produced. The ferrous salt, $Fe_5(IO_6)_2$, was obtained from $Na_2H_3IO_6$, and the salt, FeH_3IO_6, from $K_4I_2O_9$.

Copper Salts.—The green salt, Cu_2HIO_6, was obtained both from $Na_2H_3IO_6$ and $K_4I_2O_9$. On dissolving this salt in nitric acid and concentrating, a yellow salt was produced, probably $Cu(IO_4)_2$.

Nickel Salts.—No salt corresponding to HIO_4 could be obtained. The salt $Ni_3(IO_5)_2$ is greenish yellow, and $Ni_2I_2O_9$ is black and crystalline.

Cadmium Salts.—The only salt obtained was $CdHIO_5$; it is easily prepared from $Na_2H_3IO_6$, and with difficulty from $K_4I_2O_9$.

Silver Salts.—The salt $Ag_4I_2O_9$, was formed by treating $K_4I_2O_9$ with silver nitrate; by treating this with nitric

Meta-periodates. Salts of HIO_4.	Meso-periodates. Salts of H_3IO_5.	Para-periodates. Salts of H_5IO_6.	Di-periodates. Salts of $H_4I_2O_9$.
$AgIO_4 \cdot H_2O$	Ag_2HIO_5	$Na_2H_3IO_6$	$K_4I_2O_9$
$AgIO_4$	$Pb_3(IO_5)_2$	$Na_3H_2IO_6$	$K_3HI_2O_9$
$Pb(IO_4)_2$	$Ni_3(IO_5)_2$	$Ba_5(IO_6)_2$	$Ag_4I_2O_9 \cdot 3H_2O$
$Fe(IO_4)_3$	$CdHIO_5$	$Ag_2H_3IO_6$	$Ag_4I_2O_9 \cdot H_2O$
$Cu(IO_4)_2$		$Ag_3H_2IO_6$	$Ag_4I_2O_9$
		$Pb_3H_4(IO_6)_2$	$FeHI_2O_9$
		$Fe_5(IO_6)_2$	$Ni_2I_2O_9$
		FeH_3IO_6	
		Cu_2HIO_6	

	Schultz-Sellack. $B_2O_8 \cdot H_2O \cdot 3SO_8$.	$H_3BO_3 \cdot 3SO_3$.	Results of analyses.			
			(1	(2).	(3).	(4).
SO_3	73·2	79·5	78·8	79·7	78·3	80·1
B_2O_3	21·2	11·6	11·3	10·6	12·2	11·8
H_2O	5·5	8·9	9·9 (by diff.)	9·7 (by diff.)	8·9 (by diff.)	8·1 (by diff.)

acid of different degrees of concentration, other silver periodates are formed. All silver salts yielded orange crystals of $AgIO_4 \cdot H_2O$ when heated with concentrated nitric acid.

The salts described in this and a previous paper may be classified as in Table on preceding page.

4. "*Compounds of Arsenious Oxide with Sulphuric Anhydride.*" By R. H. Adie.

This paper describes in detail the preparation of a series of compounds of As_2O_3 and SO_3; the compounds are represented by the formula, $As_2O_3 \cdot xSO_3$, where, $x = 1$, 2, 4, and 8. $As_2O_3 \cdot 8SO_2$ is produced by the interaction of arsenious oxide and sulphuric anhydride; when fuming sulphuric acid is used, approximately $2H_2SO_4 \cdot SO_3$, $As_2O_3 \cdot 4SO_3$, and probably also $As_2O_3 \cdot SO_3$ are formed; $As_2O_3 \cdot 2SO_3$ is obtained by using ordinary concentrated sulphuric acid; and when acids are used approximately corresponding to the formulæ of $9H_2SO_4 \cdot 2H_2O$. $9H_2SO_4 \cdot 4H_2O$, $9H_2SO_4 \cdot 6H_2O$, and $H_2SO_4 \cdot H_2O$, the product has the composition $As_2O_3 \cdot SO_3$. Sulphuric acid of greater dilution than $H_2SO_4 \cdot H_2O$ was found not to yield any compound of As_2O_3 with SO_3. All the compounds described are easily decomposed by moisture, or by heating.

5. "*On a Compound of Boric Acid with Sulphuric Anhydride.*" By R. F. D'Arcy, B.A.

On adding an excess of sulphur trioxide to boric acid, and heating the mixture until sulphur trioxide ceases to be evolved, a substance remains which is fairly stable and possesses the composition $BH_3O_3 \cdot 3SO_3$. This formula may be written $B(HSO_4)_3$, but sufficient experiments have not yet been made to determine whether the compound is a sulphate of boron or a compound of boric acid with sulphuric anhydride. In analysing the compound, use was made of Gooch's accurate method of estimating boric acid by distillation with methyl alcohol (*Proc. Am. Acad. of Arts and Sciences*, 1886—1887). Merz and Schultz-Sellack have described compounds of the formulæ $5B_2O_3 \cdot 2SO_3 \cdot 2H_2O$ and $B_2O_3 \cdot 3SO_3 \cdot H_2O$. Attempts to obtain results similar to those obtained by these chemists were unsuccessful. The percentage composition given by the formula of Schultz-Sellack, and that given by the formula $H_3BO_3 \cdot 3SO_3$, together with the experimental numbers obtained, are stated in the Table above.

6. "*Notes on Experiments on Butter Fat.*" By A. Wynter Blyth and G. H. Robertson.

The authors have endeavoured to separate the glycerides of butter fat by (*a*) fractional crystallisation of the solid portion from alcohol; (*b*) dissolution in ether and fractional precipitation by alcohol; (*c*) electrolysis. The main result of their experiments is to show that butter fat is composed of solid crystalline fats and an oil. The proportion of the oil to the solid crystalline fats is about 45·5 of butter oil to 54·5 butter crystals. A crystalline glyceride was separated, to which the authors ascribe the formula $C_3H_5 \left\{ \begin{array}{l} C_4H_7O_2. \\ C_{16}H_{31}O_2. \\ C_{18}H_{34}O_2 \end{array} \right.$

They consider that butter is mainly made up of compound and not of simple triglycerides.

To the original paper is added a note of the electrical resistance of butter fat and olive oil.

7. "*Gawalowski's Method for the Volumetric Estimation of Sulphuric Acid.*" By Barker North, Assoc. N.S.S.

In Fresenius's *Zeitschrift für Analytische Chemie* for 1888, xxvii., 152—159, is a paper on the "Volumetric Estimation of Combined Sulphuric Acid," by A. Gawalowski. As such a method is still a desideratum among chemists, I undertook, at the request of Professor Thorpe, to make a critical examination of Gawalowski's process. The method consists in adding a quantity of a standard solution of barium chloride, more than sufficient to precipitate the sulphuric acid which may be present, and titrating the excess of barium chloride with a standard solution of sodium carbonate, using phenolphthalein as an indicator of the excess of sodium carbonate.

The barium chloride solution was made as nearly seminormal as possible by weighing, and then accurately standardised by gravimetric analysis. The sodium carbonate solution was made seminormal by weighing out recently ignited Na_2CO_3. A series of experiments were made with strict adherence to Gawalowski's instructions. The errors ranged from 2 to 27·5 per cent. It will thus be seen that the method is entirely worthless. The cause of the error doubtless is the solubility of the barium carbonate, which, even in the presence of alcohol, affects the phenolphthalein to such an extent as to render it impossible to properly detect the true end point of the interaction.

8. "*Note on the* 1 : 3 *Homo- and the Isomeric Hetero-αβ-dichloronaphthalenes melting at nearly the same Temperature.*" By Henry E. Armstrong and W. P. Wynne.

In a recent communication (*Chem. Soc. Proc.*, 1888, 104) we have specially called attention to the fact first brought under notice by one of us at the Manchester Meeting of the British Association, on September 2nd, 1887 (*B. A. Report*, 1887, 231), that *two* αβ-dichloronaphthalenes exist which melt nearly at the same temperature, slightly above 60°. Cleve, in a paper in the number of the *Berichte* issued previously in the same week as the number of the *Proceedings* containing our note, without any reference to our earlier work, corroborates our conclusion (p. 3275), but continues to assign the same melting-point (61°) to the two isomers. Cleve's earlier statement (*Ber.*, 1886, 2182) that two of the isomeric nitrosulphonic acids obtained on nitrating naphthalene-β-sulphonic acid both gave the dichloronaphthalene melting at 61° evidenced his belief, and led others to the belief, that isomeric change took place during the treatment of the sulphochlorides with PCl_5; he subsequently pointed out, however, that perhaps there were two isomeric dichloronaphthalenes melting at 61°. Our observation published in 1887 first proved that no isomeric change takes place, and thus deprived the objections which have been urged against the use of PCl_5 in determining the constitution of nitro- and sulphonic derivatives of naphthalene of their force. Erdmann, in the number of the *Berichte* just issued (1888, 3446), states that Reverdin and Nölting were the first to positively state that two dichloronaphthalenes melting at 61° exist; it is to be noted, however, that Professor Nölting was present at the meeting at which one of us brought forward the above-mentioned facts, and that Reverdin and Nölting's invaluable monograph was at that time only in the press.

In the notice referred to, Erdmann speaks of Cleve's recognition of two dichloronaphthalenes melting at 61° as an important confirmation of *his* views (*Annalen*, ccxlvii., 308) as to the stability of isomeric naphthalene-derivatives; and he states that, disregarding the changes which occur in the case of sulphonic acids when heated with water or sulphuric acid—which he has made the subject of special experimental investigation—no case is now known of the conversion of a naphthalene-derivative into a “position-isomer.” These statements afford multiple illustration of simple belief in the sufficiency of the *Berichte* and a very few other German journals as media of communication among chemists which is becoming so noticeable. The manner in which isomeric change takes place in the case of naphthalene-derivatives has been specially discussed and referred to by one of us (*Chem. Soc. Trans.*, 1887, 266, 587; *B. A. Report*, 1886, 216; 1887, 231; 1888, Chem. News, lviii., 295; *Chem. Soc. Proc.*, 1887, 143—146). A number of cases of isomeric change have been described by us, one so far back as 1881, and that, too, in the *Berichte* (1882, 204), although perhaps this case may be denied rank as one of change into a “position-isomer” by Erdmann; and we shall shortly have to describe other cases.

In the same paper Erdmann makes an acceptable addition to our knowledge in describing the synthesis of the 1 : 3-dichloronaphthalene melting at 61·5° from 1 : 3-dichlorobenzaldehyde. He, however, forgets to mention that the constitution of this dichloronaphthalene had already been determined by us: he calls attention to the existence of two dichloronaphthalenes melting at almost the same temperature as though it were an original observation; and he states that it will be his “nächste Aufgabe” to sufficiently determine the chemical differences of the two isomers in question and to discover means of discriminating between them with certainty: overlooking the fact that we have long since stated that we are engaged in further characterising the isomeric dichloronaphthalenes; and that in our recent note, to the admirable and almost verbal translation of which in that most valuable periodical the *Chemiker Zeitung* he refers and therefore has under notice, we have already described certain distinctive properties and have made the identification of the two dichloronaphthalenes in question a simple matter.

The description originally given by Erdmann and Kirchhoff of the dichloronaphthalene melting at 61·5° which they obtained from parachlorobenzaldehyde did not suffice to determine its identity, and as it was all-important to us to place the constitution of the two dichloronaphthalenes now under discussion beyond question, we have been at the pains to prepare it by Erdmann and Kirchhoff's method from parachlorotoluene: In doing this we have had cause to appreciate and value their labours. By heating the chloronaphthol with PCl_5, a product was obtained consisting of a mixture of tri- and di-chloronaphthalene: these were approximately separated by crystallising from alcohol the tri-derivative separating first in prisms melting at 120°. The residual dichloronaphthalene fused at 57—59°, and as the quantity was inconsiderable this was converted directly into sulphonic acid, from which salts and the chloride were prepared. The potassium salt was found to be sparingly soluble in water containing a little potassium carbonate, and crystallised in anhydrous scales; the sulphochloride crystallised from benzene in needles, becoming opaque on standing and melting at 117°. The dichloronaphthalene recovered from the sulphochloride by hydrolysis *melted* at 63·5°. There can be no doubt therefore that the dichloronaphthalene prepared synthetically by Erdmann and Kirchhoff's method is identical with that from Arnell's betachloronaphthalenesulphonic acid and from the betanaphthylaminesulphonic acid known as the Badische modification. Our previous conclusion that these acids are heteronucleal derivatives is thus confirmed.

Erdmann has entirely misunderstood our objections to his conclusions with respect to the oonstitution of the dichloronaphthalene melting at 63·5°, viz., that his method did not enable us to discriminate the 1 : 2′ from the 1 : 3′ modification. It is not that we think it necessary that the chlorophenylisocrotonic acid should have been isolated; our objection arises from our conviction that, as we have already said, “the origin of the hydroxyl in their acids cannot be determined.” The oxygen-atom in the naphthol may be either that which originally was present in the carbonyl and which may have remained attached to the carbonyl-carbon atom; or it may be that which was contained in the carboxylic hydroxyl; or that which was contained in the aldehyde; and in the last two cases the OH-group may ultimately become associated with either of the two para-carbon atoms with which the oxygen-atom is represented as connected in the formula of phenylparaconic acid. There is at present, moreover, no valid reason to be urged against the conclusion that in some cases the OH-group may assume the one, in some other cases the other position, according to the nature of the influence exercised by the chlorine-atom. We are specially engaged with experiments in the hope of determining the exact constitution of the dichloronaphthalene melting at 63·5°.

9. “*The Constitution of Betanaphthol-α-sulphonic Acid (Bayer's acid).*” By Henry E. Armstrong.

The number of the *Berichte* just issued contains a most valuable paper by Dr. O. N. Witt, on the reduction products of the azo-dyes derived from the various naphthol- and naphthyl-aminesulphonic acids, together with another discussing the constitution of betanaphthol-α-sulphonic acid—conventionally known as Bayer's acid. In the latter I regret to say that Dr. Witt altogether misrepresents my views, misreading an early paper of mine (*Berichte*, 1880, 200); and overlooking the discussion which took place after the reading of Mr. Green's paper on November 15th last, and the conclusions arrived at by Mr. Wynne and myself with regard to the amido-acid corresponding to Bayer's hydroxy-acid published in the same number of the *Proceedings* (p. 104).

Witt speaks of my having converted Bayer's acid into 1 : 2 bromo-betanaphthol, and of my having in consequence inferred that Bayer's acid is the 1 : 2 modification; actually, however, in my paper, I describe (p. 202) the action of bromine on *betanaphthylsulphate.* I may quote the following passages from my Report to the British Association at the Manchester meeting, in 1887, read, I believe, in Dr. Witt's presence, to show what have been my views:—

“The dichloronaphthalene obtained from Bayer's modification of β-naphtholsulphonic acid is doubtless hetero-θ-dichloronaphthalene; the conclusion arrived at by Claus that this acid is a 2 : 3 derivative is not only opposed to all that is known of the behaviour of naphthalene compounds, inasmuch as it involves the assumption that on sulphonating β-naphthol the second β-position contiguous to the hydroxyl becomes displaced; it is untrustworthy, as the dichloroquinone which he obtained may have been, and doubtless was, produced by the action of chlorine liberated during the process of oxidation.

“*Theory of the Formation of Azo-dyestuffs from β-naphthol.*—It is well-known that in the case of β-naphthol itself the α-hydrogen atom contiguous to the OH-group becomes displaced by the azo-group. This position appears to be free in all the sulphonic acids which afford azo-colours, and those naphthol derivatives in which it is not free appear to be incapable of forming such colours; it is therefore a legitimate inference that all-azo-dyes derived from β-naphthol are formed by the introduction of an azo-group in the position indicated.”

At the meeting on November 15th I “referred to Emmert's observation (*Annalen*, ccxli., 371) that the betanaphtholsulphonic acid corresponding to betanaphthylamine-α-sulphonic acid is convertible in a dihydroxynaphthalene different from hydrobetanaphthaquinone as incompatible with the conclusion that the α-acid was the 1 : 2 compound;” and I again expressed the opinion “that an acid in which the SO_3H and OH groups were in the relative positions 1 : 2 would not be capable of forming azo colours.”

The conclusion which I had arrived at as to the probable constitution of the betanaphthol (and betanaphthylamine) azo-dyes, led me, in October, 1887, to commence their study precisely in the manner in which

Witt has now done so skilfully and with such thoroughness; at my suggestion, Dr. F. Feist reduced the benzeneazobetanaphtholsulphonic acid prepared from Schaefer's acid, and found, as Witt had done, that the reduction-product was identical with Meldola's amidobetanaphtholsulphonic acid; he obtained, by hydrolysing the acid, the known amidobetanaphthol, and converted it into betanaphthaquinone. Recently, having determined that Bayer's acid corresponded to the heteronucleal dichloronaphthalene melting at 63·5°, and that it is either a 1 : 2′ or a 1 : 3′ derivative, I had commenced the study of the *Croceine* prepared from Bayer's acid and diazonaphthionic acid. Witt's results relieve me in a most welcome manner from pursuing the investigation. His discovery that the azo-group in the croceines is in the α-ortho-position is precisely what I had foreseen, and I have little doubt that when he examines the reduction products of the azo-dyes prepared from the other betanaphthol- and betanaphthylaminesulphonic acids, he will find that the azo-group is always introduced into the α-ortho-position contiguous to the OH-group of the naphthol, or the NH-group of the naphthylamine.

10. "*The Sulphonation of Naphthalene-β-sulphonic Acid.*" By Henry E. Armstrong.

The number of the *Berichte* just issued contains at p. 916 of the "Referate" an abstract of a patent secured by Ewer and Pick for a *new* naphthalenedisulphonic acid prepared by sulphonating naphthalene-β-sulphonic acid, or one of its salts, by means of fuming sulphuric acid. When this patent came under my notice some months ago I at once came to the conclusion that the *new* acid was the (?) β-disulphonic acid prepared by Mr. Wynne and myself by a similar process by means of chlorosulphonic acid instead of fuming sulphuric acid, and described at the meeting of the Society on November 4th, 1886 (*Chem. Soc. Proc.*, 1886, 230). On preparing the acid according to Ewer and Pick's directions this surmise proved correct. It may be added that this acid corresponds in constitution to η-dichloronaphthalene (m.p. 48°), and, therefore, to Dahl's modification of betanaphthylaminesulphonic acid. I am indebted to Mr. Garrett for assisting me to make the comparison.

At the next meeting on February 7th the following paper will be read:—

"Researches on the Constitution of Azo- and Diazo-derivatives. Part V. Compounds of the Naphthalene-β-series" (continued). By R. Meldola, F.R.S., and G. T. Morgan.

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. cviii., No. 2, January 14, 1889.

A New Mineral.—M. Des Cloizeau.—The author exhibited some crystals of a native platinum arsenide received from Mr. Wells, of Newhaven, Connecticut. This mineral contains 40·9 per cent of arsenic and 52·5 of platinum, along with antimony, rhodium, stannic acid, and traces of iron and palladium.

On the Oxidability and the Cleansing of Tin.—Leo Vignon.—The author's researches relate to the industrial processes of tinning iron and of soldering with tin. He has shown formerly that mixtures of metallic tin and stannous oxide, if heated in contact with air, do not melt, but burn. Such tin, however, may be made fusible by the addition of the substances which have been empirically used in tinning and soldering, such as zinc chloride, ammonium chloride, resin, borax, and caustic alkalies. Tin becomes oxidised rapidly both in moist and in dry air.

New Proximate Principle in the Ergot of Rye.—C. Tanret.—The substance in question is named ergosterine, and has the composition $C_{52}H_{40}O_2$. It is slowly oxidised on exposure to the air, becoming coloured and odoriferous. It is not attacked by strong boiling alkaline solutions. Like cholesterine it is a monoatomic alcohol. With nitric acid or hydrochloric acid and ferric chloride it gives the same reactions as cholesterine. But it dissolves completely in sulphuric acid, and chloroform, if shaken up with the mixture, remains colourless.

The Heptine of Perseite.—M. Maquenne.—This heptine is a non-saturated cyclic carbide, a kind of incomplete hydride, comparable, in its molecular structure, with the terpenes.

Zeitschrift für Physikalische Chemie, Stoechiometrie, und Verwandtschaftslehre. Vol. ii., Part 11.

The Connection between the Molecular Properties of Inorganic Compounds and their Action upon Animated Matter.—J. Blake.—The author expresses his conviction that animated matter may serve as an important reagent for the physico-chemical properties of bodies, and these properties bear an important relation to a branch of science with which they have not yet been connected. The first fact which the author establishes is that the reactions produced upon living animals depend upon the electro-positive constituent of a salt, and are little affected by the nature of the acid radicle. If introduced directly into the blood the sulphates, nitrates, chlorides, acetates, arseniates, and phosphates of one and the same base exert all the same biological action. This rule has been found to hold good with more than forty elements, the only exceptions being potassium and ammonium, to which the author refers below, and it extends not merely to compounds of the more electro-positive elements, but even to the halogens. Dr. Blake has previously shown that the atomic weight of an element is an important factor in its biological action, and has an influence upon its general character, which depends on the isomorphous relations of the substances. It was found that in bodies of one and the same isomorphous group the intensity of the action is proportional to the atomic weight. In other words, the higher the atomic weight of an element the less of it need be present to bring on the symptoms indicative of the peculiar isomorphous group to which it belongs. This rule holds good only for the electro-positive elements. In the non-metals the biological action is, indeed, determined by their isomorphous relations, but there appears no connection between the atomic weight and the intensity of their action. Another fact is the connection between the molecular constitution of inorganic substances and their effects upon living matter, the valence of an element being a factor in its biological action. It is not the general character or the intensity of the biological action, but, so to say, its *extent* which is affected by the valence of the element. As the valence rises so does the number of the organs upon which the organic substances act. Mono-valent elements are known by their effects upon the pulmonary capillaries. Even if injected into the arteries they exert no definite action upon the nerve-centres, and they kill by the changes which they occasion in the lungs. The di-valent elements, both of the Mg and the Ba group act, by destroying the excitability of the muscles of the heart. They have an influence also upon certain peripheric nerves, the Mg group upon those of the intestines and the Ba group upon those of the voluntary muscles. The biological action of the tri- and tetra-valent elements is much more extensive, as they affect the functions of all the more important nerve-centres. It is evident that the phenomena in question are not related to ordinary chemical reactions. The fact that we have in an isomorphous group of salts a series of reagents, each of which produces analogous biological effects, and that the higher the position of an element in these series the smaller is the quantity needed to produce an equally strong effect, distinguishes these effects clearly from those of an ordinary chemical transposition. In 1885 the author pronounced these reactions as catalytic, and in a recent memoir Professor Ostwald declared that the reactions taking place in living matter might be generally thus regarded. Dr. Blake is not certain that a relation can be demonstrated between these catalytic phenomena and the isomorphous characters of the elements, but we have certain indications that atomic weight and valency are factors in catalytical reactions. As to the influence of isomorphism, it seems to be the main determining factor in these biological reactions. Among all the substances examined two exceptions only have occurred, the salts of potassium and ammonium. The influence of the isomorphous relations of elements in its action upon living matter appears most conspicueus when they form the transition members between two isomorphous groups. They produce biological effects which are analogous to those occasioned by the elements of both the adjacent groups. The salts just mentioned, which have isomorphous relations both with the mono-valent metals and also with the Ba group, are distinguished by their action upon the pulmonary capillaries, like those of the Na group, whilst at the same time they bring on the most characteristic reaction of the salts of the Ba group—they delay the contraction of the voluntary muscles for several minutes after death. If one and the same element forms compounds belonging to two isomorphous groups the action of such salts is by no means mutually identical. Such are the connections manifested between the action of inorganic compounds upon living matter, and some of their most important molecular properties. From the experiments of other observers it seems as if a similar connection between molecular constitution and biological effects exists in the hydrocarbons. Dujardin-Beaumetz has shown that in homologous series of alcohols the poisonous properties increase with the molecular weight, and Schmiedeberg finds that the biological action of the esters does not depend on their electro-negative constituent. The author refers to certain researches of Gerhard Krüss; which we purpose shortly to notice, and expresses the opinion that as we have in living matter a substance in a condition of perpetual transformation, and that the result of such transformations is the production and modification of vibrations in the nervous tissue which are communicated by the nerves to the various organs, we might expect, *à priori*, that by means of the molecular vibration of our reagents the reactions occurring in the nervous tissue will undergo a direct or indirect modification. Whilst these considerations open up a new point of view for the investigation of biological phenomena, the author considers the connection between chemical constitution and biological action to be so clearly manifested that living matter forms a valuable reagent in the examination of the molecular constitution of bodies.

The Dissociation Theory of the Electrolytes.—J. H. van't Hoff and L. Th. Reicher.—The authors extended Avogadro's law to solutions if only osmotic pressure takes the place of the pressure of tension in the case of gas; or, in other words, the osmotic pressure of all dilute solutions and the pressure of tension of all dilute gases have the same value at the same molecular concentration and the same temperature. But at the same time they admitted that the aqueous solutions of most salts, acids, and bases seemed to be different, their osmotic pressure being often considerably greater than it should be expected. Arrhenius soon after sought to explain this anomaly, showing that in the substances concerned the anomalous behaviour in aqueous solutions is due to a partial splitting up, which is fully manifested in electrolysis. The authors are now able to confirm the explanation of Arrhenius.

The Dissociation of Carbonic Acid.—H. Le Chatelier.—After giving a sketch of the history of researches on this subject, that author informs us that according to the experiments of M. Mallard and himself the dissociation of carbonic acid only begins to be perceptible above 2000°. At this temperature and at a pressure of six atmospheres it is less than 0·05. At 3300° it is considerably advanced. The results obtained do not agree with the general opinion that at a sufficiently elevated temperature all substances would undergo a complete dissociation. There are cases in which the existence of a maximum of dissociation has been observed. Such are the experiments of Troost and Hautefeuille on the dissociation of silicon chloride, and those of Ditte on hydrogen selenide.

Rapidity of the Reaction in the Oxidation of Tartaric Acid.—Jean Krutwig.—This paper does not admit of useful abridgment.

Electro-chemical Studies. Sixth Memoir: Relations between the Composition of the Ions and their Rapidity of Translation.—W. Ostwald.—Isomeric ions are translated with an equal rapidity. The rapidity of translation decreases with an increase of the number of the atoms contained in the ion. The nature of the component elements has an influence on the rapidity of translation, which, however, is distinct only in ions of simple composition. If the number of the atoms in an ion is more than about twelve the rapidity of translation depends almost exclusively on this number. The totality of these results justifies the conclusion that a sufficiently approximate determination of the maximum conductivity of an acid can be arrived at from its composition alone.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Plaster of Paris.—Where can I obtain particulars as to the various details of the manufacture of the above?—Gypsum.

MEETINGS FOR THE WEEK

Monday, 4th.—Medical, 8.30.
—— Society of Chemical Industry, 8. "Some Industrial Applications of Oxygen," by Dr. T. L. Thorne. "Note on Improved Laboratory Apparatus," by Dr. T. W. Leathes.
—— Royal Institution, 5. General Monthly Meeting.
Tuesday, 5th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin —II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Pathological, 8.30.
Wednesday, 6th.—Society of Arts, 8.
—— Geological, 8.
Thursday, 7th.—Royal, 4.30.
—— Royal Institution, 3. "The Metamorphoses of Minerals," by Prof. J. W. Judd.
—— Royal Society Club, 6.30.
—— Chemical, 8. "Researches on the Constitution of Azo- and Diazo-Derivatives—Part V.," by R. Meldola, F.R.S., and G. T. Morgan. "Résume of Researches on the Laws of Substitution in the Naphthalene Series," by H. E. Armstrong. "The Action of Nitric Acid on Anthracene," by A. G. Perkin. "Note on Methyl Fluoride," by N. Collie.
Friday, 8th.—Quekett Club.
—— Astronomical, 3. (Anniversary).
—— Royal Institution, 9. "Electrostatic Measurement," by Sir William Thomson, F.R.S.
Saturday, 9th.—Royal Institution, 3. "The Character of the Great Composers and the Characteristics of their Works," by Prof. E. Pauer.
—— Physical, 3. Annual General Meeting. "On Physico-Geometrical Models," by Prof. A. S. Herschel.

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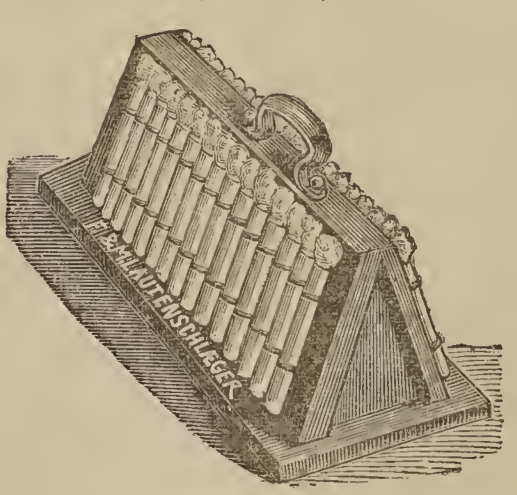

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THE CHEMICAL NEWS.

Vol. LIX. No. 1524.

THE DECOMPOSITION OF POTASSIUM CHLORATE IN CONTACT WITH METALLIC OXIDES.

By Dr. W. R. HODGKINSON and F. K. S. LOWNDES.

In the Chemical News, vol. lviii., p. 309, we mentioned a number of qualitative reactions bearing on the function of MnO_2 and other oxides in the decomposition of potassium chlorate by heat. Our work on this subject is now so far advanced that we are enabled to give a more rational explanation of this peculiar action supported by analyses.

It is usually supposed that when $KClO_3$ and MnO_2 are heated together, the MnO_2 remains as such in the vessel together with KCl. In only exceptional cases does this appear to be the case. The manganese is to a greater or less extent in the form of lower oxides. Only when the mixture has been heated until the whole of the oxygen is driven off and a gentle heat maintained for some time, is the manganese completely re-oxidised.

In one case only out of a number, 14 or 15, were we able by continuous heating to obtain MnO_2. In this series of experiments a weighed quantity of pure $KClO_3$ was heated with a weighed amount of MnO_2 in a cleaned weighed test-tube; the residue remaining in the tube was weighed after cooling.

0·2779 $KClO_3$ and 0·0328 MnO_2 gave a residue of 0·1104, consisting of KCl and oxide of manganese. The theoretical quantity corresponding to KCl and MnO_2 being 0·1110, gave a difference of only 0·0006, which could be accounted for by errors of experiment.

Altogether eight experiments on this point were made; they are numbered consecutively.

In experiments 1 and 2 (Table) the loss of oxygen appears to correspond with that contained in the chlorate only. In 6 and 7 the mixture was at first heated to such a temperature that only part of the oxygen was given off; the tube was cooled and weighed, and again heated until the whole of the oxygen was evolved. In 8, after driving off all the oxygen and weighing, a fresh portion of $KClO_3$ was added, and the tube again heated. After the first heating the loss of oxygen was nearly theoretical: experiment, 0·4074; theory, 0·4088. 0·1672 grms. of $KClO_3$ was added containing 0·0655 grm. O. After treating the second time the loss was not so great as it should have been theoretically, it being 0·0638 grm.

In all these experiments it was noticed that just before the last traces of oxygen were being driven off the mass of solidified substance in the tube began to glow as if oxidation was taking place, which passed, more or less, completely throughout the whole mass. These experiments appear to point to the conclusion that the manganese is alternately *reduced* and re-oxidised by the $KClO_3$, but only in exceptional cases is the re-oxidation complete. This reduction in a strongly oxidising atmosphere is probably due to the atomic attraction of the oxygen; in both the $KClO_3$ and MnO_2 they pull at each other, and the force of attraction combined with the decomposing effect of the temperature is sufficient to break up both compounds.

In support of this idea may be mentioned the facts that silver oxide is reduced to the metallic state by just fused $KClO_3$, and PbO_2 is reduced to Pb_3O_4.

The manganese oxide is physically altered, and in nearly all cases we find that a trace of manganate is formed, enough in fact to give a very distinct pink colour to the mass, especially when the chlorate was very largely in excess, and not heated for any length of time. What struck us as very strange, however, was the fact that when this was heated with water the pink colour of the solution was very evanescent, disappearing almost at once. We found the explanation of this peculiarity when, upon mixing with a solution of permanganate, finely divided MnO_2, the colour of the former was completely taken away, and no manganese salt went into solution. It was reduced apparently to MnO_2 and potash. This appears to account for the formation of a manganate apparently never having been particularly noticed. Having found that there was a deficiency in the weight of residue, we next endeavoured to prove that the difference was indeed due to the reduction of MnO_2. In these experiments a weighed quantity of MnO_2 was mixed with an excess of $KClO_3$, and the whole heated to drive off all the O; as soon as the tube was cooled enough water was put in and boiled, the insoluble matter filtered off and well washed on a weighed filter-paper. After drying the whole was again weighed.

	MnO_2 taken.	Residue after filtering, &c. (MnO_2).
Expt. I.	0·0647	0·0643
„ II.	0·0600	0·0618

It appears from these experiments that the manganese is in the state of dioxide, and that these experiments contradict the previous ones.

This, however, is probably not the case, as the water used for washing seems to be decomposed by the lower oxides formed, and the oxygen re-oxidising them to MnO_2. In fact, a considerable quantity of some gas is always given off as soon as the water is added. This we take to be hydrogen from the decomposed water, but have not yet been able to collect in quantity for proof.

As is partly known, a large number of other oxides enable potassium chlorate to give its oxygen up at a lower temperature. The action on the chlorate depends, however, upon the nature of the oxide. Some, in addition, cause the evolution of quantities of chlorine, but only those oxides capable of giving salts with the potassium oxide do this to any extent.

Some basic oxides act on the MnO_2, but do not give off Cl; others, such as SiO_2, TiO_2, are quite inactive, although they are to a certain extent acid-forming oxides, but only at a very high temperature. A number of analyses have been made by us to ascertain the relation between the amount of oxide used and the quantity of chlorine liberated. The following oxides were used:—$(UO_2)(OH)_2+OH_2$, U_2O_5, and V_2O_5. In these experiments 3 grms. pure $KClO_3$ were mixed in a small distilling bulb with a weighed quantity of the oxide under examination, and the gases obtained by heating sent

No	$KClO_3$.	MnO_2.	Theory O for MnO_2.	Theory O for $KClO_3$.	Total O theoretical.	Loss of O found.	Difference between theory and experiment.
1.	0·4235	0·0990	0·0091	0·1649	0·1740	0·1669	0·0071
2.	0·7109	0·1068	0·0098	0·2768	0·2866	0·2762	0·0104
3.	0·2779	0·0328	0·0030	0·1800	0·1110	0·1104	0·0006
4.	1·0161	0·0502	0·0046	0·3980	0·4026	0·3900	0·0126
5.	0·9155	0·0979	0·0101	0·3553	0·3654	0·3629	0·0025
6.	0·3383	0·0698	0·0064	0·1312	0·1378	0·1322	0·0056
7.	0·7434	0·1859	0·0170	0·2910	0·3080	0·2935	0·0145
8.	1·1930	0·1440	0·0104	0·4639	0·4733	0·4712	0·0021

through the side tube into a solution of KI; the amount of liberated I was then determined by standard thiosulphate solution, and calculated into chlorine.

I. *Yellow Hydrated Oxide of Uranium*, $(UO_2)_2(OH)_2+H_2O$.

Equation for reaction—

$$2KClO_3+2(UO_2)(OH)_2+2H_2O=2H_2O+K_2U_2O_7+ +Cl_2+O_4.$$

(3 grms. $KClO_3$ used).

α. 0·0698 uranium oxide liberated 0·00740 Cl
Theoretical amount of Cl = 0·00760 ,,

β. 0·1127 uranium oxide liberated 0·01285 Cl
Theoretical amount of Cl = 0·01227 ,,

γ. 0·1292 uranium oxide liberated 0·01443 Cl
Theoretical amount of Cl = 0·01407 ,,

II. *Red Oxide of Vanadium*, V_2O_5.

(3 grms. chlorate used).

α. 0·0202 uranium oxide liberated 0·00888 Cl
Theoretical amount of Cl = 0·009 ,,

β. 0·0304 V_2O_5 gave 0·010545 Cl
Theoretical amount of Cl = 0·0109 ,,

γ. 0·0259 V_2O_5 gave 0·00934 Cl
Theoretical amount of Cl = 0·00925 ,,

Uranium pentoxide, black or dark green, scarcely acts upon $KClO_3$, and the chlorine evolved is not a proportionate amount.

α. 0·2295 U_2O_5 gave 0·00226 Cl
Theoretical amount of Cl = 0·0284 ,,

β. 0·21615 U_2O_5 gave 0·001319 Cl
Theoretical amount of Cl = 0·0269 ,,

A number of salts, especially those of ammonia, are very active in decomposing $KClO_3$, and are of course at the same time decomposed by it. NH_4Cl, when heated with $KClO_3$, evolves an amount of chlorine equal to that contained in itself, but the nitrogen apparently is not oxidised.

0·1909 NH_4Cl evolved 0·15995 Cl
Theoretical amount of Cl = 0·15600 ,,

$$6NH_4Cl+4KClO_3=12H_2O+4KCl+3Cl_2.$$

With some other ammonium salts we are not so sure that some oxide of nitrogen or nitrogen oxychloride is not formed.

Tungstic and molybdic oxides are so eminently acid that we did not think it worth while to do any quantitative experiments with them. They no doubt expel all the chlorine. Ordinary cerium oxide, Ce_2O_3, containing La and Di, does not appreciably act on melted chlorate.

Royal Military Academy,
Woolwich.

SOLUTION FOR DEPOSITING METALLIC COBALT.

By H. N. WARREN, Research Analyst.

The cobalt salt, preferably the chloride, is dissolved in a sufficiency of water at a temperature of about 100° F., and a concentrated solution of Rochelle salt added until tha bulky precipitate at first formed has almost entirely re-dissolved. The solution, filtered if necessary from any insoluble precipitate, is electrolysed with the utmost ease by connecting the article intended to receive the deposit with the negative electrode of any single cell battery. The opposite, or positive electrode, which is composed of a zinc rod immersed in a saturated solution of either ammonium chloride or common salt, and protected from contaminating the cobalt solution by the intervention of a porous pot surrounding the zinc. On completing the circuit the cobalt is immediately deposited in a uniform layer, and at the same time presenting a perfectly bright surface. On substituting nickel chloride in place of the cobalt salt metallic nickel may be similarly deposited. It has also been observed on several occasions that by employing a solution holding both nickel and cobalt salts in solution that the deposit thus obtained was considerably darker as regards shade, and also more durable than when cobalt alone was used, the deposit thus produced consisting of both nickel and cobalt in almost exact proportions. Zinc and several other metals may be also deposited by the same means.

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18, Albion Street, Everton, Liverpool.

RESEARCHES ON COBALT AND NICKEL.

By GERHARD KRUSS and F. W. SCHMIDT.

The authors, who were engaged in a re-determination of the atomic weights of these metals, did not succeed in obtaining either the values of Zimmermann (Co=58·74, Ni=58·56), nor the almost respectively identical figures of Russell and Winkler. It was found impossible to precipitate from a neutral solution of gold chloride an equivalent quantity of absolutely pure gold by means of nickel or cobalt. In consequence of polarisation traces of cobalt and nickel were re-precipitated from the solutions of cobalt or nickel which had been formed and remained in admixture with the gold. In order to determine the quantities of metal which had entered into reaction, the precipitated gold, after being perfectly washed, dried, and ignited, was weighed. It was then re-dissolved in aqua regia, and, after expelling the excess of acid, the gold in solution was precipitated with sulphurous acid. The weight of gold thus obtained was smaller than the former weight, and the difference of both values was deducted from the weight of the cobalt or nickel originally employed.

Despite these precautions the results were so fluctuating that their differences could not be due to ordinary analytical errors. It became therefore necessary to examine the solutions and washing-waters. On washing the gold thrown down by means of sulphurous acid from a solution of the metal precipitated by cobalt, the authors observed the following phenomenon:—The red colour of the filtrate, owing to cobalt chloride, became by degrees paler, and changed then to a faint greenish shade, barely perceptible. This portion of the washings was therefore collected separately, and evaporated down in a platinum capsule. After ignition it left a slight residue, which dissolved with a fine green colour in hot and strong hydrochloric acid: on cooling the liquid became almost completely colourless.

Analogous phenomena were observed in determining the atomic weight of nickel. Here also, by concentrating the last washings and re-dissolving in hydrochloric acid, there was obtained the solution of a chloride in which neither nickel chloride nor any other known compound could be detected. The quantity of this chloride being very small, the authors instituted a number of experiments, and finally obtained a pure oxide by utilising the observation that the oxide in question was soluble in melting alkali, in which nickel and cobalt oxides are insoluble. These experiments will shortly be described in full.

The acid solution of the chloride is not precipitated by sulphuretted hydrogen, but ammonium sulphide throws down a blackish sulphide from the nentral solution. Ammonia precipitates the neutral solution of the chloride in voluminous white flakes, resembling zinc or aluminium hydroxide. An excess of ammonia does not re-dissolve the precipitate.

Semi-normal potassa also throws down a snow-white hydroxide, which cannot be re-dissolved, even by a great excess of the precipitant. This excludes alumina, of which not the slightest trace could be detected in the oxide in question. If moistened with a solution of cobalt and ignited it yielded not Thénard's blue, but took a faint light brown colour. If strongly ignited for a long time with the blast the oxide yielded a fine white powder, which dissolved readily and completely in cold hydrochloric acid at 27 per cent of strength. The strongly acid solution of the chloride displayed its peculiar greenish yellow colour. When perfectly dry and free from excess of acid the chloride is white, and forms a colourless solution in water. If the white chloride is treated with the vapour of hydrochloric acid it turns green and yields a green solution in water.

In a current of hydrogen the oxide does not behave like the nickel and cobalt oxides, since even at the strongest heat it undergoes no loss of weight. But the metal corresponding to the white oxide can be obtained by the electrolysis of an aqueous solution of the chloride. The chloride can likewise be reduced at a red heat in a current of hydrogen if it has been previously dried in a current of carbonic acid. The metal is black, or in thin layers a brownish black, readily soluble in acids if it has been obtained electrolytically in the cold; but it is much less readily soluble if it has been heated to redness or whiteness in a current of hydrogen.—*Berichte der Deutschen Chemischen Gesellschaft*, Vol. xxi., No. 1, p. 11.

INCOMPLETENESS OF COMBUSTION IN GASEOUS EXPLOSIONS.*

By Prof. HAROLD B. DIXON, F.R.S., and H. W. SMITH, B.Sc., Dalton Chemical Scholar, Owens College

In the course of an investigation in which we were engaged, on the rate of propagation of gaseous explosions, it was noticed that when a mixture of hydrogen and oxygen, in the proportions in which they combine to form water, was exploded, there remained an explosive residue in addition to the unavoidable slight excess of one or the other gas due to inaccuracy in mixing. The mixture was exploded in a leaden tube 100 m. long and 9 m.m. in diameter; after the explosion the tap at one end was opened, and air allowed to rush in. Air was then pumped in by a bellows, and the other tap was then opened. On applying a light to the out-rushing gases for the purpose of determining whether the hydrogen or the oxygen was in excess in the original mixture, the gas at first driven out proved to be rich in oxygen—supporting combustion vividly—and then the succeeding gas burnt with a series of sharp cracklings, and finally there was a flash down the tube.

From this it appeared that even in a mixture of hydrogen and oxygen, containing a slight excess of oxygen, the hydrogen was not completely burnt. If the mixture had contained an excess of hydrogen it might have been reasonably supposed that the explosive residue was made up of the excess of hydrogen and the air admitted after the explosion. This explanation could not be admitted in the present instance, as the mixture contained an excess of oxygen. A similar phenomenon was observed when a slight excess of hydrogen was employed, and the residue was swept out of the tube by a stream of carbonic acid gas.

Led by these experiments we began the investigation, an account of which is given in the following paper. Our object was to determine the conditions affecting the amount of this explosive residue, especially the influence of the surface exposed to the exploding gases.

Mixtures containing slight excess, first of hydrogen and second of oxygen, were employed, and in all cases the residues were collected and analysed. The first series of experiments was made with the tube mentioned above, which was 100 m. long and 9 m.m. in diameter, the surface exposed to the gases being about 29,000 sq. c.m. After each explosion CO_2 was admitted at one end of the tube until the pressure was equal to that of the atmosphere, and then one litre was driven out and collected over caustic soda solution at the other end of the tube. It was found that the first litre driven out contained practically all the gas left after explosion. The amount of residue varied from 100 to 250 c.c., according to the accuracy of the mixture and the amount of nitrogen as impurity in the original gas, and of air in the CO_2. We give below the mean results of analysis of a considerable number of residues; those given under A resulting from a mixture containing an excess of hydrogen, whilst in those given under B and C the original gas contained oxygen in excess.

I.

Explosions of Hydrogen and Oxygen.

(Capacity of tube, 8100 c.c.; diameter, 9 m.m.; internal surface, 29,000 sq. c.m.).

Mean composition of residue—

Average residue.		A.	B	C.
A—150 c.c.	H_2	54·3	29·5	20·5
B—160 ,,	CO		5·1	5·8
C—220 ,,	O_2	19·4	38·1	32·7
	N_2	26·3	27·3	41·0
		100·0	100·0	100·0

Per cent of original detonating gas unburnt—

Maximum	1·08	0·92	1·07
Minimum	0·69		
Mean	0·88		

With regard to the calculation of the amount of unburnt detonating gas, a slightly different method is employed according as the original gas contains excess of oxygen or hydrogen. All the residues contain a certain percentage of nitrogen, part of which is due to inleakage of air, and to air in the CO_2, used for sweeping out the tube, whilst part exists as impurity in the original gas, being chiefly derived from the water in the gas-holder. It is, however, impossible to determine accurately how much is due to each cause. In calculating the percentage of unburnt detonating gas, a maximum and minimum are taken in following way:—Firstly, assume all the nitrogen was present in the original gas, and calculate all the oxygen as belonging to the unburnt residue. This gives a maximum value for the percentage unburnt. Secondly, assume that all the nitrogen got in (as air) after the explosion, and from the percentage of oxygen deduct the amount of oxygen corresponding to the nitrogen (as air). In this way we get a minimum value for the amount of unburnt detonating gas, and the true percentage must lie between these limits. If there is a sufficient excess of oxygen we get only one value for the unburnt residue, viz., 1½ times the residual hydrogen. It will be observed that each of the residues contains a small percentage of carbonic oxide. Part of this is probably due to the grease used for the taps, and part may be due to hydrocarbons derived from the zinc used in the preparation of the hydrogen (except in cases where electrolytic gas was used). The carbonic oxide being a combustible gas must be taken into account in calculating the residual detonating gas. When there is an excess of oxygen the carbonic oxide is liable to get burnt, and therefore should be considered as a portion of the detonating gas left unburnt. When there is a deficiency of oxygen the carbonic oxide may be classed with the excess of hydrogen left over, and whether it affects the amount of unburnt detonating gas depends upon the quantity of oxygen remaining.

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* A Paper read before the Manchester Literary and Philosophical Society, Oct. 2nd, 1888.

To determine the influence of the amount of surface exposed to the gases, a tube 4 m.m. in diameter was next employed. The length was about 170 m., and the internal surface, 25,000 sq. c.m., the capacity being 2750 c.c. The method of procedure was the same as before. Under A in the following table is given the mean of several analyses of residues from mixtures containing an excess of hydrogen, and under B, the mean result from mixtures containing an excess of oxygen.

II.

	A.	B.
H_2	46·1	38·6
CO	14·9	12·4
O_2	16·3	25·4
N_2	22·7	23·6
	100·0	100·0
Average residue	75 c.c.	82 c.c.

Per cent of original detonating gas unburnt—

Maximum . ..	1·34	2·27
Minimum.. ..	0·84	1·55
Mean	1·09	1·91

The per cent unburnt under A does differ much from that obtained with the wider tube. Under B we see a rather larger percentage. In the next tables are given the means of analyses of residues obtained with a tube 19 m.m. in diameter (III.), and lastly (IV.), with an iron bomb made out of an ordinary mercury bottle attached to a firing tube. In the latter there are only about 1600 sq. c.m. of surface exposed for a volume of 3075 c.c.; that is to say, a surface only $\frac{1}{15}$ as great as that exposed in the 4 m.m. tube, the capacities being, however, nearly equal. From the analyses it would appear that although the amount of surface exposed to the gases has some influence on the amount unburnt, the influence is not very great, and therefore it seems improbable that the incompleteness of combustion is due to the cooling action of the surface of the vessel.

	III.	IV.
	C=14,000 c.c.	C=3075 c.c.
	d=19 m.m.	d=100 m.m.
	S=28,000 sq. c.m.	S=1600 sq. c.m.
Average residue	235 c.c.	100 c.c.

Mean composition of residue—

H_2	44·2	8·2
CO	18·0	1·2
O_2	22·7	31·1
N_2	15·1	59·5
	100·0	100·0

Per cent of detonating gas unburnt—

Maximum ..	1·16	0·46
Minimum ..	0·86	
	1·01	

A number of experiments were made with a mixture of carbonic oxide and oxygen.

In the first series of experiments the 9 m.m. tube was employed, and in the second series, the iron bomb. The mean results are given below.

Carbonic Oxide and Oxygen.

	I.	II.
	C=8100 c.c.	C=3075 c.c.
	d=9 m.m.	d=100 m.m.
	C=29,000 sq. c.m.	S=1600 sq. c.m.
Average residue	205 c.c.	55 c.c.

Mean composition of residue—

CO	26·0	41·4
H_2	1·7	6·7
O_2	30·2	27·1
N_2	42·1	24·8
	100·0	100·0

Per cent unburnt—

Maximum	1·06	1·17
Minimum		1·01
Mean		1·09

In this case, therefore, we have also about 1 per cent of the original detonating gas left unburnt. The surface here does not appear to have much influence, the percentages unburnt being almost the same, although the surface exposed to the gases was, with the tube, about 3½ sq. c.m. for each 1 c.c. of gas burnt, against 0·5 sq. c.m. per 1 c.c. of gas burnt with the bomb.

The fact that the incompleteness of combustion is characteristic of the explosive wave, and is not observed in the ordinary combustion in a eudiometer, has an important bearing on the theory proposed by Berthelot to explain the mode of propagation of the explosive wave, and also seems to confirm the observation made by Mallard and Le Chatelier, that the rate of cooling in this method of combustion is much more rapid than in the ordinary combustion.

THE VOLUMETRIC COMPOSITION OF NITROGEN OXIDES AND OTHER GASEOUS COMPOUNDS.

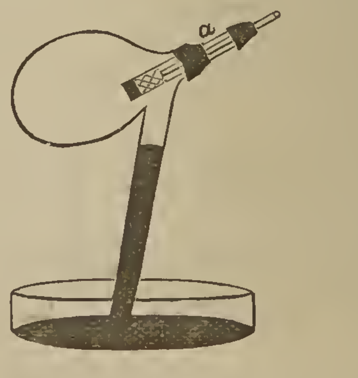
By P. HAWKRIDGE, B.A., late Scholar, Clare College, Cambridge.

CERTAIN text-book experiments have long been a puzzle to the Chemical Demonstrator, one in particular wherein it is proposed to determine the composition of certain gases by imprisoning them in a bent tube over mercury, the decomposition being affected by sodium, on the application of heat. The innocency of the pictorial representation is only equalled by the difficulty of its realisation. I think I am right in saying that few lecturers attempt these experiments, and yet they would be a welcome relief from the wearisome "Preparation and Properties" that are the bane of the chemical lecture room in so many cases.

The following description deals with practical methods for estimating the composition of several gases.

The chief trouble has been to get the metal into position without contact with the mercury. This difficulty is overcome as follows:—

Take a two-ounce retort. In the tubulure insert a closely fitting glass tube, A, and fasten it to the tubulure by external indiarubber tubing. The interior end of tube A is closed by a plug of Italian asbestos rammed tight; next to it is the metal to be used, K, Na, Sn, &c., also closely packed to exclude as much air as possible; finally insert a glass rod, fitting closely into A, occupying the remainder of its length, and projecting beyond it. This is also fastened to the tube A by external indiarubber tubing. Fill the retort with mercury, place vertically



over the mercurial trough, pass up the gas, N_2O, H_2S, &c. Close the end of the neck by the finger, cork, or cushion, and push the glass rod; the asbestos plug and metal fall into the bulb of the retort. Ligature all joints with copper wire, unclose the end of the neck, mark the height of the mercury, and effect the decomposition by heating the metal in the bulb.

As above described, the apparatus is only suitable for gases which, like N_2O and H_2S, have little or no action on the metals in the cold, and where no change of volume results. However, the system of rod, tube, and asbestos plug may be fixed on to the end of a bent tube, placed as in the text-book experiment; but, of course, the end must in that case be left open for the purpose. In this case the bent tube simply replaces the retort, and the experiment now becomes moderately well adapted for cases where the volume does not remain the same, as in the case of nitric oxide.

The method is inexpensive and efficacious.

I take this opportunity to point out that the retort, placed vertically as indicated in the above experiment, is a very good substitute for the much more expensive apparatus usually employed for demonstrating the composition of carbonic and sulphurous anhydrides. A little ingenuity will show how it should be used.

Schools of Science and Art,
Newcastle-on-Tyne.

ON A NEW THORIUM MINERAL, AUERLITE.[*]

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

While one of us was about completing a contract for twenty-six tons of zircons, to supply a recent large demand for that mineral, several crystals of the mineral forming the subject of this paper were noticed in the very last shipments from the mine. As the quantity then found was insufficient for a complete chemical and physical examination, the locality was re-visited in July last, and for five weeks a systematic and laborious search for the mineral *in situ* was carried on. We had already proved it to be a hydrous mineral rich in thoria, with silica and, strangely, a very appreciable quantity of phosphoric acid. Our interest was centered upon its apparent anomalous composition, and a series of careful analyses were made by one of us as soon as the necessary material was procured. As the result of the search at the locality, not quite 100 grms. were found, and it became necessary to mine over 200 kilos. of zircons to get even this small amount.

It has thus far been found at only two places in Henderson County, North Carolina, namely, at the well-known Freeman mine, on Green River, and on the Price land, three miles south-westerly. At both places it occurs in disintegrated granitic and gneissic rocks intimately associated with crystals of zircons, and it is often seen implanted upon them—as a second or after-growth—in parallel position.

The colour on a fractured surface ranges in different crystals from a pale lemon-yellow through various shades of orange to a deep brown-red. The form is distinctly tetragonal, only the unit pyramid and prism being observed, and, excepting a tendency to a longer prismatic development, it is much like the common type of zircon found throughout the region. The faces being very rough and uneven, no constant angles could be obtained on any of the material, but they closely approximate to those of zircon.

Fragments of the mineral resemble some varieties of gummite and deweylite, but have a more waxy or rosin-like appearance. It is sub-translucent to opaque, and has a dull yellowish-white exterior. It is very brittle and easily crumbled. The hardness varies from 2·5 to 3, some crystals barely scratching cleavage surfaces of calcite. The specific gravity has a wide range, *i.e.*, from 4·422 to 4·766, the dark orange-red crystals having the highest density.[*]

The largest mass found measured 1 c.m. through the prism, and it was evidently only part of what had been a long crystal. The bulk of what we collected is in a very fragmentary condition, down to masses and broken crystals of 1 m.m. diameter.

Our analyses have given the following results:—

	1.	2.	3.	4.	5.
H_2O }	10·7	—	11·21	—	9·88
CO_2 }				—	1·00
SiO_2	—	9·25	7·64	8·25	
P_2O_5	—	—	7·46	7·59	
ThO_2	—	69·23	70·13		
Fe_2O_3	—	1·42	1·38		
CaO	—	—	0·49		
MgO	—	—	0·29		
Al_2O_3, &c.[†] ..	—	—	1·10		
			99·70		

If the amount of CO_2 in analysis No. 3 is assumed to be the same as it is in 5, and if we take the amount of H_2O as the difference between the loss on ignition and the CO_2, the ratio of hydrogen equivalents, of bases and acids (assuming the carbonates to be admixed impurity), is nearly 2 : 1 : 2. This gives the formula—

$$ThO_2, \left\{ \begin{matrix} SiO_2 \\ \frac{1}{3}P_2O_5 \end{matrix} \right\} 2H_2O,$$

or a thorite in which part of the silica is replaced by its equivalent in phosphoric acid, when $3SiO_2 = 1P_2O_5$. The ratio of silica to phosphoric acid is variable, and is approximately 1 : 1 in hydrogen equivalents; but the P_2O_5 tends to be in excess.

We have considered it possible that this mineral is a mixture of a hydrated thorium phosphate with a hydrated thorium silicate, in some respects analogous to the occurrence of zirconium silicate (zircon) in parallel position with yttrium phosphate (xenotime),[‡] although there is nothing in the appearance to suggest this—the mineral seeming to be perfectly homogeneous, except on the exposed surfaces. It is more probable, however, that we have here an example of a partial replacement of silica by phosphoric acid, which fact has not yet, to our knowledge, been noticed in the literature of mineralogy; unless we should so regard the small proportion of P_2O_5 (4·17) which Eakins[§] observed in the xanthitane (altered titanite) from the same locality.

This occurrence of a thorium phosphate is the first instance of such a compound existing in nature, and seems to have a direct bearing upon the presence of thorium in monazite, and we believe that the idea that thorium is included in monazite as thorite—mechanically intermixed—should be modified in so much that the thoria should be considered as partially present as a phosphate, and the cerium earths partially present as silicates.

This mineral is readily soluble in hydrochloric acid, leaving a residue of gelatinous silica: after ignition it becomes insoluble. Thorium phosphate is generally regarded as a very insoluble compound, but the ready solubility of this mineral seems to disprove that opinion.

It is infusible, and upon strong ignition becomes dull brown, and, on cooling, orange again.

Thorite crystals having the form of zircon have been described by Zschau,[||] Nordenskiold,[¶] and later, Brögger,[**]

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[*] *American Journal of Science*, vol. xxxvi., Dec., 1888.

[*] Some of the crystals were much lighter in colour, softer, and of specific gravity from 3·7 to 3·8. These we propose to examine and report upon later

[†] Including other oxides with traces of thoria.

[‡] *American Journal of Science*, Nov. 1888, p. 380.

[§] *Ibid.*, vol. xxxv., p. 418, May, 1888.

[||] *Ibid.*, II., xxvi., 359; see also "Dana's Syst. Min.," Ed. 1868, p. 413.

[¶] *Geol. För. Förh.*, iii., 226, 1876; see also App. III., "Dana's Min.," p. 121.

[**] *Ibid.*, ix., 258, 1887.

have expressed the opinion that the mineral known as thorite is a pseudomorph after an original thorium silicate analogous to zircon in composition. This view is confirmed by the fact that this new mineral occurs intimately associated with and implanted upon perfectly unaltered zircon.

As this mineral was found while mining the very large quantity of zircons necessary to supply the demand caused by the invention of the system of incandescent gas-lighting of Dr. Carl Auer von Welsbach, we propose to name it *Auerlite* in his honour.

COMMITTEE[*] APPOINTED TO CONSIDER THE BEST METHOD OF ESTABLISHING INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.

Objects.

It is proposed that the Committee shall co-operate with other similar committees in the more important iron-producing countries, in order to provide standard specimens of iron and steel, the chemical composition of which shall have been carefully determined. The specimens adopted as standards shall be entrusted to some recognised official authority, such as the Standards Department of the Board of Trade, and shall be used either for reference in the determination of the accuracy of any proposed method of analysis, or for controlling the results of analyses in any cases of importance which may from time to time arise.

Suggestions.

1. Professor J. W. Langley, of the University of Michigan, U.S.A., to be requested to superintend the production of the samples; that they be prepared and preserved in accordance with the directions to be furnished by the Committee, and that an equal portion of each sample be forwarded to the several Secretaries of the respective Committees in the United Kingdom, America, France, Germany, and Sweden.

2. The specimens which are eventually to be adopted as standards to be supplied to not more than seven representative chemists of repute in each of the countries above mentioned, who shall be requested to analyse the specimens by any method or methods they may prefer.

3. In the event of the analyses giving results, which in the opinion of the Committee may be regarded as sufficiently concordant, the means of the analytical results of each of the several constituents to be adopted as representing the composition of the standards. The report on the analytical results not to be issued before the various analysts, to whom the samples have been submitted, shall have had an opportunity of examining it. The standards shall hereafter be distinguished only by letters or numbers.

4. The attention of the Committee to be for the present confined to four samples of steel, selected as containing as nearly as possible 1·3, 0·8, 0·4, and 0·15 per cent of total carbon respectively. In addition to the determination of the amount of carbon present in each condition, the phosphorus, sulphur, silicon, manganese, and chromium also to be determined.

5. 150 kilos. of the samples selected for examination as standards to be prepared in all. This would give, after allowing sufficient for the required analyses, quite 5 kilos. of each standard for each of the five countries interested. allowing say 10 grms. for each applicant who may desire to use the standards, this would permit of 500 appeals to each of the four standards in each country, or at least 10,000 appeals in all.

6. The samples to be analysed in the United Kingdom by W. Jenkins, Dowlais; Edward Riley, London; J. E. Stead, Middlesbrough: The Royal School of Mines; G. S. Packer, of the Steel Company of Scotland, and two others.

7. The metal of which the samples are to be produced to be cast in small ingots, special care being taken to prevent any irregularity of composition. After the removal of the outer skin the metal to be cut by a blunt tool in the form of thin shavings, then crushed, sieved, and intimately mixed.

8. The samples thus prepared to be preserved in separate small quantities (say of 30 grms. each), which shall be hermetically sealed in glass tubes so as to prevent oxidation.

9. These preliminary arrangements of the Committee to be communicated to the leading technical journals.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.[*]

Methods for Determining Phosphoric Acid and Moisture.

(1). *Preparation of Sample.*—The sample should be well intermixed and properly prepared, so that separate protions shall accurately represent the substance under examination, without loss or gain of moisture.

(2). *Determination of Moisture.*—(*a*). In potash salts, nitrate of soda, and sulphate of ammonia heat 1 to 5 grms. at 130° C. till the weight is constant, and reckon water from the loss. (*b*). In all other other fertilisers heat 2 grms., or if the sample is too coarse to secure uniform lots of 2 grms. each, 5 grms., for five hours, at 100° in a steam bath.

(3). *Water-soluble Phosphoric Acid.*—Weigh out 2 grms. in a small beaker, wash by decantation four or five times with not more than from 10 to 15 c.c. of water, then rub it up in the beaker with a rubber-tipped pestle to a homogeneous paste, and then wash four or five times by decantation with from 10 to 15 c.c. of water. Transfer the residue to a 9 c.c., No. 589 Schleicher and Schüll filter, and wash with water until the filtrate measures not less than 250 c.c. Mix the washings. Take an aliquot (corresponding to $\frac{1}{2}$ grm.) and determine phosphoric acid, as under total phosphoric acid.

(4). *Citrate-insoluble Phosphoric Acid.*—Wash the residue of the treatment with water into a 200 c.c. flask with 100 c.c. of strictly neutral ammonium citrate solution of 1·09 density, prepared as hereafter directed. Cork the flask securely and place it in a water-bath, the water of which stands at 65° C. (The water-bath should be of such a size that the introduction of the cold flask or flasks shall not cause a reduction of the temperature of the bath of more than 2° C.) Raising the temperature as rapidly as practicable to 65° C., which is subsequently maintained, digest with frequent shakings for thirty minutes from the instant of insertion, filter the warm solution quickly (best with filter-pump), and wash with water of ordinary temperature. Transfer the filter and its contents to a capsule, ignite until the organic matter is destroyed, treat with 10 to 15 c.c. of concentrated hydrochloric or nitric acid, digest over a low flame until the phosphate is dissolved, dilute to 200 c.c., mix, pass through a dry filter, take an aliquot and determine phosphoric acid as under total.

In case a determination of citrate-insoluble phosphoric acid is required in non-acidulated goods, it is to be made

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[*] British Association for the Advancement of Science, Section B. Committee:—Prof. Roberts-Austen, F.R.S. (Chairman), Sir F. Abel, C.B., F.R.S., Prof. Langley, Edward Riley, G. J. Snelus, F.R.S., John Spiller, Prof. Tilden, F.R.S., and Thomas Turner (Secretary).

[*] Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

by treating 2 grms. of the phosphatic material, without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, &c.), the residue insoluble in ammonium citrate is to be treated by one of the processes described below.

(5). *Total Phosphoric Acid.*—Weigh 2 grms. and treat by one of the following methods :—(1). Evaporation with 5 c.c. magnesium nitrate, ignition, and solution in acid. (2). Solution in 30 c.c. concentrated nitric acid with a small quantity of hydrochloric acid. (3). Add 30 c.c. concentrated hydrochloric acid, heat, and add cautiously and in small quantities at a time about 0·5 grm. of finely pulverised potassium chlorate.

Boil gently until all phosphates are dissolved and all organic matter destroyed; dilute to 200 c.c.; mix and pass through a dry filter; take 50 c.c. of filtrate; neutralise with ammonia (in case hydrochloric acid has been used as a solvent add about 15 grms. dry ammonium nitrate or its equivalent). To the hot solution for every decigrm. of P_2O_5 that is present, add 50 c.c. of molybdic solution. Digest at about 65° C. for one hour, filter, and wash with water or ammonium nitrate solution. (Test the filtrate by renewed digestion and addition of more molybdic solution). Dissolve the precipitate on the filter with ammonia and hot water and wash into a beaker to a bulk of not more than 100 c.c. Nearly neutralise with hydrochloric acid, cool, and add magnesia mixture from a burette; add slowly (one drop per second), stirring vigorously. After fifteen minutes add 30 c.c. of ammonia solution of density 0·95. Let stand several hours (two hours is usually enough). Filter, wash with dilute ammonia, ignite intensely for ten minutes, and weigh.

(6). Citrate-soluble phosphoric acid. The sum of the water-soluble and citric insoluble subtracted from the total gives the citrate-soluble.

Preparation of Reagents.

(1). *To Prepare Ammonium Citrate Solution.*—Mix 370 grms. of commercial citric acid with 1500 c.c. of water; nearly neutralise with crushed commercial carbonate of ammonia; heat to expel the carbonic acid; cool; add ammonia until exactly neutral (testing by saturated alcoholic solution of coralline) and bring to a volume of two litres. Test the gravity, which should be 1·09 at 20° C., before using.

(2). *To Prepare Molybdic Solution.*—Dissolve 100 grms. of molybdic acid in 400 grms. or 417 c.c. of ammonia of specific gravity 0·96, and pour the solution thus obtained into 1500 grms. or 1250 c.c. of nitric acid of specific gravity 1·20. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phospho-molybdate. Decant the solution from any sediment, and preserve in glass-stoppered vessels.

(3). *To Prepare Ammonium Nitrate Solution.*—Dissolve 200 grms. of commercial ammonium nitrate in water and bring to a volume of two litres.

(4). *To Prepare Magnesia Mixture.*—Dissolve 22 grms. of recently ignited calcined magnesia in dilute hydrochloric acid, avoiding excess of the latter. Add a little calcined magnesia in excess, and boil a few minutes to precipitate iron, alumina, and phosphoric acid; filter, add 280 grms. of ammonium chloride, 700 c.c. of ammonia of specific gravity 0·96, and water enough to make the volume of two litres. Instead of the solution of 22 grms. of calcined magnesia 110 grms. of crystallised magnesium chloride ($MgCl_2,6H_2O$) may be used.

(5). *Dilute Ammonia for Washing.*—One volume ammonia of speeific gravity 0·96 mixed with three volumes of water, or usually one volume of concentrated ammonia with six volumes of water.

(6). *Nitrate of Magnesia.*—Dissolve 320 grms. of calcined magnesia in nitric acid, avoiding an excess of the latter; then add a little calcined magnesia in excess; boil; filter from excess of magnesia, ferric oxide, &c., and bring to volume of two litres.

METHODS OF DETERMINING POTASH.

Method of Lindo as Modified by Gladding.

(1). *Superphosphates.*—Boil 10 grms. of the fertiliser with 300 c.c. of water for ten minutes. Cool the solution; add a little oxalatate of ammonia, and then ammonia in slight excess, thus precipitating all phosphate and sulphate of lime, oxide of iron, and alumina, &c.; make up to 500 c.c., mix thoroughly and filter through a dry filter; take 50 c.c., corresponding to 1 grm., evaporate nearly to dryness, add 1 c.c. of dilute H_2SO_4 (1 to 1), and evaporate to dryness and ignite to whiteness. As all the potash is in form of sulphate, no loss need be apprehended by volatilisation of potash, and a full red heat must be used until the residue is perfectly white. This residue is dissolved in hot water, plus a few drops of HCl; 5 c.c. of a solution of pure NaCl (containing 20 grms. NaCl to the litre) and an excess of platinum solution (4 c.c.) are now added. This solution is then evaparated to dryness in a small dish, the residue taken up with a little water, sufficient to dissolve it, and strong alcohol added. The precipitate is washed thoroughly with alcohol by decantation and on filter as usual. The washing should be continued even after the filtrate is colourless. 10 c.c. of the NH_4Cl solution, prepared as directed, are now run through the filter, or the washing may be performed in the dish. These 10 c.c. will contain the bulk of the impurities, and are thrown away. Fresh portions of 10 c.c. NH_4Cl are now run through the filter several times (five or six). The filter is then washed thoroughly with pure alcohol, dried, and weighed as usual. The platinum solution used contains 1 grm. metallic platinum in every 10 c.c.

(2). *Muriates of Potash.*—In the analysis of these salts an aliquot portion, containing 0·500 grm., is evaporated with 10 c.c. platinum solution plus a few drops of HCl, and washed as before.

(3). *Sulphate of Potash, Kainite, &c.*—In the analysis of these salts an aliquot portion, containing 0·500 grm., is taken, 0·250 grm. of NaCl added, plus a few drops of HCl, and the whole evaporated with 15 c.c. platinum solution. In this case special care must be taken, in the washing with alcohol, to remove all the double chloride of platinum and sodium. The washing should be continued for some time after the filtrate is colourless. 25 c.c. of the NH_4Cl solution are employed, instead of 10 c.c., and the 25 c.c. poured through at least six times to remove all sulphates and chlorides. Wash finally with alcohol, dry, and weigh as usual.

To prepare the washing solution of NH_4Cl, place in a bottle 500 c.c. H_2O, 100 grms. of NH_4Cl; shake till dissolved. Now pulverise 5 or 10 grms. of K_2PtCl_6, put in the bottle, and shake at intervals for six or eight hours; let settle over night; then filter off liquid into a second bottle. The first bottle is then ready for a preparation of a fresh supply when needed.

Alternate Method.

In case the potash is contained in organic compounds like tobacco stems, cotton-seed hulls, &c., it is to be saturated with strong sulphuric acid and ignited in a muffle to destroy organic matter. Pulverise the fertiliser (200 or 300 grms.) in a mortar; take 10 grms., boil for ten minutes with 200 c.c. water, and after cooling, and without filtering, make up to 1000 c.c., and filter through dry paper. If the sample has 10 to 15 per cent K_2O (kainite), take 50 c.c. of the filtrate; if from 2 to 3 per cent K_2O (ordinary potash fertilisers), take 100 c.c. of the filtrate. In each case make the volume up to 150 c.c., heat to 100°, and add, drop by drop, with constant stirring, slight excess of barium chloride; without filtering, in the same manner, add barium hydrate in slight excess. Heat, filter, and wash until precipitate is free from chlorides. Add to filtrate 1 c.c. strong ammonium hydrate, and then a saturated solution of ammonium carbonate until excess of barium is precipitated. Heat. Add now, in fine powder, 0·5 grm. pure oxalic acid or 0·75 grm. ammonium oxalate. Filter, wash free of chlorides, evaporate filtrate to dryness in a platinum dish, and, holding dish with crucible tongs, ignite carefully over the free flame below red heat until all volatile matter is driven off.

The residue is now digested with hot water, filtered through a small filter, and washed with successive small portions of water until the filtrate amounts to 30 c.c. or more. To this filtrate, after adding two drops of strong hydrochloric acid, is added, in a porcelain dish, 5 to 10 c.c. of a solution of 10 grms. of platinic chloride in 100 c.c. of water. The mixture is now evaporated on the water-bath to a thick syrup, or further, as above treated with strong alcohol, washed by decantation, collected in a Gooch crucible or other form of filter, washed with strong alcohol, afterwards with 5 c.c. ether, dried for thirty minutes at 100° C., and weighed.

It is desirable, if there is an appearance of foreign matter in the double salt, that it should be washed, according to the previous method, with 10 c.c. of the half-concentrated solution of NH_4Cl, which has been saturated by shaking with K_2PtCl_6, as recommended by Gladding.

The use of the factor 0·3056 for converting K_2PtCl_6 to KCl and 0·19308 for converting to K_2O are continued.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

January 26, 1888.

Prof. Fuller, F.R.S., in the Chair.

The thanks of the Society were tendered to Mr. Freeman for presenting to the Library a rare and interesting work —"Réflections sur la Puissance Motrice du feu et Sur les Machines propres a dévellopper cette puissance, Par S. Carnot, ancien élèvede L'Ecole Polytechnique.

Dr. S. P. Thompson read three notes on Polarised Light entitled respectively:—"*The Structure of Natural Diffraction Gratings of Quartz*;" "*Ahrens's Modification of Delezenne's Polariser*;" and "*The Use of Two Quarter Wave Plates in Combination with a Stationary Polariser*."

Two microscope slides of iridescent quartz (prepared by the late Mr. Darker), which have recently come into possession of the author, exhibit remarkable peculiarities. Both act like diffraction gratings, one as if the rulings were about 12,000 and the other about 26,000 to the inch. On examining the specimens by the microscope it was found that the parts which exhibited the grating effect showed a spindle-like structure, and by micrometer measurements the dimensions of the spindle-shaped bodies were determined to be from 1-1000th to 1-3000th of an inch in diameter and 1-100th to 1-300th of an inch long. These were much too large to cause the effects noticed, but on closer examination it was found that the bodies were crossed at right angles by fine markings, the distances between which are in close accordance with those deduced from the spectra produced. As a probable cause of the phenomenon the author mentioned a recent paper by Prof. Judd "On the Production of a Lamellar Structure in Quartz by Pressure," and suggested the possibility of making diffraction gratings by such means.

Ahrens's modification of Delezenne's polariser consists of a total reflection prism combined with glass plates and black glass mirror arranged so that the polarised beam is parallel to the original one. The combination of plates and mirror is adopted so as to give enough light and still keep the polarisation sufficiently good. One or two plates laid over the mirror are found to give the best results.

The fact that a beam polarised by reflection is not coincident with the original beam renders it inconvenient, if not impossible, to rotate the polariser, and to overcome this defect the author has arranged two quarter wave plates, one of which may be rotated. The first plate circularly polarises the plane polarised beam, and the second (or rotating one) re-plane polarises it in any desired plane. Objects were shown on the screen to illustrate the degree of perfection attainable by using the new polariser in combination with the two quarter wave plates.

A "*Note on a Relation between Magnetisation and Speed in a Dynamo Machine*" was read by the same author.

In a note presented to the Society in June last it was shown that $\Sigma\rho.\Sigma R = 4\pi n CS$, where $\Sigma\rho$ and ΣR are the magnetic and electric resistances respectively, n = speed, and C and S the numbers of armature and field windings. By writing the equation in the form—

$$\frac{4\pi CS}{\Sigma R} = \frac{\Sigma\rho}{n}$$

it is seen that *when the electric resistance is maintained constant the magnetic resistance is proportional to speed.*

Prof. Herroun read selections from a paper "*On the Divergence of Electromotive Forces from Thermochemical Data.*"

The fact that the electromotive forces of voltaic cells does not always coincide with calculated values has not hitherto received a satisfactory explanation, and this paper describes an experimental research bearing on the question. Several suggested explanations are given. In some cells the anticipated chemical change does not occur, and some metals become coated with oxide or subsalts; others are affected by dissolved gases, and the hydration or solution of the salts formed may supplement or diminish the E.M.F. of a cell, as well as the absorption or evolution of sensible heat.

The question of absorption and evolution of heat is the one chiefly dealt with. If such actions do take place the total heat evolved by passing a definite current through the cell must depend on the direction of the current, and by enclosing the cell in a calorimeter the difference should be detected. The total heat developed by a current, C, in t seconds is—

$$\frac{C^2rt \mp eCt}{J},$$

where r is the resistance of the cell and e the divergence of the observed from the calculated E.M.F., the − or + sign depending on the direction of the current. In the case of mercury cells, which are usually said to give about half a volt excess E.M.F., the heat was found to be independent of the direction of the current. The heats of formation of mercury salts were then re-investigated, and the results showed that Julius Thomsen's numbers (the ones usually accepted) were greatly in excess of the true values. This accounts for the difference between the observed E.M.F.'s and those calculated from Thomsen's numbers. A copper silver-nitrate cell was tested in the calorimeter, and the reversible heat effect agreed closely with that deduced from the "thermo-voltaic constant," or divergence of observed from calculated E.M.F. Other experiments on tin, lead, nickel, and cadmium cells are described, and the chief conclusions arrived at are:—(1) The primary factor in determining the E.M.F. of a voltaic cell is the relative heat of formation of the anhydrous salts of the two metals employed. (2) That this E.M.F. may set up chemical changes of a different direction and character from those predicable from the heat of formation of the dissolved salts. (3) That the E.M.F. set up by (1) may be, and usually is, supplemented by the energy due to the hydration or solution of the solid salts, and may have values which accord with the heat of formation of the dissolved salts. The absorption or evolution of sensible heat depends primarily on the attraction between the salts and water, combined with the heat of solution. Finally, the author states that the E.M.F. of a cell gives a more accurate measurement of chemical affinity than data derived from calorimetric observations.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, February 4, 1889.

Sir JAMES CRICHTON BROWNE, M.D., F.R.S.,
Vice-President, in the Chair

THE following were elected Members of the Royal Institution :—John Tomlinson Brunner, M.P., Augustus Stroh, Sir Charles Tennant, Bart., and John Tennant.

Sixteen candidates for Membership were proposed for election.

The special thanks of the Members were returned to Mr. William Anderson for his present of a portrait of Professor Mendeleeff.

The special thanks of the Members were returned for the following donation to the Fund for the Promotion of Experimental Research :—Professor Dewar, £50.

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 Retrospect of Medicine: Being a Half-yearly Journal containing a Retrospective View of every Discovery and Practical Improvement in the Medical Sciences. Edited by JAMES BRAITHWAITE, M.D. Vol. xcviii., July—December, 1888. London: Simpkin and Marshall.

IN this valuable miscellany we find mention of a reagent producing a peculiar colour-reaction in the urine of patients suffering from typhoid fever. Two solutions are necessary; the one, called A, consists of 1 part of pure hydrochloric acid, 20 parts of water, and saturating with sulphurous acid. Mixture B consists of 1 part sodium nitrite, and water 200 parts. The test solution is made by adding 1 part of B to 25 parts of A, when wanted for use. Equal parts of the urine and of the test solution are mixed in a test-tube. and strong ammonia is freely added to make the whole alkaline. In normal urine the addition of the ammonia merely deepens the colour or produces a light reddish tint, and the deposit of phosphates, after 12 to 24 hours, retains its ordinary grey colour. In typhoid urines there is produced, on the addition of the ammonia, an intense scarlet, carmine, reddish orange, or even purple. The phosphatic deposit is coloured green, violet, or greenish black.

A new anæsthetic, discovered by Lewin, is put forward under the name of erythrophlaeine. Some doubt appears to exist whether this compound—if it is a definite chemical individual—is the active principle of *Erythrophlaeine judiciale*, or an extract from the venom of *Naja Najé*, better known as the cobra. In the latter case great care will doubtless be required in its administration.

For the detection of the bacillus of tubercle, Mr. Fargan recommends a Leitz oil-immersion object-glass of one-twelfth inch focus as quite equal in its performance to the Zeiss of the same power, and at nearly one-fourth of the price.

We find here no reference to any progress in the study of the ptomaines and leucomaines, which compounds a medical contemporary stigmatises as the "great unwashed."

A Year Book of Pharmacy: Comprising Abstracts of Papers relating to Pharmacy, Materia Medica, and Chemistry, contributed to British and Foreign Journals from July 1st, 1887, to June 30th, 1888, with the Transactions of the British Pharmaceutical Conference at the Twenty-fifth Annual Meeting, held at Bath, September, 1888. London: J. and A. Churchill.

WE are happy to perceive that the abstracts in this volume are much better classified than it was in the case of its predecessors a few years ago. We no longer find placed under the general head "pharmacy" notices of manufacturing processes for substances which are not used in the treatment of disease. Many of the abstracts here inserted will have been already seen by most of our readers, but they are here collected in a form very convenient for reference.

The address of the President of the Conference contains not a few passages worth remembrance. We note especially a saying quoted from Nasmyth, of Manchester—"Touch and handle, remembering that gloves, especially kid gloves, are non-conductors of knowledge." Rarely, if ever, have we seen the necessity of experimental training and the impotence of mere book-study and paper-philosophy put so happily.

Those persons who think that everything is managed better abroad than in Britain may look at the course imposed in Belgium alike upon medical men and pharmacists. It includes zoology, which may be useful, but logic and *proh pudor* rhetoric! As we in England are already overrun with rhetoricians, we hope that this act will never be forced upon our medical men and pharmacists.

Elementary Inorganic Chemistry: Theoretical and Practical. With a Course of Chemical Analysis, and a Series of Examples in Chemical Arithmetic. By A. HUMBOLDT SEXTON, F.R.S.E., F.I.C., F.C.S., London: Blackie and Son.

WE do not see that the work before us differs in any striking manner from many other elementary manuals of chemistry. It embraces only a portion of the recognised simple bodies, with their respective compounds; phosphorus, iodine, fluorine, silicon, along with some of their less important congeners, being omitted, whilst of the metals a few only are noticed. The least satisfactory feature of the work is its decidedly examinational character. We had hoped that, in prospect of a change in the educational wind, the compilers of elementary treatises on the sciences would have ventured to turn over a new leaf. We are very sorry to say that Mr. Sexton has made no such attempt. As he informs us in his preface, he "has thought it advisable to keep the requirements of the syllabus of the Department before him in preparing his book." In other words, he tacitly acquiesces in the "sacrifice of education to examination."

Sell's Dictionary of the World's Press. 1889 Edition. London: Sell's Advertising Agency, 167 Fleet Street.

A WORK of 1452 pages, full of important, useful, and, with rare exceptions, accurate information, and published at the low price of two shillings, may be considered as a prodigy, even in these days of enterprise. But we have here more, much more than a mere enumeration of journals of all kinds, with their places of publication and times of appearance.

We find here a careful abstract of the law of libel brought down to the present date, and rendered as intelligible as the subject admits. There are comments on the influence of the Press upon language and style—by no means exclusively favourable. There is a commercial geography of the Indian Empire, and an essay on South Africa as a field for emigration. We find reminiscences of "Printers' Land," that district of London bounded north by Holborn, south by the Thames, and extending from St. Paul's on the east to Waterloo Place on the west, and a quantity of miscellaneous information which must be seen to be fully appreciated.

The weakest side of the work is that which deals with the scientific Press, British and especially foreign. Improvements have, indeed, been effected in this department in comparison with last year's edition, but some of the best known scientific and technical journals are still conspicuous by their absence. This is a point to be regretted, and we trust the proprietor will, in future editions, see his way to bring this part of his great compilation up to the level of the rest.

CORRESPONDENCE.

NICKEL AND COBALT.

To the Editor of the Chemical News.

Sir,—I have read with great interest the results of Krüss's experiments, published in the Chemical News and *Berichte*, on cobalt and nickel. I do, however, *not agree* with Krüss that the atomic weights of these metals, as found by Zimmermann, are in accordance with the periodic system, viz., Co = 58·74 and Ni = 58·56. On the contrary, the atomic weight of cobalt ought to be smaller than that of nickel, *i.e.*, about 57, as its highest oxide is an acid, and that of nickel not, so that the following will be the order of the atomic weights in the periodic system:—

Mn	Fe	Co	Ni	Cu
55	56	57	58·5	63
Mn_2O_7	Fe_2O_6	CO_2O_4 ?		

The atomic weight 58·7 hitherto found for cobalt may be due to the admixture of an element with the atomic weight of 153 or 248, most probably the new element discovered by Krüss.—I am, &c.,

B. Brauner.

Bohemian University, Prague,
February 3, 1889.

SEXTON'S INORGANIC CHEMISTRY.

To the Editor of the Chemical News.

Sir,—I am much obliged to "A Benighted Teacher" for calling my attention to an error which has unaccountably crept into my little book. The sentences should read:—"The composition of the gas may be determined by the first of the methods described for nitrous oxide, potassium being used in place of sodium."

"Leaves half its own volume of N on decomposition with K."

Apologising for occupying your valuable space, I am, &c.,

A. Humboldt Sexton.

Determination of an Alloy of Lead and Tin.—After treating such alloy with nitric acid in order to convert the tin into insoluble stannic acid, it is necessary to neutralise the excess of nitric acid by adding a very dilute solution of sodium hydroxide until a slight precipitate of lead begins to appear. This precipitate is then re-dissolved by means of a few drops of acetic acid, and the analysis is conducted as above.—*Journ. de Pharm.*, Vol. xix., No. 1.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 3, January 21, 1889.

On the Electric Conductivity of Melted Salts.—Lucien Poincaré.—The author concludes that the coefficients of variation are inversely as the densities of the corresponding salts.

On Inverted Sugar.—E. Jungfleisch and L. Grimbert.—The facts observed by the authors lead to the conclusions that powerful acids modify the rotatory power of levulose, increasing it more or less according to circumstances. The levulose of sugar inverted by the procedures in common use is not identical with crystalline levulose, of which it may be considered an alteration-product.

The Extraction of Sorbite.—C. Vincent and M. Delachanal.—Sorbite forms an acetal with benzoic aldehyd. This acetal, by reason of its insolubility in water, renders it possible to extract sorbite rapidly in a pure state, and to detect it in vegetable liquids.

The Dibenzoic Acetal of Sorbite.—J. Meunier.—This compound is represented by the formula $C_{20}H_{22}O_6$, and contains two mols. of aldehyd.

Bulletin de la Société Chimique de Paris.
Vol. li., No. 1.

Preparation of Iodoform.—H. Suilliot and H. Raynaud.—The authors take a solution containing 50 parts potassium iodide, 6 parts acetone, and two parts sodium hydroxide in one or two litres of cold water. Into this they pour, drop by drop, and with constant stirring, a dilute solution of sodium hypochlorite. Iodoform is quickly produced and precipitated. Further additions of the hypochlorite are made until all the acetone or all the iodide has disappeared.

On Tin.—Leo Vignon.—Already noticed under *Comptes Rendus.*

Conversion of Terpilene into a Menthene.—G. Bouchardat and J. Lafont.—It results from these researches that natural menthol should be connected with the terpilene series. This menthol has, with tepilenol or terpilene monohydrate, relations of composition like those which connect allylic alcohol to propylic alcohol.

Identity of the Active Principle of the Strophantus Glabrus of the Gaboon with Ouabaine.—M. Arnaud.—Already noticed.

On Dioxethylic Acetone.—E. Grimaux and L. Lefèvre.—This compound, $C_7H_{14}O_3$, is a colourless liquid of an aromatic odour, which distils at 195°. Its specific density is 0·980 at 17·8°. Its vapour density is 4·95, the theoretic figure being 5·05. It is soluble in alcohol and ether, moderately soluble in water, and volatilises along with watery vapour. It reduces the cupro-potassic liquor energetically, and in heat it reduces ammoniacal silver nitrate, yielding a mirror. It restores the colour of magenta which has been decolourised by sulphurous acid. It represents a mixed function, which has no analogues, being at once an acetone and the ethyl-ether of a bi-primary glycol.

Syntheses of Hydropyridic Bases.—A. and Ch. Combes.—The reactions indicated allow of the formation the derivatives of any closed chain whatever containing a single atom of nitrogen, excepting the pyrrol derivatives.

Reclamation of Priority on the Subject of the Process of M. l'Abbé Godefroy for the Disinfection of Alcoholic Phlegms by Hydrogenation.—Laurent Naudin.

Reply to L. Naudin.—M. Godefroy.—Of this stale controversy no further notice can be taken than to protest against the abuse of the term "disinfection" by both contending parties.

Volumetric Determination of Sulphates. — H. Quantin.—The author dissolves in 200 c.c. of distilled water 19·48 grms. of neutral potassium sulphate and 50 to 100 c.c. of pure hydrochloric acid and pours in slowly, stirring to dissolve the precipitate formed, 24·35 grms. barium chloride previously dissolved. He makes up to 1 litre and filters. Of this solution 50 c.c. precipitate from 0·3 to 0·4 of sulphuric acid. The excess of alkaline chromate involves a deduction as correction in all the readings. This correction is ascertained by precipitating with ammonia, in a total volume equal to that in which the determination is effected, the same quantity of barium chromate as in the analysis itself. Taking afterwards an equal fraction of the filtrate, we add a ferrous solution until a complete reduction is effected. The correction should be about 0·2 to 0·5 c.c. This correction may be determined once for all by precipitating in a flask marked at 1000 c.c. 100 c.c. of the solution with an excess of ammonia, and reducing with the ferrous liquid 100 c.c. of the filtrate mixed with 5 c.c. of pure sulphuric acid. The ferrous liquid is prepared by dissolving 20 grms. double iron and ammonium sulphate and 10 c.c. of pure sulphuric acid in 1 litre of water. The operation is conducted as follows :—1 grm. pure dry potassium sulphate is dissolved in 600 c.c. of water in a flask marked at 1 litre, 100 c.c. of the barium chromate are added and shaken up. When the liquid begins to grow clear it is supersaturated with ammonia, when the liquid becomes of a sulphur yellow. It is filtered, and 100 c.c. of the perfectly clear liquid are taken, and to them are added 5 c.c. of pure sulphuric acid. The solution of iron is dropped in from a burette holding 50 c.c. The liquid turns from red to olive-brown green, and at last bluish green. At this moment little drops of the liquid are taken up with a glass rod and placed upon drops of ferricyanide on a white slab, stopping as soon as there is a blue tint. The solution of ferricyanide must be fresh and so dilute as to appear colourless. The salt must not be used as a dry powder. The actual determination is performed in the same way. Chlorides and nitrates do not interfere; chlorates must not be present and phosphates must be previously eliminated. All such cases may be previously prepared as follows :—The organic matter, if any, is destroyed by projecting the matter in small portions into pure melting sodium nitrate. The mass is dissolved in boiling water, and precipitated with a slight excess of ammonia along with calcium chloride. Lastly there is added a little sodium carbonate and the liquid is filtered.

Journal de Pharmacie et de Chemie.

Vol. xix., No. 1.

Researches on Rhodium.— E. Leidié.— Already noticed.

On the Solom (*Dialium nitidum*).—E. Heckel and Fr. Schlagdenhauffen.—A botanical paper.

On Anagyrine.—E. Hardy and N. Gallais.—Already noticed.

Volumetric Determination of Lead by means of Potassium Ferrocyanide.—M. Yvon.—The author's process is expeditious. It involves neither the separation of tin nor the washing of precipitates. It is founded upon the action of potassium ferrocyanide upon lead salts. The precipitation is complete in the absence of free nitric acid. Free nitric acid does not interfere. The end of the operation is indicated by means of spotting with ferric chloride. The use of heat presents no advantage. Three solutions are needed. 1. A normal lead solution made with 15·987 crystalline lead nitrate and water enough to make up 1000 grms. Each c.c. represents 1 centigrm. of metallic lead. 2. Semi-normal solution of potassium ferrocyanide made with 10·201 grms. of the crystalline salt, and water to make up 1000 grms. Each c.c. represents a centigrm. of lead. The solution of ferric chloride must be so dilute that a drop when deposited upon the porcelain plate is not perceptibly coloured. For titrating the ferrocyanide solution the author pours into a large test-glass 10 c c. of the normal lead solution, and drops in with a burette the ferrocyanide solution, stirring meanwhile with a glass rod. The precipitate deposits rapidly; but it is not necessary to wait until the liquid is clear. When nearly 10 c.c. of the ferrocyanide solution have been added a series of drops of the ferric solution is placed upon a white plate, and a drop of the mixture is applied to one of these with a glass rod. As soon as a blue colour appears the addition of the ferrocyanide is stopped, and the number of degrees consumed is noted. Ten more c.c. of the lead solution are then added, and ferrocyanide is again added until the blue colour appears anew. If the process has been properly managed the second number of degrees read off on the burette will be exactly double the first, and the standard of the ferrocyanide solution is thus found.

No. 2.

On Solom (*Dialium nitidum*).—MM. Heckel and Schlagdenhauffen.—A pharmaceutical paper continued from the previous number. It is interesting to note that this fruit contains free tartaric acid and potasssium bitartrate, unaccompanied as in the tamarind by citric and malic acids.

On the Homopterocarpine and Pterocarpine of Red Santal Wood.—MM. P. Cazeneuve and L. Hugounenq.—From the *Bulletin de la Société Chimique*.

MISCELLANEOUS.

Separation of Stannic Oxide from Tungstic Acid.—E. Donath and F. Müllner.—The ignited and weighed mixture of both bodies as resulting in the analysis of the alloys by decomposition with nitric acid is ground in an agate mortar with twice its bulk of zinc powder or zinc filings, and ignited for fifteen minutes in a covered crucible. The spongy mass is treated with dilute hydrochloric acid (1 part acid and 2 parts water) in a covered beaker until there is no further escape of hydrogen. When it is cold potassium chlorate is added until the tungstic oxide is oxidised to yellow tungstic acid, diluted with 1½ vols. of water, let stand for twenty-four hours. The tungstic acid is washed first with water containing nitric acid, and finally with a dilute solution of nitric acid, and weighed. The tin may be either determined as difference, or directly by precipitating the filtrate with sulphuretted hydrogen.—*Chem. Centralblatt.*

The Oxidation of Hydrogen Iodide by the Oxy-acids of the Halogens.—Oskar Burchard.—In this investigation the author shows that the oxidation of hydrogen iodide by the oxy-acids of the halogens is a regularly progressive movement, the course of which is essentially determined by the concentration of the solution employed. The time requisite for the oxidation of a given quantity of substance depends on concentration in the same manner as Landolt has shown it to be the case in the oxidation of sulphurous acid. Of all the three oxy-acids used the one which acts most energetically upon hydrogen iodide is iodic acid, whilst chloric acid is least disposed to undergo any transformation with hydrogen iodide. The course and the duration of all these processes of oxidation depends on concentration, and it is extremely retarded in mixtures where both the components diminish in equal proportion. The rapidity of the oxidation is greatly increased by an excess of either of the reacting acids, equal equivalents of either producing like effects.—*Zeitschrift für Physikalische Chemie, Stoechiometrie, und Verwandtschaftslehre*, Vol. ii., Part 11.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Plaster of Paris.—(Reply to "Gypsum").—Short account in Bloxam's "Chemistry" (Churchill, London). Longer account in the "British Encyclopædia" (Black, Edinburgh). May be consulted probably at the large Free Libraries.—G. A. KEYWORTH, Hastings.

MEETINGS FOR THE WEEK

MONDAY, 11th.—Medical, 8.30.
— Society of Arts, 8. Cantor Lectures. "Wood Engraving," by W. J. Linton.
TUESDAY, 12th.—Institute of Civil Engineers, 8.
— Royal Institution, 3. "Before and After Darwin —II. Evolution," by Prof. G. J. Romanes, F.R.S.
— Royal Medical and Chirurgical, 8.30.
WEDNESDAY, 13th.—Society of Arts, 8. "Salt; its Production and Consumption at Home and Abroad," by P. L. Simmonds, F.L.S.
— Microscopical, 8. (Anniversary).
— Pharmaceutical, 8.
THURSDAY, 14th.—Royal, 4.30.
— Royal Institution, 3. "The Metamorphoses of Minerals," by Prof. J. W. Judd.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
FRIDAY, 15th.—Royal Institution, 9. "Electrical Stress," by Prof. A. W. Rücker, F.R.S.
— Society of Arts, 8. "The Ruby Mines of Burmah," by G. Skelton Streeter, F.R.G.S.
— Geological, 1. (Anniversary).
SATURDAY, 16th.—Royal Institution, 3. "The Character of the Great Composers and the Characteristics of their Works," by Prof. E. Pauer.

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TAR.

The Directors of the Reading Gas Company are prepared to receive Tenders for the purchase of their TAR for one year from the 1st of April next.

Specifications for the Contracts can be seen at my Office or will be sent on application. Rail and Water communication direct to the Works.

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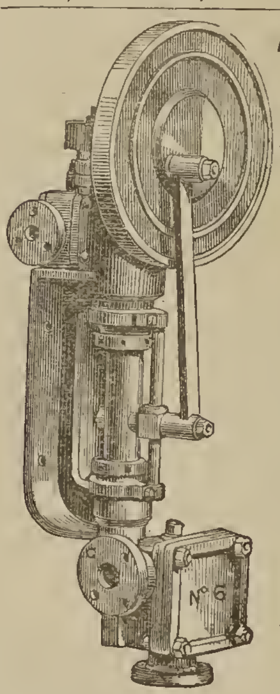

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THE CHEMICAL NEWS.

Vol. LIX. No. 1525.

A NEW SERIES OF ALUMINIUM COMPOUNDS.

Hitherto no substance has been known in which aluminium is present, not as aluminicum, but as aluminosum. A recent discovery has removed this anomaly. On fusing 58 parts of cryolite with 29½ parts of aluminium a double fluoride was obtained having the composition $2NaF,AlF_2$. The operation was first attempted in a crucible of gas-coke, atmospheric air being excluded during the entire process by means of a current of hydrogen. The product being found to be contaminated with aluminium carbide, the experiment was repeated in an iron crucible, polished internally and cased in platinum. The fusion was kept up for five hours, atmospheric air being excluded during the whole time, as before mentioned. The result was a homogeneous white compound, resembling cryolite in appearance, and having the exact composition stated above. It is to be hoped that other aluminous compounds will be obtained.

FERRO-MANGANESE WITH A LOW PERCENTAGE OF CARBON.

By SERGIUS KERN, M.E., St. Petersburg.

The late Mr. R. Hadfield produced a very useful metal, known as manganese steel. The less carbon there was in manganese steel the better it would be. Ferro-manganese containing 80 to 84 per cent of manganese contains also 5 to 6 per cent of carbon. How to eliminate the latter? Manganese is so easily oxidised that use of the refining furnace is out of question.

We desire to propose the use of the decarbonising process, used for the production of malleable castings from pig-iron.

The ferro-manganese, high in manganese, is cast from blast-furnaces into as thin as practically possible flat pigs. These pigs are heated in cast-iron boxes filled with a mixture of three-fourths of hematite powdered iron ore and one-fourth of lime, also in the form of powder.

We made several experiments on a small scale, which proved to be successful.

NOTES ON THE EXPLOSION OF A GAS CYLINDER.

By W. N. HARTLEY, F.R.S., Royal College of Science, Dublin.

On January 28th a lamentable and fatal accident happened to Mr. Thomas Arthur Bewley by the explosion of a cylinder of compressed gas at the shipbuilding yard of Messrs. Bewley and Webb, East Wall, Dublin. The deceased gentleman established machinery for the compression of gases, and supplied the trade with compressed coal-gas and oxygen in wrought-iron cylinders. Owing to the uncertainty of the exact cause of the explosion a good deal of anxiety has been excited amongst the public.

The combustible gas, whether hydrogen or coal-gas, was stored in cylinders painted red and the oxygen in cylinders painted black. This rule was intended to be invariable. On December 27 Mr. Chancellor, of Sackville Street, sent an urgent request for a bottle of oxygen, but there being none of the black cylinders available, owing to the excess of business at Christmas-time, Mr. Chancellor was informed that he could be accommodated with oxygen in a red cylinder. This cylinder was returned on January 15. Afterwards, an application was made for a bottle of hydrogen and one of oxygen. It had been forgotten by the deceased that this bottle was charged with oxygen, and, being red, it was simply filled up and sent out as hydrogen.

It was attached to a lime-light apparatus, when the discovery was made that it contained mixed gases, for the indiarubber connecting tube was blown off as soon as the gas was ignited at the burner. It was placed on one side and labelled "mixed gases." Two days afterwards the bottle was sent back to Mr. Bewley and was placed on a table in the drawing office, where it remained until the fatal occurrence.

Instead of allowing the gas to blow off he tested a small quantity of the gas in a tube in presence of one of his foremen, who described the "spirt" with which it went off when a lighted match was applied to the mouth of the tube. The flame seen was a small blue one. He stated to the foreman that as the amount of inflammable gas was so small he intended to use the cylinder himself as an oxygen cylinder. As the pressure was higher than he required, a portion of the gas was allowed to pass into another black cylinder, which reduced its tension from 800 to 400 lbs. (the breaking strain of the bottle is well over 2000 or 2500 lbs.). It must be remarked that the connecting tube did not fit satisfactorily, and that at the time (2 o'clock) a small gas jet was burning in the room. At 4.25 the explosion occurred, but as no one had been in the drawing office but Mr. Bewley himself the conditions under which the explosion took place are not precisely known. The evidence, however, is fairly conclusive.

In the first place it must be stated that the metal of the cylinder was perfectly sound, and in the interior there was no appearance either of oil or of rust. While the upper part of the cylinder was blown to pieces, the body of it struck the arch over a window and caused the wall to bulge; it then ricocheted apparently against the wall, and passed through a window opposite to where it had first struck. The upper end of the cylinder was found at a much greater distance from the building.

One witness, who saw a gauge on the bottle marking 800 lbs., believed that the cylinder had been overcharged, and that disruption occurred simply by the elastic force of the gas. Having examined the premises, I was in a position to state at the inquest that the nature of the explosion was most certainly that of a detonation. The table and drawers were splintered into match-wood, and the glass from the window, as it lay on the ground, presented the peculiarities of fracture which are characteristic of such an explosion.

The examination of the top of the cylinder just below the shoulder showed that the fractured metal at this part had a different appearance from the other fractured surfaces. Instead of being bright it was burnt all the way round, that is to say, covered with magnetic oxide. Moreover, the medical evidence showed that death was caused by shock, and the force of the explosion threw the body out of the room. While the left hand was severed from the arm at four inches above the wrist, the right was charred, and singeing was noticed on the right leg, and the air was crisp from the same cause.

Without doubt the explosion occurred from the detonation of mixed gases within the cylinder.

The valves of both cylinders, which had been connected by a tube previously, were found wide open. The ignition of the gases was most probably caused, not by any chemical action spontaneously taking place within the cylinder, but either by a leakage, which was tested by applying a match, or, the leakage being serious, the gases were fired by a lighted gas jet. It must be remembered that what was believed to be the same gas had previously exploded in the limelight apparatus, merely blowing off the indiarubber tube, but, the valve being but slightly open, the explosion was not communicated to the interior of the cylinder because the pressure was higher and the issuing gas was travelling at too great a speed for the temperature of ignition to be maintained in the stream issuing from the small orifice in so large a mass of metal.

For the better understanding of this explanation I will refer to a very simple experiment. Carbon monoxide stored in a gas-holder under a pressure of six inches of water cannot be burnt from an ordinary gas jet, but if the size of the orifice is enlarged to 1-16th or 1-8th of an inch it can be made to burn when the pressure is somewhat reduced. There is no material alteration in the conditions of the experiment if the gas be mixed with air or oxygen. In fact, the temperature of ignition cannot be maintained in contact with the cooling mass which surrounds a small orifice, or with the gas under a very rapid rate of flow.

We cannot precisely ascertain the temperature of ignition or the rapidity of explosion of the mixture of gases contained in the cylinder, but it certainly contained a large excess of oxygen, and the conditions under which it was first found to be dangerous were different and less favourable to explosion than after the pressure was reduced.

The verdict of accidental death was coupled with a recommendation that the public should be protected from similar accidents by a Government stamp being fixed to all cylinders used for such purposes. But greater safety would be secured by making the fittings for hydrogen and oxygen cylinders so entirely different that it would be practically impossible to charge a cylinder with wrong gas.

USE OF HYDROGEN PEROXIDE IN ANALYSIS.

By F. P. DUNNINGTON.

Lead peroxide may be most readily dissolved by treatment with dilute nitric acid and a solution of hydrogen peroxide. Half of the oxygen from each of the two peroxides unite to produce an effervescence of oxygen, even when cold, resulting in the formation of a solution of lead nitrate.

A similar action of hydrogen peroxide, I have frequently found of advantage in effecting the solution of a precipitate produced by ammonia and consisting mainly of ferric and alumina hydrates, in which, however, after washing, a little manganese is retained as Mn_2O_3. The latter body will resist solution in dilute acid, and under these circumstances a drop or two of hydrogen peroxide will instantly clear up the solution.

In the same manner, ignited oxide of cerium or oxide of manganese may be readily dissolved by cold dilute acids mixed with hydrogen peroxide.—*Journal of Analytical Chemistry*, Vol. ii., Part 4.

University of Virginia, Sept. 10, 1888.

THE USE OF AMMONIUM DITHIOCARBAMINATE IN ANALYSIS.

By JOSEPH KLEIN.

Ammonium dithiocarbaminate is formed if we pass the ammonia evolved from 150 parts ammonium chloride and 300 parts caustic lime into 600 parts alcohol at 95 per cent, and add to the solution 96 parts carbon disulphide. At 30° ammonium dithiocarbaminate crystallises out alone, and may be collected on a filter, washed with a little alcohol, and dried between blotting-paper. The salt is dissolved in water to a 5 per cent solution, which is very permanent, while the crystals readily decompose.

Determination of Copper.

If a solution of copper sulphate is mixed with the reagent there falls a yellow precipitate of copper dithiocarbaminate. If the solution is hot and is boiled for a few seconds, the precipitate deposits very well. It is soluble on prolonged boiling with an excess of hydrochloric acid, and is decomposed if heated with nitric acid. It is not changed on exposure to the air or on washing. If the precipitate is mixed with sulphur and ignited in a current of hydrogen sulphide it is converted into copper sulphide.

For the quantitative determination of copper the slightly hydrochloric solution is precipitated with ammonium dithiocarbaminate, boiled up, filtered, and washed with hot water; the precipitate is then dried and converted into copper sulphide. No other metals of the fifth group and no metals of the sixth group must be present along with the copper.

Determination of Zinc.

If a solution of zinc sulphate is mixed with ammonium dithiocarbaminate there is formed a white precipitate of zinc dithiocarbaminate soluble in an excess of the precipitant. If the clear solution is then boiled there again occurs precipitation. Zinc dithiocarbaminate is soluble in hydrochloric and nitric acids, but not in acetic acid if the solution is sufficiently dilute. Hence ammonium dithiocarbaminate throws down zinc from a weak acetic solution on gentle heating. On exposure to the air and on washing with hot water zinc dithiocarbaminate undergoes no change. On admixture with sulphur and ignition in a current of hydrogen it is converted into zinc sulphide. On prolonged boiling in an acetic liquid it is decomposed with formation of zinc sulphide, which does not run clear through the filter. Thus, the complete precipitation of zinc as dithiocarbaminate depends on conditions which may be gathered from the following case:—

50 c.c. of a solution of zinc sulphate containing 3·5826 grms. zinc oxide per litre were mixed with a quantity of sodium acetate sufficient for the formation of zinc acetate, 100 c.c. distilled water, and 1 to 1·5 c.c. acetic acid of sp. gr. 1·02. The liquid was heated to a boil and 30 c.c. of a 5 per cent solution of ammonium dithiocarbaminate were added and the boiling was continued for a short time. As soon as no further deposition of the zinc salt took place it was allowed to settle, filtered while still hot, and washed with hot water. The dried precipitate was converted into zinc sulphide.

The filtrate generally passes through clear from the beginning, but it afterwards becomes turbid in consequence of the decomposition of residual ammonium dithiocarbaminate or of sulphuretted hydrogen. When all the filtrate is passed through and the precipitate is washed with hot water we obtain a clear filtrate which no longer becomes turbid. If the filtrate passes through turbid from the beginning some zinc sulphide may have been formed. The filtration is then completed without regarding the turbidity, the precipitate is washed with hot water, the filtrate and washings are concentrated with the addition of a few drops of hydrochloric acid, acidulated with acetic acid, and the remnant of zinc is thrown down with ammonium dithiocarbaminate.

Separation of Copper and Zinc.

The precipitability of copper dithiocarbaminate and the solubility of the corresponding zinc salt might point to the possibility of a direct separation of copper and zinc. Experiment showed, however, that a complete separation of the two metals can be effected only by repeated precipitations, so that the use of ammonium dithiocarbaminate presents no advantage over the ordinary methods.

Behaviour of Ammonium Dithiocarbaminate with Some other Saline Solutions.

Iron, nickel, cobalt, and manganese are not thrown down if the precipitant is added to the hot solutions and sufficient hydrochloric acid is present.

The earthy-alkaline and alkaline dithiocarbaminates are soluble in water. Still, in determining copper in presence of considerable quantities of the alkaline earths or the alkalies, a repeated precipitation of the copper is needful.—*Zeitschrift fur Analytische Chemie* (Vol. xxviii., Part 1, p. 90).

RE-CALCULATIONS OF THE ATOMIC WEIGHTS.[*]

By F. P. VENABLE.

Within the last five years several attempts have been made by chemists of prominence to re-calculate the many atomic weight determinations upon a uniform basis and by uniform methods, and so secure, if possible, a trustworthy table of these most important constants of nature. Our better knowledge of these elements and the increased accuracy of modern methods promised favourably for the success of such an undertaking. That such a revision was called for a glance at the text-books of the time will abundantly show. The greatest variance was shown in the tables of atomic weights given. They seemed to be chosen most arbitrarily. No single authority was recognised, and in many cases it would have been difficult to trace the source of the numbers given. Especially were the differences notable in text-books of different nationalities. Taking two nearly contemporaneous text-books widely used in England, America, and Germany—Watts (1878) and Richter (1881)—I find that out of 64 elements 37 per cent only have the atomic weights the same in both; 22 per cent differ by from 0·10 to 0·25; 20 per cent differ from 0·25 to 0·50; 10 per cent differ from 0·50 to 1·00; and 11 per cent differ by more than 1, the difference in several cases ranging from 25 to 40.

To call such a list a table of constants seems ridiculous, nor does it speak well for chemistry as a science that these, the very foundation stones on which its building is reared, should be so unstable and little trustworthy. Analyses calculated by numbers so different, as in these two tables, must give very different results, one or the other, or perhaps both, of which must be erroneous.

The evil was and is a crying one, and demands the best energies of the wisest chemists to rectify.

The general acceptation of the Law of Periodicity has been another potent factor in drawing attention to the need for careful revision, and in many cases re-determination, of the atomic weights. Those who have undertaken this revision have met with many serious obstacles which are still very far from being overcome. This, I think, will be seen as we proceed in the discussion of the results obtained.

The Unit or Basis.

The first essential is the adoption of a unit of calculation or basis, and this has proved one of the great obstacles in the way of uniformity. Two elements suggest themselves as bases for these calculations—hydrogen and oxygen. For fifty years or more the strife has raged as to which of these should be adopted. Hydrogen has been practically adopted and used, but the opposition to it has only slumbered at times and seems rising again in the past few years. Dalton and Gmelin were the advocates of the hydrogen unit in early days, and Wollaston and Berzelius advocated oxygen. Among the late revisers and recalculators Becker[*] refers all the atomic weights to oxygen = 16. Clarke[†] gives tables calculated either for oxygen = 16 or hydrogen = 1. Sebelien[‡] uses the units hydrogen = 1 or oxygen = 100, as also do Meyer and Seubert.[§] Ostwald[||] uses hydrogen = 1, giving to oxygen the value 16. Van der Plaats[¶] has selected oxygen = 16 as the basis for his re-calculation.

There is a decided predominance of authority in favour of oxygen as the standard and of giving it the value 16, though some would make it appear that this is the same thing as adopting hydrogen = 1.

What points should decide the choice of our unit? They have been ably discussed by Meyer and Seubert,[**] but I must confess they seem to me somewhat blinded themselves by the partisanship of which they accuse their opponents, and I cannot agree with them in all of their conclusions.

I would state as the essentials for the unit element:

1st. That it must be one with which the greatest number of the other elements can be directly compared, thus avoiding the multiplication of error.

2nd. Its own atomic weight must be reasonably small so as not to make too great the higher atomic weights.

3rd. The atomic weights of the other elements got by comparison with it should be, as many of them as possible, integers, or nearly so, rendering calculation easier. In spite of all the tabular and other aids at the command of the chemist of the present day, calculations with an atomic weight having an awkward fraction cause the loss of much time.

Now on examining with a view to these requisites the two elements proposed as units, oxygen alone will be found to answer every requirement.

Nearly all of the present atomic weights have been determined by the aid of oxygen.

Few can be directly compared with hydrogen, and this forms the almost insuperable objection to hydrogen as a standard.

Hydrogen has been used for the past half century for the two last reasons cited among the requisites. As it has the smallest atomic weight, all the others would be above unity if it were taken as the unit. Thus fractional atomic weights were avoided, and again a large number of the other atomic weights compared with it are approximately integers. I am confidant that this is mainly made use of as a matter of convenience and of custom at the present day, and that no special weight is attached to the coincidences with whole numbers. It did give rise to a visionary sort of hypothesis, first enunciated by the Rev. Mr. Prout in 1815, and hence called Prout's hypothesis, that all of the atomic weights were multiples of that of hydrogen, and, as an inference to be drawn, that hydrogen was the primal element of which they were made.

This hypothesis has had many valiant defenders and a large number of most determined opponents, and it has called forth work that has been of immense benefit to the science. It is well that this one good thing can be spoken of so many false suppositions and theories. As an hypothesis it is based on a few coincidences which were to be naturally looked for in the light of mathematics and the law of probabilities. One may say that no absolute proof in its favour has ever been advanced, nor does it seem capable of proof at the present day. A cursory examination would reveal proportionately similar coincidences for some of the other elements. I say proportionately for, of course, the smaller the atomic weight the greater the number of its multiples, and the greater the probability of coincidences within the limits given.

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[*] From the *Journal of the Elisha Mitchell Scientific Society*, Vol. v., Part 2.

[*] "Constants of Nature," Part IV., Smithsonian Institution, 1880.

[†] *Ibid.*, Part V., Smithsonian Institution, 1887.

[‡] "Beiträge zur Geschichte der Atomgewichte," 1884.

[§] "Die Atomgewichte der Elemente," 1883.

[||] "Lehrbuch der Allgemeinen Chemie," 1885.

[¶] *Annales de Chimie et de Physique* (6 serie) 7 April, 1886.

[**] *Berichte der Deutschen Chem. Gesell.*, xviii., 1089.

TABLE No. I.

Factor.	Multiples of 7·98=½ O.	Elements.	Differences.	Multiples of 3·52=½ Li.	Elements.	Differences.	Multiples of 6=½ C.	Elements.	Differences.
2.	15·96	O	0	7·04	Li	0	12·00	C	0
3.	23·94	Mg	0	10·56	Be	+0·44	18·00	—	—
4.	31·92	S	+0·06	14·08	Ni	−0·04	24·00	Mg	+0·38
5.	39·90	Ca	+0·01	17·60	—	—	30·00	—	—
6.	47·88	Ti	+0·13	21·12	—	—	36·00	Cl	−0·55
7.	55·86	Fe	+0·02	24·64	Mg	−0·26	42·00	—	—
8.	63·84	Cu	−0·66	28·16	Si	−0·10	48·00	Ti	+0·12
9.	71·82	Ge	+0·50	31·68	S	+0·38	54·00	—	—
10.	79·80	Br	−0·04	35·20	Cl	+0·25	60·00	Co	−0·90
11.	87·78	Sr	−0·48	38·72	K	+0·41	66·00	Zn	−0·62
12.	95·76	Mo	+0·14	42·24	—	—	72·00	Ger	+0·32
13.	103·74	Ru	−0·24	45·76	—	—	78·00	—	—
14.	111·72	Cd	0	49·28	—	—	84·00	—	—
15.	119·70	Sb	−0·10	52·80	Cr	−0·50	90·00	Zr	+0·70
16.	127·68	—	—	56·32	Fe	−0·32	96·00	Mo	−0·10
17.	135·66	—	—	58·82	Co	+0·28	102·00	—	—
18.	143·64	—	—	63·36	Cu	−0·03	108·00	Ag	+0·06
19.	151·62	—	—	66·88	—	—	114·00	Ir	−0·30
20.	159·60	—	—	70·40	Ga	−0·50	120·00	Sb	+0·29
21.	167·58	—	—	73·92	—	—	126·00	Te	−0·80
22.	175·56	—	—	77·44	—	—	132·00	Cs	+0·88
23.	183·54	W	+0·06	80·96	—	—	138·00	La	+0·50
24.	191·52	—	—	84·48	—	—	144·00	—	—
25.	199·50	Hg	+0·30	88·00	Sr	−0·48	150·00	Sm	+0·20
26.	207·48	Bi	−0·18	91·52	Zr	−0·92	156·00	—	—
27.	215·46	—	—	95·04	Mo	+0·86	162·00	—	—
28.	223·44	—	—	98·56	—	—	168·00	—	—
29.	231·42	Th	+0·54	102·08	—	—	174·00	Yb	−0·80
30.	239·40	U	+0·40	105·60	Pb	−0·60	180·00	—	—
31.	—	—	—	109·12	—	—	186·00	—	—
32.	—	—	—	112·64	Cd	−0·56	192·00	—	—
33.	—	—	—	116·16	—	—	198·00	—	—
34.	—	—	—	119·68	Sb	+0·61	204·00	Tl	+0·15
35.	—	—	—	123·20	—	—	210·00	—	—
36.	—	—	—	126·72	I	+0·14	216·00	—	—
37.	—	—	—	129·24	—	—	222·00	—	—
38.	—	—	—	132·76	Cs	+0·12	228·00	—	—
39.	—	—	—	136·28	Ba	+0·76	234·00	Th	−1·00
40.	—	—	—	140·80	Ce	+0·70	240·00	U	−1·00
41.	—	—	—	144·32	Di	+0·68	—	—	—
49.	—	—	—	172·48	Yb	+0·72	—	—	—
52.	—	—	—	183·14	Ta	−0·34	—	—	—
55.	—	—	—	193·70	Ir	−0·59	—	—	—
56.	—	—	—	197·22	Au	−0·48	—	—	—
57.	—	—	—	200·74	Hg	−0·30	—	—	—
58.	—	—	—	204·26	Tl	−0·11	—	—	—
59.	—	—	—	207·78	Bi	+0·23	—	—	—
62.	—	—	—	218·34	Ng	+0·66	—	—	—
68.	—	—	—	239·46	U	+0·54	—	—	—

I cannot believe that Meyer and Seubert* are serious when they state it as a "striking fact that the atomic weights of more than one-fourth of all the elements are very nearly multiples of the half atomic or equivalent weight of oxygen," giving a table to show this, and adding that "such regularities are worthy of note." They can scarcely be worthy of much note, for such regularities or coincidences would be exceedingly probable where we have sixty or seventy elements with atomic weights under 240, and take a small number with thirty or more multiples in the same range. The smaller the number the more numerous will be the multiples, and consequently the coincidences. To show this I have added to the table of Meyer and Seubert two other lists of multiples and "regularities."

I cannot think that these authors really mean this as in any way a plea for oxygen = 15·96. It must be intended to show the ridiculous nature of the grounds upon which Prout's hypothesis has been based. Certainly they are correct in their deduction that "to attempt to correct the atomic weights by them (*i.e.*, these regularities) would be just as incorrect as to round them off into whole numbers." With such glaring and persistent exceptions as chlorine, chromium, copper, strontium, gold, and others, the hypothesis of Prout must fail to take its place as a law, since no law could be accepted with so large a percentage of exceptions.

It is not necessary to discuss the modifications of Prout's hypothesis which have been proposed—the half-atom or fourth-atom of hydrogen as unit, &c. Such changes really do away with all meaning to the hypothesis, and the valuable idea which Meyer and Seubert acknowledge may lie concealed in it, is lost.

That the hypothesis is still doing yeoman's service to science is shown by the number of new determinations, within the past two years, of the ratio between hydrogen and oxygen. It is evidence of the struggle to retain the old unit hydrogen, and at the same time secure accuracy for it by fixing definitely its relation to oxygen, by means of which nearly all comparisons with the other elements must be made. I fear that much of this work would not have been done if it had been made to appear that the

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* *Loc. cit.*

atomic weight of hydrogen, and not of oxygen, was aimed at. The atomic weight of hydrogen has only the ordinary interest of that of any of the elements. With the atomic weight of oxygen they all stand or fall, no matter which we choose as our theoretical unit. The new determinations referred to are—

Rayleigh (Chemical News, vol. lvii., p. 73), O=15·912.

Cooke and Richards (*Am. Chem. Journal*, vol. x., p. 81), O=15·953.

Cooke and Richards (*Am. Chem. Journal*, vol. x., p. 91), O=15·869.

Keiser (*Am. Chem. Journal*, vol. x., p. 250), O=15·949.

None of them come up, indeed, to the present assumption of O=15·96, so if these investigators are correct, or more nearly correct than those who have preceded them, the whole table of atomic weights must be again shifted.

It is time then that hydrogen were finally discarded as the unit. Oxygen is in every way preferable, and nothing like uniformity will be attained until it is adopted.

With oxygen as the standard, what value shall be assigned to it? Four values have been suggested: 1st, O=1; 2nd, O=10; 3rd, O=16; 4th, O=100.

If O=1 we should have nearly 10 per cent of the elements represented by decimal fractions, and the following partial table would show other inconveniences:—

Al	1·694	Cr	3·284
F	1·194	Fe	3·501
Mg	1·500	Co	3·67
Na	1·4408	Cu	3·95
P	1·940	Mn	3·43
S	2·0037	Ni	3·67
		Ti	3·15
Si	1·754	V	3·20

The differences between the elements are too small for speedy recognition or for easy memorising. O=1 is manifestly too small.

Considering next the fourth suggestion, O=100, we see that just the opposite objection holds good. Over one-fifth of the elements would be represented by numbers exceeding 1000. Few of these could be accurately given as far as the fourth place. For instance, shall gold be represented by the number 1229·4, or 1225·1, or 1234·0, or 1249·0, all of which are actual determinations? From long custom we have come to regard a whole number as being correct and the decimals as indicating approximations. It would seem to be best still to hide our imperfections under the decimals.

The only claim that can be adduced in favour of O=10 is that we will then have the atomic weights on the decimal system. This is not true, however, unless the other atomic weights are multiples of ten. A glance at a few of the elements will show that the numbers would be complicated, rather than simplified, by such an unit.

H	=6·265	F	=11·94
Li	=4·39	Na	=14·408
Be	=5·89	Fe	=35·01
B	=6·83	Co	=36·70
C	=7·502	Mn	=34·30
N	=8·779	Cu	=39·50

That is, the eight first elements, which in our present tables are approximately whole numbers, and in ordinary calculations commonly taken as such (especially in technical analyses, and we must not let theoretical considerations take us out of sight of the practical side of chemistry), are, when compared with O=10, burdened with cumbrous fractions and brought inconveniently near to one another. This last consideration is of especial weight when the clearness of the Periodic Law is considered.

There remains then only O=16 to be considered. The advantage of this unit may be summed up as follows:—

1st. Every atomic weight is above unity and yet not inconveniently large.

2nd. The distance between the atomic weights renders them easy to memorise, and is more convenient for the illustration of the "Periodic Law."

3rd. About two-thirds of the atomic weights are either whole numbers or vary from whole numbers by fractions of $\frac{1}{10}$ or less.

4th. The adoption of this as a unit practically means the retention of most of the numbers so long in use. The valuable literature of the past three or four decades need not be rendered less useful and intelligible to the chemists of the present and the future, as it would be by radical changes in these combining numbers.

Some chemists seem to feel an especial repugnance to this unit because it is too arbitrary and unusual, not bearing upon its face the fact that it is the unit, and again because hydrogen is then represented by the number 1·0025. The arbitrariness of it seems unavoidable: as to why they should be troubled by the number given hydrogen is not very apparent. The fraction is an easy one to handle and may often be neglected. It can make no possible difference in the close calculations of organic chemistry cited by Meyer and Seubert, whether H=1 and O=15·96 or H=1·0025 and O=16. The only thing is to keep the ratio which most exact research reveals as existing between the two. The tendency of the day is toward O=16, and it should be universally adopted. To avoid dangerous assumptions the other atomic weights should be rigidly put down in accord with the most accurate determinations available. This brings us to consider another difficulty and cause of variation.

(To be continued).

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

(Continued from p. 70).

Methods for the Determination of Nitrogen.

The Absolute or Cupric Oxide Method.

(Applicable to all nitrogen determinations).

The apparatus and reagents needed are as follows:—

Apparatus.

Combustion tube of best hard Bohemian glass, about 26 inches long and one-half inch internal diameter.

Azotometer of at least 100 c.c. capacity, accurately calibrated.

Sprengel mercury air-pump.

Small paper scoop, easily made from stiff writing-paper.

Reagents.

Cupric Oxide (coarse).—Wire form; to be ignited and cooled before using.

Fine Cupric Oxide.—Prepared by pounding ordinary cupric oxide in mortar.

Metallic Copper.—Granulated copper or fine copper gauze reduced and cooled in stream of hydrogen.

Sodium Bicarbonate.—Free from organic matter.

Caustic Potash Solution.—Dissolve commercial stick potash in less than its weight of water so that crystals are deposited on cooling. When absorption of carbonic acid ceases to be prompt solution must be discarded.

Loading Tube.

Of ordinary commercial fertilisers take 1 to 2 grms. for analysis. In the case of highly nitrogeneous substances the amount to be taken must be regulated by the amount

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* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

of nitrogen estimated to be present. Fill tube as follows:—(1). About 2 inches of coarse cupric oxide. (2). Place on the small paper scoop enough of the fine cupric oxide to fill, after having been mixed with the substance to be analysed, about 4 inches of the tube; pour on this the substance, rinsing watch-glass with a little of the fine oxide, and mix thoroughly with spatula; pour into tube, rinsing the scoop with a little fine oxide. (3). About 12 inches of coarse cupric oxide. (4). About 3 inches of metallic copper. (5). About 2½ inches of coarse cupric oxide (anterior layer). (6). Small plug of asbestos. (7). Eight-tenths to 1 grm. of sodium bicarbonate. (8). Large, loose plug of asbestos; place tube in furnace, leaving about 1 inch of it projecting; connect with pump by rubber stopper smeared with glycerin, taking care to make connection perfectly tight.

Operation.

Exhaust air from tube by means of pump. When a vacuum has been obtained allow flow of mercury to continue, light gas under that part of tube containing metallic copper, anterior layer of cupric oxide (see 5th above), and bicarbonate of soda. As soon as vacuum is destroyed and apparatus filled with carbonic acid gas, shut off the flow of mercury and at once introduce the delivery tube of the pump into the receiving arm of the azotometer, and just below the surface of the mercury seal off the azotometer, so that the escaping bubbles will pass into the air and not into the azotometer, thus avoiding the useless saturation of the caustic potash solution.

When the flow of carbonic acid has very nearly or completely ceased, pass the delivery tube down into the receiving arm, so that the bubbles will escape into the azotometer. Light the jets under the 12-inch layer of oxide, heat gently for a few moments to drive out any moisture which may be present, and bring to red heat. Heat gradually mixture of substance and oxide, lighting one jet at a time. Avoid too rapid evolution of bubbles, which should be allowed to escape at rate of about one per second or a little faster.

When the jets under mixture have all been turned on, light jets under layer of oxide at end of tube. When evolution of gas has ceased turn out all the lights except those under the metallic copper and anterior layer of oxide, and allow to cool for a few moments. Exhaust with pump, and remove azotometer before flow of mercury is stopped. Break connection of tube with pump, stop flow of mercury, and extinguish lights. Allow azotometer to stand for at least an hour or cool with stream of water until permanent volume and temperature are reached.

Adjust accurately the level of the KOH solution in bulb to that in azotometer, note volume of gas, temperature, and height of barometer; make calculations as usual. The labour of calculation may be much diminished by the use of the tables prepared by Messrs. Battle and Dancy, of the North Carolina Experiment Station (Rayleigh, N.C).

The above details are, with some modifications, those given in the *Report of the Connecticut Station* for 1879, (p. 124), which may be consulted for details of apparatus, should such details be desired.

THE KJELDAHL METHOD.

(Not applicable in presence of nitrates).

Apparatus and Reagents.

(1). Hydrochloric acid, whose absolute strength has been determined (*a*) by precipitating with silver nitrate and weighing the silver chloride, (*b*) by sodium carbonate, as described in Fresenius's "Quantitative Analysis," second American edition, page 680, and (*c*) by determining the amount neutralised by the distillate from a weighed quantity of pure ammonium chloride boiled with an excess of sodium hydrate. Half normal acid, *i.e.*, containing 18·25 grms. hydrochloric acid to the litre, is recommended.

(2). Standard ammonia whose strength, relative to the acid, has been accurately determined. One-tenth normal ammonia, *i.e.*, containing 1·7 grms. ammonia, to the litre, is recommended for accurate work.

(3). "C. P." sulphuric acid, specific gravity 1·83, free from nitrates and also from ammonium sulphate, which is sometimes added in the process of manufacture to destroy oxides of nitrogen. Eimer and Amend's "Strictly C. P." is good.

(4). Mercuric oxide, HgO, prepared in the wet way. That prepared from mercury nitrate cannot safely be used.

(5). Potassium permanganate tolerably finely pulverised.

(6). Granulated zinc.

(7). A solution of 40 grms. of commercial potassium sulphide in one litre of water.

(8). A saturated solution of sodium hydrate free from nitrates, which are sometimes added in the process of manufacture to destroy organic matter and improve the colour of the product. That of the Greenbank Alkali Company is of good quality.

(9). Solution of cochineal prepared according to Fresenius's "Quantitative Analysis," second American edition, page 679.

(10). Kjeldahl digestion flasks of hard, moderately thick, well annealed glass. These flasks are about 9 inches long, with a round, pear-shaped bottom, having a maximum diameter of 2½ inches, and tapering out gradually in a long neck, which is three-fourths of an inch in diameter at the narrowest part, and flared a little at the edge. The total capacity is 225 to 250 c.c.

(11). Distillation flasks of ordinary shape, 550 c.c. capacity, and fitted with a rubber stopper and a bulb tube above to prevent the possibility of sodium hydrate being carried over mechanically during distillation. The bulbs are about 1½ inches in diameter, the tubes being the same diameter as the condenser and cut off obliquely at the lower end. This is adjusted to the tube of the condenser by a rubber tube.

(12). *A Condenser.*—Several forms have been described, no one of which is equally convenient for all laboratories. The essential thing is that the tube which carries the steam to be condensed shall be of block-tin. The upper ends of the tin tubes should be bent so that the glass connections may have a slope towards the distilling flasks. All kinds of glass are decomposed by steam and ammonia vapour, and will give up alkali enough to impair accuracy. (See Kreussler and Henzold, *Berichte*, xvii., 34). The condenser in use in the laboratory of the Connecticut Experiment Station, devised by Professor Johnson, consists of a copper tank, supported by a wooden frame, so that its bottom is 11 inches above the workbench on which it stands. This tank is 16 inches high, 32 inches long, and 3 inches wide from front to back, widening above to six inches. It is provided with a water supply tube, which goes to the bottom, and a larger overflow pipe above. The block-tin condensing tubes, whose external diameter is three-eighths of an inch, seven in number, enter the tank through holes in the front side of it near the top, above the level of the overflow, and pass down perpendicularly through the tank and out through rubber stoppers tightly fitted into holes in the bottom. They project about 1½ inches below the bottom of the tank, and are connected by short rubber tubes with glass bulb tubes of the usual shape, which dip into precipitating beakers or Erlenmeyer flasks of about 300 c.c. capacity. The titration can be made directly in them. The distillation flasks are supported on a sheet-iron shelf, attached to the wooden frame that supports the tanks in front of the latter. Where each flask is to stand a circular hole is cut, with three projecting lips, which support the wire gauze or asbestos under the flask, and three other lips, which hold the flask in place and prevent its moving laterally out of place while distillation is going on. Below this sheet-iron shelf is a metal tube carrying seven Bunsen burners, each with a stop-cock like those of a gas-combustion furnace. These burners are of a larger diameter at the top, which prevents smoking when covered with a fine gauze to prevent the flame from striking back.

(13). The stand for holding the digestion flasks consists of a pan of sheet-iron 29 inches long by 8 inches wide, on the front of which is fastened a shelf of sheet-iron as long as the pan, 5 inches wide and 4 high. In this are cut six holes 1⅝ inches in diameter. At the back of the pan is a stout wire running lengthwise of the stand, 8 inches high, with a bend or depression opposite each hole in the shelf. The digestion flask rests with its lower part over a hole in the shelf and its neck in one of the depressions in the wire frame, which holds it securely in position. Heat is supplied by low Bunsen burners below the shelf. With a little care the naked flame can be applied directly to the flask without danger.

The Determination.

(1). *The Digestion.*—Seven-tenths to 2·8 grms. of the substance to be analysed, according to its proportion of nitrogen, is brought into a digestion flask with approximately 0·7 grm. of mercuric oxide and 20 c.c. of sulphuric acid. The flask is placed on the frame above described in an inclined position, and heated below the boiling-point of the acid for from five to fifteen minutes, or until frothing has ceased. If the mixture froths badly, a small piece of paraffin may be added to prevent it. The heat is then raised until the acid boils briskly. No further attention is required until the contents of the flask have become a clear liquid, which is colourless, or at least has only a very pale straw colour. The flask is then removed from the frame, held upright, and, while still hot, potassium permanganate is dropped in carefully and in small quantity at a time till, after shaking, the liquid remains of a green or purple colour.

(2). *The Distillation.*—After cooling, the contents of the flask are transferred to the distilling flask with about 200 c.c. of water, and to this a few pieces of granulated zinc and 25 c.c. of potassium sulphide solution are added, shaking the flask to mix its contents. Next add 50 c.c. of the soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 c.c. of the distillate will generally contain all of the ammonia. This operation usually requires from forty minutes to one hour and a half. The distillate is then titrated with standard ammonia.

The use of mercuric oxide in this operation greatly shortens the time necessary for digestion, which is rarely over an hour and a half in cases of substances most difficult to oxidise, and is more commonly less than an hour. In most cases the use of potassium permanganate is quite unnecessary, but it is believed that in exceptional cases it is required for complete oxidation, and in view of the uncertainty it is always used. Potassium sulphide removes all mercury from solution, and so prevents the formation of mercuro-compounds which are not completely decomposed by soda solution. The addition of zinc gives rise to an evolution of hydrogen and prevents violent bumping. Previous to use the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates that are present which might otherwise escape notice.

KJELDAHL METHOD MODIFIED TO INCLUDE THE NITROGEN OF NITRATES.*

(Applicable to all fertilisers containing nitrates).

Besides the reagents and apparatus given under the Kjeldahl method there will be needed—

(1). Zinc dust. This should be an impalpable powder; granulated zinc or zinc filings will not answer.

(2). Commercial salicylic acid.

The Determination.

Bring from 0·7 to 1·4 grms. of the substance to be analysed into a Kjeldahl digesting flask, add to this 30 c.c. of sulphuric acid containing 2 grms. of salicylic acid, and shake thoroughly; then add *gradually* 3 grms. of zinc dust, shaking the contents of the flask at the same time. Finally place the flask on the stand for holding the digestion flasks, where it is heated over a low flame until all danger from frothing has passed. The heat is then raised until the acid boils briskly, and the boiling continued until white fumes no longer pour out of the flask. This requires about five or ten minutes. Add now approximately 0·7 grm. mercuric oxide, and continue the boiling until the liquid in the flask is colourless, or nearly so. (In case the contents of the flask are likely to become solid before this point is reached, add 10 c.c. more sulphuric acid). Complete the oxidation with a little permanganate of potash in the usual way, and proceed with the distillation as described in the Kjeldahl method. The reagents should be tested by blank experiments.

THE RUFFLE METHOD.

Apparatus and Reagents.

(1). Standard solutions and indicator the same as for the Kjeldahl method.

(2). A mixture of equal parts by weight of fine soda-lime and finely powdered, crystallised sodium hyposulphite.

(3). A mixture of equal parts by weight of finely powdered granulated sugar and flowers of sulphur.

(4). Granulated soda-lime, as described under the soda-lime method.

(5). Combustion-tubes of hard Bohemian glass, 20 inches long and ½ inch in diameter.

(6). Bulbed "U" tubes or Wills's bulbs, as described under the soda-lime method.

Preparation.

(1). Clean and fill the U-tube with 10 c.c. of standard acid.

(2). Fit cork and glass connecting tube. Fill the tube as follows:—(1). A loosely fitting plug of asbestos, previously ignited, and then 1 to 1½ inches of the hyposulphite mixture. (2). The weighed portion of the substance to be analysed is intimately mixed with from 5 to 10 grms. of the sugar and sulphur mixture. (3). Pour on a piece of glazed paper, or porcelain mortar, a sufficient quantity of the hyposulphite mixture to fill about 10 inches of the tube; then add the substance to be analysed, as previously prepared; mix carefully and pour into the tube; shake down the contents of the tube; rinse off the paper or mortar with a small quantity of the hyposulphite mixture and pour into the tube; then fill up with soda-lime to within 2 inches of the end of the tube. (4) Place another plug of ignited asbestos at the end of the tube, and close with a cork. (5). Hold the tube in a horizontal position, and tap on the table until there is a gas channel all along the top of the tube. Make connection with the U-tube containing the acid, aspirate, and see that the apparatus is tight.

The Combustion.—Place the prepared combustion-tube in the furnace, letting the open end project a little so as not to burn the cork. Commence by heating the soda-lime portion until it is brought to a full red heat. Then turn on slowly jet after jet toward the outer end of the tube, so that the bubbles come off two or three a second. When the whole tube is red hot and the evolution of the gas has ceased and the liquid in the U-tube begins to recede towards the furnace, attach the aspirator to the other limb of the U-tube, break off the end of the tube, and draw a current of air through for a few minutes. Detach the U-tube and wash the contents into a beaker

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* Described by Prof. M. A. Scovell.

or porcelain basin, add a few drops of the cochineal solution, and titrate.

The Soda-Lime Method.

(Not applicable in presence of nitrates).

Apparatus and Reagents.

(1). Standard solutions and indicator the same as for the Kjeldahl method.

(2). Granulated soda-lime, fine enough to pass a 10-mesh sieve, and thoroughly dry.

(3). Fine soda-lime, fine enough to pass a 20-mesh sieve, also thoroughly dry.

To prepare soda-lime of the required fineness, the coarse granulated article of the trade may be ground until it will pass through a sieve of about 0·10-inch mesh. It is then sifted on a sieve of about 0·20-inch mesh to separate the fine from the coarse. The two portions are then thoroughly dried in the air-bath or by heating in a porcelain dish or iron pan over a lamp, stirring constantly.

Excellent soda-lime may be easily and cheaply prepared according to the directions of Professor Atwater (*Am. Chem. Journal*, vol. ix., p. 312) by slaking $2\frac{1}{2}$ parts of quick-lime with a strong solution of 1 part commercial caustic soda (such soda as is used in the Kjeldahl process), care being taken that there is enough water in the solution to slake the lime. The mixture is then dried and heated in an iron pot to incipient fusion, and, when cold, ground and sifted as above.

Instead of soda-lime, Johnson's mixture of carbonate of soda and lime or slaked lime may be used.

Slaked lime may be granulated by mixing it with a little water to form a thick mass, which is dried in the water-oven until hard and brittle. It is then ground and sifted as above. Slaked lime is much easier to work with than soda-lime, and gives excellent results, though it is probable that more of it should be used in proportion to the substance to be analysed than is the case with soda-lime.

(4). Asbestos which has been ignited and kept in a glass-stoppered bottle.

(5). Combustion tubes about 40 c.m. long and about 12 m.m. internal diameter, drawn out to a point and closed at one end.

(6). Large bulbed "U" tubes with glass stop-cock, or Wills tubes with four bulbs.

The Determination.

The substance to be analysed should be powdered fine enough to pass through a sieve of 1 m.m. mesh; 0·7 to 1·4 grms., according to the amount of nitrogen present, is taken for the determination. Into the closed end of the combustion-tube put a small loose plug of asbestos, and upon it about 4 c.m. of fine soda-lime. In a porcelain dish or mortar mix the substance to be analysed, thoroughly but quickly, with enough fine soda-lime to fill about 16 c.m. of the tube, or about 40 times as much soda-lime as substance, and put the mixture into the combustion-tube as quickly as possible by means of a wide-necked funnel, rinsing out the dish and funnel with a little more fine soda-lime, which is to be put in on top of the mixture. Fill the rest of the tube to about 5 c.m. of the end with a granulated lime, making it as compact as possible by tapping the tube gently while held in a nearly upright position during the filling. The layer of granulated soda-lime should not be less than 12 c.m. long. Lastly, put in a plug of asbestos about 2 c.m. long, pressed rather tightly, and wipe out the end of the tube to free it from adhering soda-lime.

Connect the tube by means of a well-fitting rubber stopper or cork with the "U" tube or Wills bulbs, containing 10 c.c. standard acid, and adjust it in the combustion furnace so that the end projects about 4 c.m. from the furnace, supporting the "U" tube or Wills tube suitably. Heat the portion of the tube containing the granulated soda-lime to moderate redness, and when this is attained, extend the heat gradually through the portion containing the substance, so as to keep up a moderate and regular flow of gases through the bulbs, maintaining the heat of the first part until the whole tube is heated uniformly to the same degree. Keep up the heat until gases have ceased bubbling through the acid in the bulbs and the mixture of substance and soda-lime has become white or nearly so, which shows that the combustion is finished. The combustion should occupy about three-quarters of an hour, or not more than one hour. Remove the heat, and when the tube has cooled below redness, break off the closed tip and aspirate air slowly through the apparatus for two or three minutes to bring all the ammonia into the acid. Disconnect, wash the acid into a beaker or flask, and titrate with the standard alkali.

During the combustion, the end of the tube projecting from the furnace must be kept heated sufficiently to prevent the condensation of moisture, yet not enough to char the stopper. The heat may be regulated by a shield of tin slipped over the projecting end of the combustion-tube.

It is found very advantageous to attach a Bunsen valve to the exit tube, allowing the evolved gases to pass out freely, but preventing a violent "sucking back" in case of a sudden condensation of steam in the bulbs.

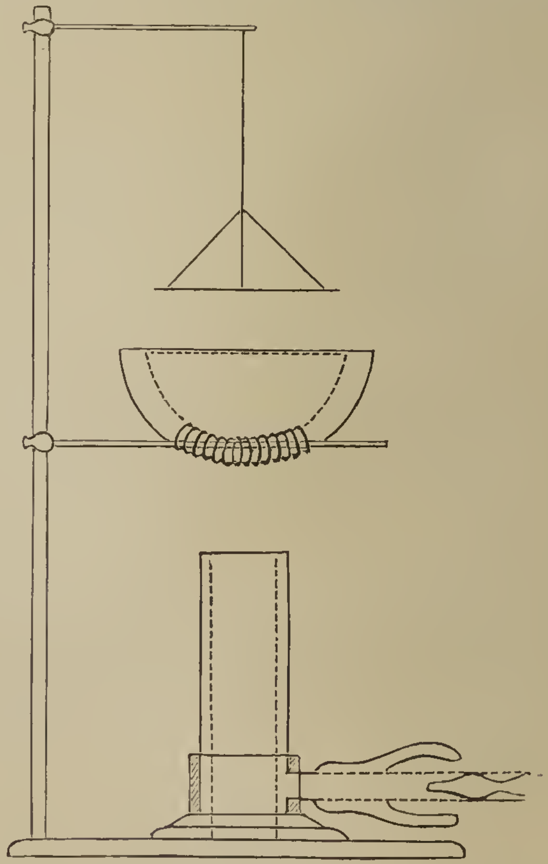
(To be continued).

ON THE

"LOSS ON IGNITION" IN WATER ANALYSIS.

By THOMAS M. DROWN, M.D.

The loss of weight resulting from the ignition of the total solid residue of evaporation of a water was, before the introduction of modern methods of water analysis, supposed to represent the amount of organic matter present in the water. It is now known that this loss, as ordinarily obtained, by heating the platinum dish containing the residue with the free flame of a Bunsen burner, is a very uncertain quantity. Two chemists will often get widely



different results, in consequence of varying practice in the temperature employed and the time of heating.

In order to eliminate this personal equation, as well as to control the temperature of the ignition, I make use of a large platinum dish as a radiator, inside of which the dish containing the residue is heated.

The accompanying sketch shows the arrangement. The radiator is 4⅛ inches in diameter and 2 inches deep. The dish in which the water residue is heated is one inch less in diameter, and rests on a coil of platinum wire, half an inch high. A triangle of platinum wire may be used instead of the coil. A flat disk of platinum foil is suspended one inch over the inner dish, in order to radiate back the heat and hasten the combustion of the organic matter. The radiator is maintained at a moderate red heat by means of an argand gas-burner.

Careful experiments have proved that when solutions of sodium chloride, potassium nitrate, and calcium carbonate, either alone, or in solution together, are evaporated to dryness and heated in this way for half an hour or more, there is no loss in weight. When carbonaceous matter, like sugar, is burned off in the presence of calcium carbonate, the latter loses no carbon dioxide. Organic matter would doubtless decompose nitrates, but the quantity of nitrates present in surface waters is so small that the weight of the fixed solid residue would seldom be affected by their partial or entire decomposition. In fact, nitrates are to some extent reduced to nitrites by the heat of the radiator alone, when no organic matter is present; but the amount of this reduction is generally too slight to be appreciated by the balance.

The following determinations were made on the same sample of filtered Cochituate water, in order to compare the loss on ignition in the radiator with that obtained by cautiously heating the dish to dull redness with the Bunsen burner held in the hand. In both cases the brown residue of evaporation was heated until the carbonaceous matter was completely burned off, leaving a white residue; and after this ignition, the residue was moistened with a dilute solution of ammonium carbonate, dried, and the residue again very gently heated to drive off the excess of ammonium salt.

Amount taken.	Loss in radiator.	Loss over free flame.
	Parts per 100,000.	
100 c.c.	1·20	2·00
200 ,,	1·10	1·95
200 ,,	1·10	1·75
200 ,,	1·15	1·65
500 ,,	1·10	1·70
1000 ,,	1·17	1·77
1100 ,,	1·18	1·68

These results show that not only is the loss much lower in the radiator, but that it is much more uniform.

It has been found that moistening the ignited residue with ammonium carbonate solution is unnecessary when the ignition is carried out in the radiator, since no carbon dioxide is driven off; moistening with water and drying at 100° C. answers the purpose—restoring any water of combination which may have existed in the total residue—quite as well.

The determination of the total solid residue and loss on ignition in ground waters is an entirely different problem from that presented in surface waters. In uncontaminated ground waters there is little or no organic matter, and the mineral matters, consisting in part, it may be, of lime, magnesia, chlorine, and nitric acid, are generally present in large amount. On the evaporation of a solution of this character to dryness there is loss of chlorine due to the decomposition of the magnesium chloride, and the solid residue is difficult to weigh owing to its deliquescence. On ignition there is loss of water of crystallisation and of chlorine and nitric acid: indeed, the "loss on ignition" under these circumstances bears no relation whatever to organic matter.

This difficulty can be remedied by adding an amount of sodium carbonate solution, of known strength, to the water in the platinum dish before evaporation, sufficient to make it slightly alkaline. The lime and magnesia are then precipitated as carbonates—compounds which are not deliquescent, do not contain any water of crystallisation, and are permanent at the temperature to which they are exposed in the radiator. The chlorine and nitric acid combine with the alkali and give compounds which are likewise permanent. When the "loss on ignition" is obtained under these conditions in ground waters or in the effluents from the purification of sewage by filtration, it will represent approximately the organic matter. In good ground waters the loss is nothing. The amount of sodium carbonate added is, of course, to be deducted from the weight of the total and fixed residue.

One cannot expect the same sharpness of results in determining the solid matters and loss on ignition in water analysis as is obtained in the determination of the nitrogen compounds. If 200 c.c. of water are taken for evaporation, an error of weight of one milligrm. is equivalent to 0·5 part in 100,000. When we consider the number of conditions which may affect the weight of the residue of evaporation, both before and after ignition,—such as the temperature of the air-bath, the time of heating, the character of the residue, the hygroscopic condition of the atmosphere, the condition of the air of the laboratory, whether containing much dust, or acid or ammoniacal fumes,—the lack of agreement among chemists in this simple determination is not surprising.

The practice in the chemical department of the Massachusetts Institute of Technology is as follows:—200 c.c. of a surface water, or 100 of a ground water which contains considerable mineral contents in solution, are evaporated to dryness on a water-bath in a hood which is used for no other purpose. To the ground water is added, if necessary, sodium carbonate, as above described. When the water is all evaporated the platinum dish is placed in the air-bath, connected with the water-bath, for about one hour. The temperature of this air-bath is 95° to 98° C. The dish is then transferred to a desiccator and cooled over sulphuric acid for half an hour: it matters not how long it stays in the desiccator after it is cool. It is then weighed, and in order that the residue may not absorb moisture during weighing, there are placed in the balance case four beakers of sulphuric acid, which is frequently renewed. This is essential in those cases in which the residue has a tendency to absorb moisture. The dish is next heated in the radiator until all the organic matter is burned off, moistened with water, and put again into the air-bath, that it may be at the second weighing precisely under the conditions as at the first weighing.

The loss of weight in surface waters, which blacken on ignition, may, under these conditions, be regarded as a close approximation to the organic matter present, both vegetable and animal; and the residue or "fixed solids" represents fairly well the mineral matters of the water.—*Technology Quarterly*, Dec., 1888.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Moniteur Scientifique, Quesneville.
December, 1888.

Improvements Effected in the First Half of 1888 in Dyeing and Printing.—Dr. P. Julius.—This valuable paper is too extensive for useful abridgment.

The Chemical Reactions in the Ammonia-Soda Process.—H. Schreib.—This paper will be inserted in full as soon as practicable.

Process of Purification for Alcoholic Liquids and Especially for Spirituous Liquous.—Dr. J. Traube.—A detailed specification of a German patent.

Session of the Academy of Medicine, October 16, 1888.—The conclusion of a medical discussion on the poisonous character of alcohol, on the higher alcohols, and on the artificial bouquets.

The Non-Explosive Character of Commercial Kerosene Oils.—Spencer B. Newbury and W. P. Cutter.—From the *American Chemical Journal.*

Use of Oxygenated Water for Bleaching Wool, Wood, &c.—Alf. Delmart and P. Ebell.—The oxygenated water of the firm of Haen contains very small quantities of foreign bodies, *e.g.*, barium phosphate, but these impurities have a favourable action, as absolutely pure hydrogen peroxide has less bleaching power. The wool is treated in a cold bath, working in a wooden tub. The room should be cool but not exposed to frost during the winter. The wools must be perfectly scoured. The oxygenated water may either be used pure or may be diluted with five to six volumes of rain-water. A little ammonia is added, about 20 grms. of sp. gr. 0·910 to 100 litres. A slip of red litmus-paper should be turned very slightly blue in a few seconds. The wool should not be left heaped up in the bath, but should be turned continually. The process may last from five to six hours. The colouring-matter is totally destroyed, so that the wool does not become yellow in course of time like that which has been bleached with sulphurous acid. P. Ebell contradicts the assertion of Delmart that a pure oxygenated water is less effective than such as contains barium phosphate, which, if present, must be precipitated on the addition of ammonia. He denies also that a cold bath is always necessary, and he maintains that dilution is not advantageous, the liquid, as supplied, containing 3 per cent of actual hydrogen peroxide, giving the best results. —(*Chemiker Zeitung*).

Recent Researches on the Fulminates.—H. N. Warren.—From the CHEMICAL NEWS.

On Griqualandite.—B. H. Brough.—From the CHEMICAL NEWS.

Determination of Microbia in Air.—Prof. Carnelley and Ch. Wilson.—From the CHEMICAL NEWS.

Detection of Iron in Turkey-red Oils.—Dr. B. Ernde.—The author agitates in a graduated cylinder 100 c.c. of the oil along with water acidified with sulphuric acid (100 c.c. of water and 100 c.c. of sulphuric acid), adding a few drops of solution of ferrocyanide. He then adds 25 to 50 c.c. of ether and agitates again. The solution of oil in ether separates readily from the aqueous liquid, and at the line of contact there appears a stratum of Prussian blue.—(*Zeitschrift angew. Chimie*).

Accidental Presence of Mercury in Commercial Tin.—E. Kayser.—The tin used in a manufactory at Nürnberg was found to contain 1·3 per cent of mercury. All the ingots bore the well-known "lamb" brand of S. A. Stone and Sons. This dangerous fraud had been committed in Germany, where a dealer had bought up the waste from a looking-glass works and had melted it down, and apparently had marked it with Messrs. Stone's brand.—(*Chemiker Zeitung*).

Volumetric Determination of Stannous Salts.—Dr. A. Jones.—The author titrates with a solution of permanganate made by dissolving 4 to 5 grms. permanganate and 8 to 10 grms. caustic potassa in 1 litre of water. To standardise this test-liquor he measures exactly 5 to 10 c.c. and adds a solution containing exactly 10 grms. of tartar emetic per litre until the green colour turns to a light brownish yellow. For the determination 0·2 to 0·4 grm. of tin crystals or half the quantity of metallic tin is dissolved in hydrochloric acid in a current of carbonic acid gas. The solution is made up exactly to 250 c.c. 5 or 10 c.c. of the permanganate liquid are put in a test-glass, and the solution of tin is let flow in gently until the change of colour is observed. The liquid must be kept alkaline and in case of need a few c.c. of caustic potassa must be added. For the calculation we have 1 mol. tin salt = 1 mol. permanganate = 1 mol. tartar emetic.—(*Chemiker Zeitung*).

Antimony Mordant with Whey.—M. Kretzschmar.—The author dissolves the antimony mordant in the whey from cheese works, removing the albuminous matters in the usual manner. The liquid is then filtered whilst still hot and abandoned to the lactic fermentation. For use it is diluted with 13 vols. of water and furnishes a mordant equivalent to that given by dissolving 5 grms. of tartar emetic per litre.—(*Chemiker Zeitung*).

The Alkaline Aluminates.—Dr. K. J. Bayer.—The author has obtained a new aluminate of the formula $Al_2O_36Na_2O$.—(*Chemiker Zeitung*).

Oxalic Acid as a By-product of the Manufacture of Aniline.—Dr. R. Hirsch.—The acid which has served for the nitration of benzenes and toluenes contains from ½ to 1½ per cent of nitric adid. If allowed to stand for some time it deposits crystals of oxalic acid, formed at the expense of the carbide nitrated and of the *nitrous* acid. Hence it is necessary, in producing aniline, to use benzenes as free as possible from thiophenes, and nitric acid free from nitrous vapours.—(*Chemiker Zeitung*).

The Absorption of Reagents by Textile Fibres.—Dr. E. Knecht.—This memoir does not admit of useful abridgment.

Biedermann's Central-Blatt fur Agricultur Chemie.
Vol. xviii., No. 1.

Injuries in "Moor-Dam" Cultivation.—Prof. M. Fleischer.—A study of parasitic diseases encountered in the cultivation of reclaimed peat-lands.

Action of Ferrous Sulphate upon Different Soils.—P. Marguerite-Delacharlonny and L. Destremx.—An application of ferrous sulphate is beneficial if the iron oxide in the soil falls below 3·5 to 4 per cent, but useless or hurtful if the proportion is greater.

Manurial Value of Nitrogen in Soda Saltpetre and Sulphate of Ammonia as Applied to Potatoes.—Dr. Baessler.—On sandy soils the action of the sulphate of ammonia seems less certain than that of Chilian nitre as far as potatoes are concerned, but the experiments performed are not as yet decisive. For oats the two salts are equal.

Composition and Properties of the Peat of South Bohemia.—Prof. Farsky.—The author concludes that fibrous peat is a very advantageous litter for stables, &c., while peat siftings (turf-mull) is very useful as an addition to cess-pools.

Experiments at Rothamsted on the Growth of Turnips.—From the *Agricultural Student's Gazette.*

Experimental Field of the Danish Agricultural High School in 1860-1882 and 1883-1884.—P. S. Jörgensen and V. Maar.—The object of the experiments was to judge of the value of certain rotations of crops. In all the rotations the yield of barley was the smaller the larger the wheat harvest had been.

Researches on Smut, Mildew, and Canker in Grain.—J. L. Jensen.—The author criticises the means recommended for destroying the spores of these fungi in seed-corn. He finds that steeping for five minutes in water at 53° to 56° destroys the spores of the parasites without interfering with the germinating power of the grain.

Communications from the Laboratory of the Aylesbury Dairy Company.—Dr. P. Vieth.—In 1887 18,611 samples of milk were analysed and the sp. gr. of 80,000 samples was determined. The sp. gr. ranged generally from 1·030 to 1·034. The average total dry matter was 12·94 per cent, and the fat 3·82.

Application of the Reichert-Meissl-Wollny Analytical Process to Italian Butter and to Mixed Butters.—Professor C. Besana.—The melting-point in 114 samples of butter ranged from 33° C. to 37·7° C., and in one sample it reached 40·5° C. The proportion of volatile fatty acids in butter was found not to be constant. Differences were observed in butters made from the milk of the same set of cows at intervals of a few days. The quantity of decinormal alkali required for titrating the volatile fatty acids obtained from 5 grms. butter varied from 29 to 30·19 c.c. to 21·8 to 22 c.c., the latter figures being rare.

Zeitschrift fur Physikalische Chemie.

Vol. ii., Part 12.

Formation of Amide from Ester and Ammonia and the Inversion of this Reaction..—Albert Bonz.—The author's experiments confirm the incompleteness of the formation of amide from ester and ammonia, and explain it by the invertibility of the reaction; the limits of the condition of equilibrium of both reactions depend on the molecular weight, the temperature, and the relations of mass. The limits of the formation of esters rise with the increase of the molecular weight as well of the amide as of the alcohol.

Determination of the Basicity of Acids from the Electric Conductivity of their Sodium Salts.—W. Ostwald.—The author works out the principle that at corresponding degrees of dilution the conductivity increases proportionally to the basicity of the sodium salts. The particulars are given in a tabular form.

Outlines of a New Theory of Volume- and Refraction-Equivalents.—E. Ketteler.—This paper does not admit of useful abridgment.

The Molecular Volume of Sulphur.—H. Blitz.—This paper requires the two accompanying woodcuts.

The Kinetics of Bodies in Solution (Second Treatise).—Morris Loeb and Walther Nernst.—The authors find that the coefficient of temperature decreases with increasing mobility.

Apparatus for Determining the Depression of the Freezing-point.—J. F. Eykman.—The author gives his results in a tabular form.

Bulletin de la Société Chimique de Paris.

Vol. li., No. 2.

The Reduction of Copper Salts by Saccharine Matters.—L. Monnet.—The various sugars have the property of reducing the copper salts to the metallic condition if they are applied in concentrated solutions. In neutral liquids the reduction is produced at all temperatures, and heat merely facilitates the operation. The copper is always obtained in a crystalline condition. In alkaline solutions the reduction is effected only at a boiling heat, and the deposit is amorphous. Saccharose acts more easily than lactose or dextrose in neutral solutions; in alkaline liquids the reverse holds good.

Assay of Alcohols: Separation of the Aldehyds by Amines, and Especially by Metaphenylendiamine.—Ch. Girard and X. Rocques.—The authors dissolve in 200 c.c. of alcohol at 50° 3 grms. of metaphenylen-diamine hydrochlorate and boil for half an hour with an ascending condenser. The liquid takes a pale yellow colour. It is let cool for half an hour and slightly stirred towards the end of this time. The colour of the liquid darkens, and if aldehyd is present it takes a fine green fluorescence. It is then distilled quickly and 125 c.c. of distilled alcohol are collected, marking 75°. This is then submitted to Savalle's test and the tints obtained are compared with those given by alcohol at 75°, to which known quantities of pure amylic alcohol have been added.

On Hydrated Metallic Chlorides.—Paul Sabatier.—The stability of the hydrates examined agrees exactly with thermo-chemical indications.

Journal de Pharmacie et de Chemie.

Vol. xix., No. 3.

A Novel Sophistication of Saffron.—M. Adrian.—The fraud consists in the addition of sodium borate, sulphate, and chloride, with potassium tartrate and ammonium nitrate together in the proportion of 43·75 per cent.

Determination of Oil of Mustard in the Seeds of Cruciferous Plants.—M. O. Foerster.—The author places in a retort 25 grms. of the substance previously pulverised and triturated with water. A current of steam is caused to traverse the retort and condense in a descending refrigerator, the end of which plunges for some centimetres below the surface of 50 c.c. of alcohol saturated with ammonia and placed in a ½-litre flask. The distillation is stopped when the volume of the condensed liquid amounts to 200 c.c. This liquid contains the thiosinnamine, and it is left for 12 hours in the stoppered flask. It is then heated in a beaker with an excess of mercuric oxide (freshly prepared by precipitating mercuric chloride with potassa), and heated, with constant stirring. Before cooling a sufficiency of potassium cyanide is added and the liquid is stirred until the precipitate of sulphur is freed from all foreign matters. It is then filtered, washed, dried, and weighed. The weight multiplied by 0·4266 gives the weight of thiosinnamine.

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Water-Gas *v.* Coal-Gas.—Would some correspondent kindly inform me the relative amounts of carbonic acid gas evolved during combustion from water-gas and coal-gas, the former being represented by H_2CO, and the latter by the constituents of an ordinary coal-gas?—F. W.

Sulphate of Lime.—(1). In the case of a solution containing sulphate of lime in suspension which is the quickest way of separating same from the liquid? (2). After above is done, then the quickest and best way of condensing the liquid and obtaining crystallisation?—G. W.

MEETINGS FOR THE WEEK

Monday, 18th.—Medical, 8.30.
—— Society of Arts, 8. Cantor Lectures. "Wood Engraving," by W. J. Linton.
Tuesday, 19th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Pathological, 8.30.
—— Society of Arts, 8. "Slavery in relation to Trade in Tropical Africa," by Commander V. Lovett Cameron.
Wednesday, 20th.—Society of Arts, 8. "The Forth Bridge," by Benjamin Baker, M.Inst.C.E.
—— Meteorological, 7.
—— Geological, 8.
Thursday, 21st.—Royal, 4.30.
—— Royal Institution, 3. "The Venom of Serpents and Allied Poisons," by Sidney Martin, M.D.
—— Chemical, 8. Ballot for the Election of Fellows.
—— Royal Society Club, 6 30.
—— Institute of Electrical Engineers, 8.
Friday, 22nd.—Royal Institution, 9. "In the Heart of the Atlas," by Harold Crichton-Browne, F.R.G.S.
—— Quekett Club. (Anniversary).
Saturday, 23rd.—Royal Institution, 3 "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.
—— Physical, 3. "Note on the Measurement of Electrical Resistance," by Dr. J. W. Waghorn. "Notes on Polarised Light," by Prof. S. P. Thompson. "On Electrical Measurements," by Prof. Ayrton, F.R.S., and Prof. J. Perry, F.R.S.

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THE CHEMICAL NEWS.

Vol. LIX. No. 1526.

A METHOD OF VAPOUR DENSITY DETERMINATION.

By THEO. W. RICHARDS, of Harvard University, U.S.A.

In making some experiments upon the determination of the specific gravity of vapours, a method was recently stumbled upon which was apparently new, and which, when tried, gave excellent results; but, after the matter was wholly ready for publication, Professor Meyer called the writer's attention to the fact that methods based upon the same principle had already been published by Gibson Dyson,[*] and W. Bott and D. S. Macnair.[†] However, as the apparatus used in the present case differed in several respects from that heretofore used, and as the gentlemen mentioned above had apparently omitted an important correction from their calculation, it was deemed not wholly without purpose to publish the present investigation.

The method of determining the specific gravity of vapours which it is the object of this paper to describe is excessively simple. A cylindrical bulb and tubes of known volumes, with a dropping apparatus exactly like that described by Grünwald and Meyer[‡] is attached to a barometer tube, while a water-pump is connected with the fine tube coming from the bottom of the bulb. After the latter is partially exhausted the pump is separated from the rest of the apparatus by a pinch-cock, and the bulb is heated to a constant known temperature. When the tension in the apparatus becomes also constant the height of the mercury supported is carefully noted.

The substance, which was placed in the drop apparatus before the exhaustion, is now allowed to fall into the heated bulb, and is vapourised; and the fall of the mercury column in the barometer indicates the tension of the vapour formed by the substance in filling the bulb of known volume at the known temperature.

Naturally the vapour remains at the bottom of the bulb in a much more concentrated condition than is indicated by this increase of tension, but the final effect is the same; and of course from the given weight, temperature, and volume, and the observed tension, the specific gravity of the vapour is easily deduced.

The underlying principle of this method, which it holds in common with those of Dyson, Bott, and Macnair, lies in the fact that here the pressure is the only variable, which it is the object of the experiment to observe. The fall of mercury will be the same with the same amount of a given substance, no matter what the tension of the residual air may have been. It will be noticed that the method is in no sense a modification of Victor Meyer's.

As before said, there is an important correction involved, which has apparently been heretofore omitted. The vapour as formed compresses the air in the bulb, and drives some of it up into the cold tube above; and of course this displaced air diminishes in volume on cooling, making the fall of the mercury less than it should be, and hence the specific gravity greater.

For this serious difficulty there are two methods of correction. The first is to determine by calculation first the amount of the air driven up (from the ratio of the air and vapour tensions as indicated by the barometer tube), then the amount of contraction of this volume in cooling from the higher temperature to the temperature of the room, and finally to find the influence of this contraction upon the fall of the mercury. The other method is experimental, and consists simply in sliding the bulb more deeply into the constant temperature bath, so that *just that volume* of air which was displaced into the tube will be heated to its previous temperature. This method is much simpler, and apparently is more reliable than the former.

The correction itself may be made much smaller than in the results published below, by diminishing the volume of the upper tubes, in an apparatus especially constructed for the purpose.

The apparatus may now be described more closely. The volume of the bulb and adjacent tubes was 189·2 c.c at 0° or 189·5 c.c. at 100 degrees, calculated, as usual, from its water capacity at a known temperature, and the coefficient of expansion of glass. To this value must be added 2·4 c.c., the average capacity of the connecting tube and upper part of the barometer tube to obtain the complete volume (191·9 c.c.) at 100°.

The bulb was surrounded by a vapour jacket closed at the top with a cork, through which passed its tubes and a wide air condenser. The total internal volume of the former, including the upper part of the barometer tube, was 15·3 c.c., and the cubic contents 0·33 c.c. for each centimetre of height.

The change of volume of the bulb, due to the elasticity of glass under pressure, is so small that it may be neglected.

The barometer tube was 2 m.m. in internal diameter. If it is much larger than this the fall of mercury will produce a sensible alteration in the volume, while, if it is much smaller, unequal capillarity will have too much effect on the readings. By rough measurement the capillary repulsion of this tube was found to be about 4·5 m.m.; of course this correction affects all readings equally, and must be applied only when we wish to compare them with an ordinary barometer. Naturally, the barometer tube must be clean, and of even diameter, and must be gently rapped before each reading. It was made of thick glass, and was clamped with the greatest rigidity, with its lower end in a large basin of mercury, whose level remains sensibly constant. The very slight error produced by the increase in volume, owing to the descent of the mercury (averaging 0·12 c.c.), might easily be corrected by the use of a cathetometer with two telescopes, and a deep vessel for mercury which could be raised or lowered; but it is so very slight that in practice it may be wholly neglected. In fact, it is quite sufficient to mark the mercury levels with a fine pencil upon labels pasted to the barometer tube, and to measure the distances between these marks with a centimetre rule, thus dispensing with a cathetometer altogether. All of the determinations given below were measured in this simple way.

The expansion of the mercury itself by the heat of the room may, of course, also be taken into account, but on so small a column it is less than the necessary experimental errors, and being in the opposite direction from the other infinitesimal corrections it may be, like them, neglected in practice. It must, of course, be considered when comparing with the outside pressure.

The method of conducting a determination is as follows:—After breaking off the end of the small sealed tube containing the substance, it is placed in the dropping apparatus. If we are dealing with a liquid it must contain no bubbles; if it is very volatile it may be necessary to surround the drop apparatus with a freezing mixture. The stopper is then applied, and the bulb is exhausted somewhat beyond the required point. The pump is then shut off by a pinch-cock, the height of the mercury marked, and the apparatus allowed to stand for some minutes as a test of air-tightness. When all is right the liquid of the bath is boiled, and, of course, the internal pressure of the apparatus rises, and the mercury falls, soon reaching constancy. This fall of mercury might, and probably will, be used, after suitable correction, as a

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[*] Chemical News, lv., 88.

[†] *Berichte d. D. Ch. G.*, 1887, 916.

[‡] *Ibid.*, xxi. (1888), 688.

method of determining the temperature, which must be known with some accuracy—otherwise the latter is determined by a thermometer in the vapour-bath.

When all has reached complete constancy, the tube containing the substance is allowed to drop into the bulb, and the increase of tension produced by its vapourisation is measured on the mercury column. The vapourisation is rapid, and after perfect constancy is once more attained the following calculation must be made:—As the total tension of the mixed air and vapour is to the tension of the vapour produced, so is the total volume of the tubes outside the bath to the volume of air driven up into them. This approximation, when divided by the capacity of the tubes per c.m., will give the number of c.m. which the bulb must be lowered into the bath, in order to correct for the cooling of the displaced air. After performing this operation, and waiting once more for constancy, which can be held for a long time, the fall of the mercury is carefully measured, and the whole apparatus is cleaned out by a stream of air and made ready for the next experiment. The whole operation does not last more than ten minutes, and is very easy in manipulation.

In the eight experiments which were tried, toluol was used as the test substance, and a steam-bath formed the source of heat. The first series of four was corrected by calculation; while the second series was corrected experimentally, and may be taken as a much better criterion of the method.

Density of Toluol Vapour.

First series, corrected by calculation.

T = 99·6°, Bar. = 749·5 m.m.

No. of experiment.	Weight.	Obs. fall.	Corr. fall.	Final tension.	Result.
	Grms.	M.m.	M.m.	M.m.	
1.	0·0333	42·10	42·94	225	3·24
2.	0·0216	27·85	28·40	118	3·18
3.	0·0430	53·63	54·70	332	3·28
4.	0·0195	24·40	24·90	82	3·27
			Average		3·242
			Theory		3·187

Second series, corrected experimentally.

T = 100°, Bar. = 760·9 m.m.

No. of experiment.	Weight.	Lowered bulb.	Corr. fall.	Final tension.	Result.
	Grms.	C.m.	M.m.	M.m.	
5.	0·0328	9·3	43·0	210·5	3·19
6.	0·0391	12·0	50·5	181·0	3·24
7.	0·0284	16·0	37·7	111·0	3·16
8.	0·0352	11·0	46·8	194·5	3·15
			Average		3·185
			Theory		3·187

The chief advantages of the method are its simplicity, the low tension and consequently low temperature required, the small amount of substance necessary, and the comparatively slight influence of impurity, the saving of time, and the complete absence of all mercurial or aqueous vapour. The chief disadvantage is that the temperature must be known with some exactitude, but it is probable, as before said, that the apparatus may itself form an air thermometer of just the degree of accuracy required.

In conclusion, the writer would once more express his warmest thanks to his friend Mr. W. P. Bradley for his interest and his assistance in the experimental work, and to Professor Victor Meyer for the use of his new laboratory.

Mention was omitted in a previous article* of papers by Dr. W. La Coste† and Dr. Schall.‡ These papers, which describe apparatus having the same end, but differing radically in principle and construction from that there described, were unknown to the author at the time of writing.

Göttingen, Jan. 18th, 1889.

SEPARATION OF ZINC AND NICKEL.

By H. BAUBIGNY.

THE author has shown in a former paper that zinc may be completely precipitated by sulphuretted hydrogen from its saline solutions if they are dilute, and that if to the solution of a given weight of zinc sulphate we add sulphuric acid, the weight of the free acid necessary to overcome the action of the sulphuretted hydrogen decreases or increases with the volume of the solvent.

Since, for a given acid solution of zinc sulphate, the phenomenon varies with the degree of dilution, it seemed useful to ascertain if it would not be possible to effect the complete separation of this metal by fixing the liquid volume at what it ought to be for a weight of neutral salt containing a weight of acid equal to the sum of the free acid and of that in combination. Experiment verified the correctness of this principle.

It must be remarked, however, that the application of this fact becomes difficult, because the total precipitation of the zinc takes place so much the more slowly as the conditions of the medium differ from those obtained on setting out from the neutral, since the sulphide formed interferes in the action upon the undecomposed sulphate.

But if the weight of free acid is not greater than 5 to 6 times that in combination in the salt the method is applicable. Thus, 0·06 grm. of neutral sulphate, dissolved in 200 c.c. of water containing 0·27 grm. of SO_3 (= 9 times the weight of the acid in the salt) is completely decomposed in eight hours if the liquid is fully saturated with hydrogen sulphide. The water does not retain more than 0·0015 grm. of zinc sulphate.

As to acetic acid, if we add it to the solution of a neutral zinc salt it exerts no similar action. All takes place as in a neutral liquid, and even if the liquid of the solution contains from 20 to 25 per cent of actual acetic acid, all the zinc is thrown down by a current of sulphuretted hydrogen.

According to these observations, and to what the author has already established in the case of nickel and cobalt (*Comptes Rendus*, xciv., pp. 1183 and 1715; and cv., pp. 751 and 806), we have conditions which seem sufficient to permit the separation of zinc from these metals, and, *à fortiori*, ftom those which do not form sulphides in presence of water, such as aluminium and chromium, or less sulphurable, such as iron and manganese.

We have therefore to operate upon the acetic solution of the sulphates in the proportion of 0·3 grm. of the salts in 100 c.c. of liquid, treating them with a current of sulphuretted hydrogen.

In the case of zinc and nickel the mixed salts are dissolved in water containing 100 c.c. of glacial acid per litre, and the liquid treated at the common temperature with sulphuretted hydrogen is let stand two or three hours and then filtered. The deposit is then complete, and is perfectly white. The operation is completed by washing with water containing 10 per cent of acetic acid and containing sulphuretted hydrogen. The nickel is precipitated from the filtrate in the ordinary manner, raising the temperature to 70°—75°, and then letting it cool in presence of sulphuretted hydrogen in a stoppered flask. The free acid must be *exclusively* acetic acid, which is secured by adding to the liquid ammonium acetate. If we filter when the liquid is clear and cold all the nickel is separated as a dense sulphide, which is washed with water charged with sulphuretted hydrogen

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* CHEMICAL NEWS, vol. lix., p. 39.

† *Berichte d. D. Ch. G.*, 1885, 2123.

‡ *Ibid.*, 1887, 1435, 1759, 1827, 2127.

and acidulated with one or two per cent of acetic acid. The sulphides are then converted into sulphates and weighed after drying at 400°.

Experiment proves that if the mixed sulphates contain little nickel, one-third at most, the addition of acetic acid is useless.—*Comptes Rendus* (vol. cviii., p. 236).

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.[*]

(Continued from p. 82).

Method for the Analysis of Cattle Food.

Hygroscopic Moisture.—Dry 2 to 3 grms. at 100° C. to constant weight.

Ash.—Char the substance at a low red heat, exhaust the charred mass with water, burn the insoluble residue, add the ash to the residue from the evaporation of the aqueous extract obtained above, dry the whole at 110°, and weigh. Determine carbonic acid and insoluble matter (sand and charcoal) in the product for the estimation of the pure ash.

Ether Extract.—Pulverise the air-dry substance till all of it will pass through a sieve with less than one-sixtieth inch mesh; dry about 5 grms. at 100°, and take about 2 grms. for each extraction. Exhaust with anhydrous ether of specific gravity 0·720 to 0·725, not less than eight hours continuously. Dry ether extract at 100° in a current of dry hydrogen to a constant weight.

Crude Protein.—Determine nitrogen by the Kjeldahl method in the manner recommended by the Nitrogen Committee, and multiply the result by 6·25 for the crude protein.

Albumenoid Nitrogen, Stutzer's Method.—Prepare cupric hydrate as follows:—Dissolve 100 grms. of pure cupric sulphate in 5 litres of water and add 2·5 c.c. of glycerin; add dilute solution of sodium hydrate till the liquid is alkaline; filter, rub the precipitate up with water containing 5 c.c. of glycerin per litre, and then wash by decantation or filtration till the washings are no longer alkaline. Then rub the precipitate up again in a mortar with water containing 10 per cent of glycerin, thus preparing a uniform gelatinous mass that can be measured out with a pipette. Determine the quantity of cupric hydrate per 1 c.c. of this mixture.

To 1 grm. of the substance, pulverised as for the determination of the ether extract, add 100 c.c. of water in a beaker, heat to boiling, or in case of substances rich in starch heat on the water-bath ten minutes, add a quantity of the cupric hydrate mixture containing 0·7 to 0·8 grm. of the hydrate, stir thoroughly, filter when cold, wash with cold water, and without drying put the filter and its contents into the concentrated sulphuric acid for the determination of the nitrogen after Kjeldahl. For filtering use either Schleicher and Schull's No. 589 filter paper or Swedish paper, either of which contains so little nitrogen that it can be left out of account.

If the substance examined consists of seed of any kind or residues of seeds, such as oil-cake or anything rich in alkaline phosphate, add a few c.c. of a concentrated solution of alum just before adding the cupric hydrate, and mix well by stirring. This serves to decompose the alkaline phosphate, precipitating aluminum phosphate; if this is not done cupric phosphate and pure alkali may be formed, and the protein copper may be partially dissolved in this alkaline liquid.

Crude Fibre, Weende Method.—Pulverise as for the ether extract, and extract the fat, at least nearly completely. To 2 grms. of the substance in an Erlenmeyer flask add 200 c.c. of boiling 1·25 per cent sulphuric acid, boil immediately and for thirty minutes continuously with as much rotary motion as may be necessary to keep all the substances that may tend to adhere to the sides of the flask in contact with the liquid, throw on a filter of finest linen, and rinse the flask and wash the contents of the filter thoroughly with boiling water. Wash the contents of the filter back into the flask with 200 c.c. of a 1·25 per cent solution of sodium hydrate, at once raise to boiling, and boil continuously for thirty minutes with rotary motion as above described, filter through a Gooch crucible or according to some similar device, and wash very thoroughly with boiling water. Such thorough washing has been found to be essential to success. Wash then with alcohol and finally with ether, dry at 100°, weigh, incinerate, and give the loss of weight for crude fibre.

Statement of Results.

	In the substance in its natural condition (or as received).	In the dry substance.
Moisture		
Crude ash		
Ether extract		
Crude fibre..		
Crude protein		
Nitrogen: Total ..		
Albumenoid..		

(To be continued).

RE-CALCULATIONS OF THE ATOMIC WEIGHTS.[*]

By F. P. VENABLE.

(Concluded from p. 79).

Methods of Calculation.

Clarke, Sebelien, and others, who have worked over this problem, have been greatly troubled as to what data should be used in the re-calculations and what rejected. Manifestly the results of many of the older experimenters can lay no great claims to accuracy. Some, as Clarke says, are "chemically worthless because of constant errors." Many have neglected proper precautions or necessary corrections. And yet there are reasons for retaining much of this, and the retention or rejection is a point of judgment on which chemists may, and do, legitimately differ. An additional sentence of Clarke's reveals the extent of the trouble. "In fact it is doubtful," he says, "whether any two chemists, working independently, would handle all the data in precisely the same way, or combine them so as to produce exactly the same final results."

The accompanying tables, giving the calculations of Clarke, Meyer and Seubert (the $O = 16$ table was worked out from their $O = 1$), Van der Plaats, and Ostwald,[†] show the truth of this. The two last agree more nearly than the others, and yet the variations are numerous and sometimes as large as 5 in the case of osmium; 3 in the case of mercury; 1 in the case of uranium, &c. Unanimity in regard to an atomic weight does not always mean that the weight is correct. Paucity of data sometimes limits the chances for variation. Indium, for instance, and gallium and beryllium have been subjected to few investigations.

The mathematical side of the question, whether the method of least squares should be adopted, or by what

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[*] Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

[*] From the *Journal of the Elisha Mitchell Scientific Society*, Vol. v., Part 2.

[†] Ostwald's table is put down under the head of $O = 16$. He gives it as $H = 1$ and also $O = 16$, but the numbers most nearly correspond with the latter.

Table No. II.

Oxygen = 16.

Symbol.	Clarke.	Meyer and Seubert.	Van der Plaats.	Ostwald.
Ag	107·923	107·929	107·93	107·938
Al	27·075	27·107	27·08	27·08
As	75·090	75·087	75·0	75·0
Au	196·606	196·690	196·7	196·7
B	10·966	10·927	11·0	11·0
Ba	137·007	137·202	137·1	137·04
Be	9·106	9·103	9·1	9·10
Bi	208·001	208·019	208·0	208·01
Br	79·951	79·954	79·955	79·963
C	12·0011	11·999	12·005	12·000
Ca	40·082	40·009	40·0	40·00
Cd	112·092	111·979	112·1	112·08
Ce	140·747	141·553	141·5	141·5
Cl	35·451	35·458	35·456	35·453
Co	59·023	58·746	58·8 or 60	59·1
Cr	52·127	52·581	52·3	52·3
Cs	132·918	133·032	132·8	132·88
Cu	63·318	63·338	63·33	63·33
Di	144·906	145·362	145·0	145·0
Er	166·273	166·415	166·0	166·0
F	19·027	19·109	19·0	19·01
Fe	56·042	56·015	56·0	56·00
Ga	68·963	70·072	70·0	69·9
Ge	72·32	= Determination of Winkler.		
H	1·0023	1·0024	1·00	1·00
Hg	200·171	200·299	200·1	200·4
I	126·848	126·856	126·86	126·864
In	113·659	113·683	113·7	113·7
Ir	193·094	192·981	193·0	193·11
K	39·109	39·128	39·144	39·136
La	138·844	138·846	138·0	138·5
Li	7·0235	7·028	7·02	7·030
Mg	24·014	23·999	24·4	24·38
Mn	54·029	54·937	55·0	55·02
Mo	95·747	96·139	96·0	95·9
N	14·029	14·045	14·05	14·041
Na	23·051	23·052	23·05	23·058
Nb	94·027	93·934	9·40	94·2
Ni	58·062	58·746	58·0 or 58·8	58·5
O	16·000	16·000	16·000	16·00
Os	198·951	195·487	195·0	200·0
P	31·029	31·037	30·95	31·03
Pb	206·946	206·906	206·91	206·911
Pd	105·981	106·465	106·5	106·0
Pt	194·867	194·826	194·9	194·83
Rb	85·529	85·413	85·4	85·44
Rh	104·285	104·360	104·0	103·05
Ru	104·457	103·759	104·0	103·8
S	32·058	32·059	32·06	32·063
Sb	120·231	119·899	120·0	120·29
Sc	44·081	44·079	44·0	44·09
Se	78·978	79·067	79·0	79·07
Si	28·260	28·07	28·0	28·06
Sm	—	—	150·0	150·2
Sn	117·968	117·643	118·1	118·12
Sr	87·575	87·518	87·5	87·52
Ta	182·562	182·455	182·8	182·8
Te	128·254	128·019	125·0	125·2
Th	233·951	232·539	233·0	233·0
Ti	49·961	50·373	48·1	48·12
Tl	204·183	204·209	204·2	204·146
U	239·030	240·399	240·0	239 0
V	51·373	51·228	51·3	51·21
W	184·032	184·059	184·0	184·0
Y	90·023	89·824	89·5	89·0
Yb	173·158	173·081	173·0	173·2
Zn	65·054	65·042	65·3	65·38
Zr	89·573	90·626	90·5	90·7

Hydrogen = 1.

Symbol.	Clarke.	Meyer and Seubert.
Ag	107·675	107·66
Al	27·009	27·04
As	74·918	74·9
Au	196·155	196·2
B	10·941	10·9
Ba	136·763	136·86
Be	9·085	9·08
Bi	207·523	207·5
Br	79·768	79·76
C	11·9736	11·97
Ca	39·990	39·91
Cd	111·835	111·7
Ce	140·424	141·2
Cl	35·370	35·37
Co	58·887	58·6
Cr	52·009	52·45
Cs	132·583	132·7
Cu	63·173	63·18
Di	144·573	145·0
Er	165·891	166·0
F	18·984	19·06
Fe	55·913	55·88
Ga	68·854	69·9
Ge	—	—
H	1·0000	1·00
Hg	199·712	199·8
I	113·398	113·4
In	113·398	113·4
Ir	192·651	192·5
K	39·019	39·03
La	138·526	138·5
Li	7·007	7·01
Mg	23·959	23·94
Mn	53·906	54·8
Mo	95·527	95·9
N	14·021	14·01
Na	22·998	22·995
Nb	93·812	93·7
Ni	57·928	58·6
O	15·963	15·96
Os	198·494	195·0
P	30·958	30·96
Pb	206·471	206·39
Pd	105·737	106·2
Pt	194·415	194·34
Rb	85·251	85·2
Rh	104·055	104·1
Ru	104·217	103·5
S	31·984	31·98
Sb	119·955	119·6
Sc	43·980	43·97
Se	78·797	78·87
Si	28·195	28·0
Sm	—	—
Sn	117·698	117·35
Sr	87·374	87·3
Ta	182·144	182·0
Te	127·960	127·7
Th	233·414	231 96
Ti	49·846	50·25
Tl	203·715	203·7
U	238·482	239·8
V	51·256	51·1
W	183·610	183·6
Y	89·816	89·6
Yb	172·761	172·0
Zn	64·9045	64·88
Zr	89·367	90·4

formulæ the probable errors should be calculated, and by what the results combined, is of course of great importance and the subject of varying views, but cannot be discussed here.

Out of 66 elements the revisers agree on 29 to the tenth place of decimals, differing in the hundredth place only. In the remaining 37 or 56 per cent the differences are more or less great.

The increased interest in these re-determinations of atomic weights, giving fresh data for calculation and enabling us to throw off some of the burden of faulty determinations, gives promise of an approximately correct table in the near future.

I cannot close without adverting to the speculations of some authors as to the question whether we are to expect these atomic weights to be fixed quantities. In other words,

Are the Atomic Weights Constant?

This question Stas proposed to himself before starting upon his classic work on the atomic weights. The conclusion he drew from his experiments was that they were unchangeable. The question has been raised again by Schützenberger and Butlerow.[*] Butlerow does not doubt the results obtained by Stas, but suggests that under changed conditions or with different bodies the results might have been otherwise.

Of course if the atomic weights are not constant the law of constant proportions is without support and must be given up, and this would necessitate a revolution in chemistry as a science.

These authors suppose the range of variation in the weights to be very slight, yet distinctly to be detected by analysis. The theories of both are supported by analytical data, in which the authors seem to place the utmost confidence. If their results are not accurate the variability of the atomic weights stands unproven. To show the nature of their experiments, Sebelien quotes from Schützenberger's work his synthesis of water. According as this is carried out with copper oxide at red heat, or by the lowest possible temperature, or with lead chromate, the relation between the oxygen and hydrogen varies from 7·89 to 7·98. Or again, the atomic weight of iron, determined from the nitrate, he finds to be 54, whilst that from the oxalate is 56. He found also that carbon dioxide prepared by burning pure carbon at a high temperature contained more oxygen than that prepared by means of carbon monoxide from organic bodies.

The generality of chemists will be more apt, I think, to suppose the analytical work of these investigators faulty than to accept their conclusions as to the inconstancy of the atomic weights. Yet the matter is of the utmost importance and should be decided with as great freedom from preconceived notions as possible. It is a question exceedingly difficult to decide, and will require great nicety and accuracy of work. Many of the most trusted leaders of work and thought in the science will have to concur in testimony derived from their own experiments before any attempt at altering the science to suit the new facts will be made.

We must not say, because we are mentally satisfied with the present theories, and dread the trouble which so radical a change would cause, that the supposition is impossible and need not be considered.

Butlerow offers three possible explanations of his own and Schützenberger's observations:—

1. The absolute amount of matter has been increased in that the so-called force or energy has been changed into matter.

2. The absolute amount of matter is unchanged, but its weight is increased by means of a temporary increase in the intensity with which the earth attracts matter.

3. The weight of matter is not increased in either way, but the chemical value is changed. The atomic weight of carbon, for instance, may be temporarily changed from 12 to 11·8, and thus the saturation capacity of carbon raised by about $\frac{1}{60}$. The amount of carbonic acid made from the same amount of carbon would thus be increased and would be richer in oxygen.

The first two suppositions would be subversive of Natural Philosophy generally. The last would simply be subversive of chemistry as now systematised. As Sebelien says, we must give up under the third supposition our idea of atoms, for an atom is nothing if not a fixed weight of something. Vogel[*] has also come to the conclusion that the atomic weights vary because those got by the use of certain compounds differ throughout from those derived from other compounds. By this assumption he also explains the cases in which analyses result in a sum total of over 100 per cent. It seems much more plausible to explain these variations on the ground of errors of analysis, constant errors of method, impurities of materials, and the many other difficulties and obstacles which a chemist meets in such work, than by the radical assumption of an inconstancy in the very constants on which the science is founded and built up.

At any rate, until much more proof is forthcoming, the matter must rest in abeyance.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1888.

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.,
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, 1889.

SIR,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

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

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

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

The results furnished by the examinations of the water supplied to the Metropolis, made daily during the month of January, are extremely good, and indeed exceptionally good for the period of the year. Thus, in the case of the Thames-derived waters, for example, the mean proportion of organic carbon was found to be only 0·170 part in 100,000 parts of the water, with a maximum in any one sample examined of 0·197 part; this maximum result for January, 1889, being almost identical with the mean result, or 0·196 part, for the previous month of December, 1888. That this last mean result was not at all excessive for the period of the year may be gathered from the consideration that even a proportion of 0·280 part of organic carbon in 100,000 parts of the water corresponds as nearly as may be to about half a grain only of organic matter per gallon. Of the 189 samples of water examined, two of the

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[*] *Bull. de la Soc. Chim. de Paris*, xxxix., 258. *Ibid.*, xxxix, 263 (cited in *Zeitschrift fur Anal. Chemie*, xxii., 640, and Sebelien, "Geschichte der Atomgewichte," 54.

[*] *Nature*, vol. xli., p. 42.

Thames-derived samples were alone recorded as exhibiting a very slight turbidity.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 7th, 1889.

Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. Albert Cooper, W. Hepworth Dixon, F. C. Garrett, F. B. Guthrie, John Percival, and R. W. Woosnam were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. T. D. Collis, Barry, Asirgarh, Central India; Harry Broadbent, 31, Victoria Terrace, Belle Vue Road, Leeds; Edward Barnwell Cook, Clifton College, Bristol; Francis Edward John Cridland, Mayfield, Southboro, Surbiton; Alexander Archie Cunningham, American Sugar Refinery, Battery Street, San Francisco, U.S.A.; Thomas Hill Easterfield, Clare College, Cambridge; Joseph T. Freestone, 33, Brownlow Road, New Ferry, Cheshire; Richard Ashworth Hoyle, 11, Market Square, Lytham; Herbert Ingle, Poole, near Leeds; Christopher J. McNally, M.D., Medical College, Madras; William Beattie Nesbitt, University of Toronto; Charles Proctor, 192, Barry Road, Dulwich, S.E.; Arthur Avery Read, Owens College, Manchester; Ernest Reckitt, Caen Wood Towers, Highgate, N.; Henry Charles Anslie Vine, 15, Old Pond Street, Bath; Walter Arthur Voss, Oak House, Croydon Road, Anerley; John Tsawoo White, Rangoon College, Rangoon.

The following papers were read:—

11. "*Researches on the Constitution of Azo- and Diazo-derivatives. V. Compounds of the Naphthalene-β-series*" (*continued*). By R. Meldola, F.R.S., and G. T. Morgan.

The authors describe the preparation of benzoyl-derivatives of azo-β-naphthol compounds by the displacement of the amido-group in the corresponding amido-derivatives by $C_7H_5O{\cdot}O$—by means of the diazo-interaction in the presence of benzoic acid. The method is analogous to that described last year by one of the authors and F. J. East (*Berichte*, 1888, 601; *Chem. Soc. Trans.*, 1888, 465) for the preparation of azophenylic acetates, action takes place in accordance with the equation—

$$R{\cdot}N_2{\cdot}OH + HO{\cdot}C_7H_5 = R{\cdot}OC_7H_5O + N_2 + H_2O.$$

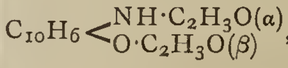
The *metanitrobenzeneazobenzoate*,—

$$(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OC_7H_5O(\beta),$$

has been prepared by the foregoing method, as well as by the direct benzoylation of metanitrobenzeneazo-β-naphthol by means of dry sodium benzoate and benzoyl chloride; it crystallises in orange needles melting at 171°. Benzeneazo-β-naphthol, when similarly treated with benzoyl chloride and sodium benzoate, gives *benzeneazo-β-naphthyl benzoate*, $C_6H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OC_7H_5O$, which crystallises in dense orange prisms melting at 125°. The greater portion of the paper is devoted to a study of the products of reduction of the azo β-naphthol-derivatives containing acid radicles. When violently reduced with tin and chlorhydric acid, benzeneazo-β-naphthol acetate yields aniline and α-amido-β-naphthol, mixed with a small quantity of a monacetyl-derivative of the base diamidohydroxynaphthyl-phenyl,—

$$NH_2{\cdot}C_6H_4{\cdot}C_{10}H_5(OH^{\beta})(NH_2{}^{\alpha}),$$

the acetyl-group being most probably present in the α-amido-group in consequence of intramolecular transference in the ortho-position (Böttcher, *Berichte*, 1883, 1933). The triacetyl-derivative of the hydroxynaphthyl-phenyl base crystallises in white needles melting at 252°. If benzeneazo-β-naphthyl acetate be reduced in cold alcoholic solution with stannous chloride the monacetyl-derivative of the hydroxynaphthyl-phenyl base is the chief product; but the instability of this compound does not allow of its being isolated. In a similar manner, it has been found that when boiled with tin and chlorhydric acid in alcoholic solution, benzeneazo-β-naphthyl benzoate gives aniline and α-amido-β-naphthol, the benzoyl being split off. α-Amido-β-naphthol and aniline are the chief products of mild reduction with stannous chloride, but the monobenzoyl-derivative of the naphthyl-phenyl base is also formed; the latter crystallises in white needles melting at 172—173°: the authors assign to it the formula $NH_2{\cdot}C_6H_4{\cdot}C_{10}H_5(OH^{\beta})(NH{\cdot}Bz^{\alpha})$, and suppose that the benzoyl is transferred to the amido-group as before by the intermediate formation of the anhydro-base. The diacetyl- and dibenzoyl-derivatives of α-amido-β-naphthol,



$$C_{10}H_6 < \begin{matrix} NH{\cdot}C_2H_3O(\alpha) \\ O{\cdot}C_2H_3O(\beta) \end{matrix},$$

and

$$C_{10}H_6 < \begin{matrix} NH{\cdot}C_7H_5O(\alpha) \\ O{\cdot}C_7H_5O(\beta) \end{matrix},$$

are also described. The first crystallises in colourless rhombic prisms melting at 206°, and the second in whitish needles melting at 226·5°. The authors are engaged in investigating the products of reduction of the alkyl-derivatives of azo-β-naphthol compounds.

12. "*The Action of Nitric Acid on Anthracene.*" By A. G. Perkin.

Experiments on the preparation of nitro-derivatives of anthracene have up to the present failed, owing to the fact that when anthracene is treated with nitric acid oxidation and nitration take place simultaneously, the products being anthraquinone and nitroanthraquinones. Nitro-derivatives of anthracene may, however, readily be prepared, provided that during the interaction of the anthracene and the nitric acid care is taken at once to decompose any nitrous acid which may be formed. If anthracene be gradually added to strong nitric acid (which has been carefully freed from nitrous compound by boiling it with urea), it is quickly converted into a new yellow substance, which after re-crystallisation from coal-tar naphtha proved on analysis to be *dinitroanthracene*. This may also be prepared by the addition of anthracene to nitric acid diluted with nitrobenzene or the nitrates of the pyridine bases.

Dinitroanthracene crystallises in long, brilliant, yellow needles, which are difficultly soluble in the ordinary solvents. When carefully heated in a test-tube, it sublimes apparently without decomposition, but on long heating it is converted quantitatively into anthraquinone, with evolution of nitrous fumes, a proof that its constitution is represented by the formula $C_6H_4{\cdot}C_2(NO_2)_2{\cdot}C_6H_4$. The same change takes place when dinitroanthracene is oxidised with chromic acid, and also when it is exposed for some weeks to the action of sunlight.

Mononitroanthracene is contained, together with anthraquinone, in the mother-liquors from the preparation of dinitroanthracene. It crystallises from naphtha in small yellow needles, which are more readily soluble in this solvent than dinitroanthracene, but not so soluble as anthraquinone.

Diamidoanthracene is readily obtained by adding dinitroanthracene to a boiling solution of sodium sulphide in alcohol, and precipitating the resulting violet solution with chlorhydric acid. The orange powder thus produced is dissolved in hot alcohol, a little potash is added, and the solution allowed to cool. In this way beautiful silky, orange needles are obtained, which on analysis give numbers agreeing with those required for the formula $C_{14}H_8(NH_2)_2$. Diamidoanthracene is readily soluble in benzene and carbon bisulphide, less soluble in alcohol

It melts at 146°, and on oxidation with chromic acid yields anthraquinone.

The author is engaged in the further investigation of these substances.

13 "*The Preparation of Glyceric Acid.*" By T. Lewkowitsch, Ph.D.

Debus (*Annalen*, cvi., 79) and Sokoloff (*Annalen*, cvi., 85) recommend preparing glyceric acid from its repeatedly re-crystallised calcium salt by means of the requisite quantity of oxalic acid; Mulder (*Ber.*, xiii., 1902), however, has proposed the use of lead glycerate and its treatment with sulphuretted hydrogen.

When recently preparing a quantity of glyceric acid, the author has found that it is impossible to completely convert the lead salt in the way indicated by Mulder, part of the lead remaining dissolved. A great number of experiments, carried out under various conditions, led all to the same result.

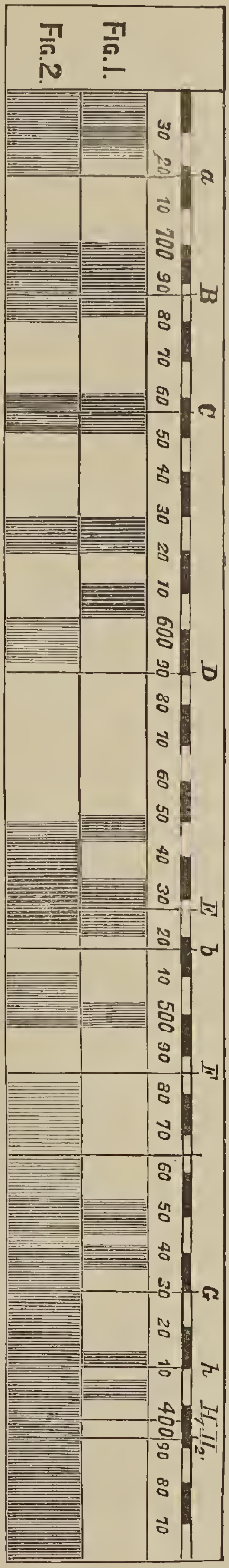
It is therefore necessary to return to the old prescription of Debus and Sokoloff, viz., to prepare glyceric acid from its calcium salt by means of oxalic acid.

14. "*The Relation of Cobalt to Iron as Indicated by Absorption-spectra.*" By W. J. Russell, Ph.D., and W. J. Orsman, Junr.

It is well known that when examined spectroscopically, some coloured metallic compounds are found only to produce a general absorption, but from previous observations it seemed possible to the authors that in some cases at least this might be resolved into bands by employing more powerful chemical agents than are generally used in such cases; experience had indicated that the chloride is usually the most suitable salt, and that it should be dissolved in chlorhydric acid and the liquid saturated with hydrogen chloride, also that, if possible, ether should be taken as solvent.

Applying these views to iron, it was found that ferric chloride gave a banded spectrum strikingly similar to that of cobalt chloride. Irons of all kinds were examined: pig iron, commercial cast iron, and various manufactured articles; steel in the form of wire, needles, and knives; and a number of specimens of reputed pure iron, viz., Demidorft's sheet iron, a sample of which was kindly given to the authors by Mr. Crookes, electro-deposited iron, and some ancient Indian iron from Professor Roberts-Austen, and iron prepared by the late Dr. Matthiessen. Also a large number of iron ores—hæmatite Elba ore, Welsh bog ore, micaceous ore, ordinary spathic ore, a spathic ore found in cryolite, for which the authors have to thank Dr. Müller; Siderite, pyrites from the chalk, wolfram and rouge. Iron was also separated from the ignited residue of blood. All the specimens examined gave the same result.

Fig. 1 represents the bands seen in a solution of cobalt chloride to a scale of wave-lengths; the three most refrangible bands are easily photographed, but are not visible to the eye under ordinary conditions. The iron spectrum (Fig. 2) in general appearance closely resembles the cobalt spectrum, but the band which in cobalt is at 605 is slightly shifted nearer the blue, as shown in the diagram; there appears also to be a shift in the 501 band, but in the opposite direction. It was found that ether always dissolved out of the ferric chloride a substance which gave a band of extraordinary intensity, exactly agreeing in position with the 530 band in the cobalt spectrum; further, that on increasing the strength of the ethereal solution, other bands became visible, agreeing with the bands observed in the strong chlorhydric solution of ferric chloride, and differing only in the case of the 690 and 655 bands, which in the ethereal solution were nearer the blue. Fig. 2 is the spectrum observed in a solution of iron in chlorhydric acid, peroxidised by any ordinary means.



For a variety of reasons the authors believe that this spectrum (Fig. 2) does not arise from the presence of cobalt in the iron. In the first place there is a constant difference between the two spectra, as shown in the position and appearance of the band at 597. A trace of cobalt dissolved along with the iron gives the same spectrum as pute cobalt dissolved in chlorhydric acid. Again, on gradually increasing the strength of a pure cobalt chloride solution, the bands in the red are the first to appear, and the band at 530 is not visible until the general absorption has crept up as far as 580, completely blocking up the red end of the spectrum; in an ethereal solution from iron, on the contrary, this 530 band is the first to appear, and the bands in the red only become visible in comparatively strong solutions. Ether extracts the band-giving substance from the ferric chloride with great ease; but it abstracts nothing from the cobalt chloride. Again, on dissolving iron in chlorhydric acid, no bands are visible, and so long as the iron is in the ferrous state, even ether extracts no band-giving substance; but on converting the ferrous into ferric chloride by nitric acid or potassium chlorate, &c., the band-yielding substance is at once apparent. A known weight of Mr. Crookes's Demidorff iron was converted into chloride and dissolved in a known volume of ether, and the intensity of the bands, compared with those given by cobalt chloride dissolved in a similar bulk of chlorhydric acid; it was found that approximately it required a weight of cobalt equal to that of the iron to give bands of similar intensity.

DISCUSSION.

Mr. J. NORMAN LOCKYER said that some years since, in a paper communicated to the Royal Society, he had suggested that there were many different molecular groupings of the same element possible, and that spectrum analysis would disclose these; if the same molecular grouping were demonstrated in several substances, then undoubtedly there was a common constituent. If the bands described by the authors represent a substance common to iron and cobalt, it should be possible to obtain spectroscopic evidence of its presence at some temperature on volatilising the metals; although he had not fully studied cobalt and nickel comparatively, he had, in fact, found that under certain special conditions some of the spectroscopic appearances were common to both, and in such a marked degree as to render it improbable that they were caused by impurities.

Dr. PERKIN referred to the non-appearance of bands in an alcoholic solution of purpurin and their appearance in an ethereal solution, as an illustration of the influence of the solvent.

Dr. ARMSTRONG remarked that the slight shift of the bands which had been referred to did not necessarily indicate that different substances were primarily the cause of the absorptions, as it was well known that such effects were observed on employing different solvents; the absorbing substance might, in the one case, be held in combination more firmly than in the other; this view was in harmony with the statement that ether did not extract the band-yielding substance in all cases.

Dr. RUSSELL, in reply, said that not the spectrum as a whole, but only one of the bands, was shifted. His view was that the solvents had broken up the substance into a finer state.

15. "*Note on Methyl Fluoride*," By NORMAN COLLIE, Ph.D.

MM. Moissan and Meslans have recently described (*Comp. Rend.*, Dec. 31, 1888) a new method of preparing methyl fluoride; but they do not seem to be aware that this substance had already been obtained in a state of purity (Lawson and Collie, *Chem. Soc. Trans.*, 1888, 626); the opportunity is therefore now taken to describe further experiments made with the gas.

The measurements of some of the physical constants of methyl fluoride have been made in conjunction with Professor Ramsay. The vapour pressures, taken at temperatures varying from −5° C. to 45° C. are as follows:—

Temp.	Press. M.m.	Temp.	Press. M.m.	Temp.	Press. M.m.
−5° C.	11365	15° C.	23003	35° C.	36204
0	14696	20	25621	40	40496
5	17740	25	28840	45	46010
10	20091	30	32756	—	—

The substance assumes the critical state at 44·9° C. and at a pressure of 47123 m.m. This pressure is probably slightly too high, owing to a trace of air, and the temperature too low. The error in pressure probably does not exceed 1500 m.m., and of temperature 0·2° C.

A determination of the relative density of the gas gave 17·38, the theoretical number being 17·05. On exposing a mixture of equal volumes of methyl fluoride and chlorine to sunlight, it became colourless in a few hours, the interaction being $CH_3F + Cl_2 = CH_2ClF + HCl$. The further action of chlorine was found to take place much more slowly, and attempts to prepare CCl_3F were without success.

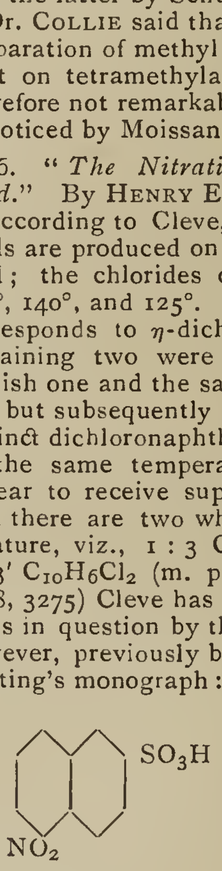
DISCUSSION.

Professor THORPE, after remarking on the importance of Moissan's researches on fluorine and its compounds, said that he feared that our Continental colleagues were less prone to take note of our work than we were of theirs. Moissan was generally said to be the discoverer of phosphorus trifluoride and oxyfluoride, but as a matter of strict history the former was first described by J. MacIvor, in the CHEMICAL NEWS (1875, xxxii., 232), and the latter by Schulze (*J. Pr. Chem.*, 1880, xxi., 442).

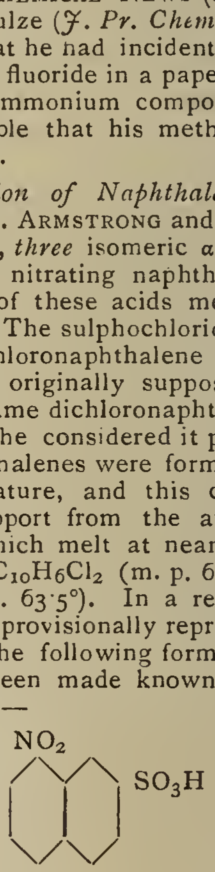
Dr. COLLIE said that he had incidentally described the preparation of methyl fluoride in a paper on the action of heat on tetramethylammonium compounds, and it was therefore not remarkable that his method had remained unnoticed by Moissan.

16. "*The Nitration of Naphthalene-β-Sulphonic Acid.*" By HENRY E. ARMSTRONG and W. P. WYNNE.

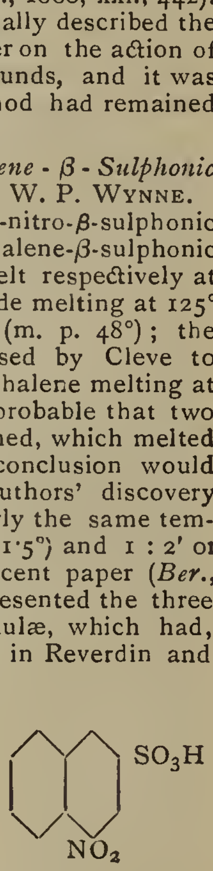
According to Cleve, *three* isomeric α-nitro-β-sulphonic acids are produced on nitrating naphthalene-β-sulphonic acid; the chlorides of these acids melt respectively at 169°, 140°, and 125°. The sulphochloride melting at 125° corresponds to η-dichloronaphthalene (m. p. 48°); the remaining two were originally supposed by Cleve to furnish one and the same dichloronaphthalene melting at 61°, but subsequently he considered it probable that two distinct dichloronaphthalenes were formed, which melted at the same temperature, and this conclusion would appear to receive support from the authors' discovery that there are two which melt at nearly the same temperature, viz., 1 : 3 $C_{10}H_6Cl_2$ (m. p. 61·5°) and 1 : 2′ or 1 : 3′ $C_{10}H_6Cl_2$ (m. p. 63·5°). In a recent paper (*Ber.*, 1888, 3275) Cleve has provisionally represented the three acids in question by the following formulæ, which had, however, previously been made known in Reverdin and Nölting's monograph:—



Sulphochloride: M. p. 125°.



M. p. 140°.



M. p. 169°.

A variety of considerations have led the authors to attempt the preparation of these acids: in the first instance they became specially interested in them on account of the supposed occurrence of isomeric change on treating two of them with PCl_5; then, when it was discovered that two dichloronaphthalenes existed which melted at nearly the same temperature, corresponding, it was to be presumed, to two of the acids, it became of importance to ascertain which of the acids corresponded to the one and which to the other dichloronaphthalene, as their constitution would thereby be determined; and lastly because, in the event of one of the acids being found to yield 1 : 3 dichloronaphthalene, the direct production of meta-derivatives of naphthalene would be established, a result of considerable theoretical importance, inasmuch as hitherto it has always been found that a heteronucleal α-derivative is formed in cases in which the corresponding benzene-derivative would afford a meta-derivative.

The authors have nitrated potassium naphthalene-β-sulphonate by grinding it up with 2·5 mol. proportions of nitric acid (1·5), and then heating on the water-bath; as soon as dissolution was effected, water was added, and the solution evaporated on the water-bath, water being frequently added. A partial separation of the isomeric acids by means of the barium salts was first effected in the manner recommended by Cleve; the various fractions were subsequently treated with PCl_5, and the sulphochlorides crystallised alternately from benzene, acetic acid, and carbon bisulphide. It was found that the nitration was complete. Both on account of the large proportion of the chloride melting at 169° which is obtained, and of its high melting-point, the authors were led to expect that this compound would prove to correspond to the heteronucleal dichloronaphthalene melting at 63·5°, rather than to the 1 : 3-derivative, as indicated by Cleve's formula, and they actually find this to be the case; on heating the sulphochloride with PCl_5 at 220°, then steam distilling, re-steaming the product, and crystallising it from alcohol, a dichloronaphthalene was obtained which melted at 62·5 to 63°; the sulphonic acid prepared therefrom gave an anhydrous potassium salt and a sulphochloride which, soon after its separation, when only partially opaque, melted at 115°, but subsequently, when entirely opaque, at 117·5°. Cleve's two nitrosulphochlorides, melting at 125° and 169°, therefore correspond respectively to the Dahl and Badische modifications of beta-naphthylamine sulphonic acid.

All attempts to separate a third sulphochloride have been unattended with success: products of intermediate melting-point have indeed been obtained, but on recrystallisation have been resolved into the two chlorides melting at 125° and 169°. This result is perhaps significant, if the theoretical improbability of the formation of a meta-compound be borne in mind; but the authors are loth to accept the apparently logical interpretation of their results, as they are unacquainted with the precise conditions under which Cleve worked—only a very brief statement of his method having been made public—especially as the third acid is said by Cleve to be sparingly produced, and as it is within their own experience that slight variations in treatment, such as may escape notice, may materially affect the result. It is, however, noteworthy that Palmaer (*Ber.*, 1888, 3260) has obtained only the two heteronucleal β-sulphonic acids on sulphonating α-nitronaphthalene. In view of the importance of the question raised, it is hoped that Cleve will ere long communicate a detailed account of his method which will make it easy to verify his conclusions.

17. "*The Action of Bromine and Chlorine on the Salts of Tetrethylphosphonium.*" By ORME MASSON, M.A., D.Sc. (Edin.), and J. B. KIRKLAND, the University of Melbourne.

An account is given of experiments in continuation of those on the action of halogens on the salts of organic bases by Dobbin and Masson (*Chem. Soc. Trans.*, 1885 and 1886). The results show a very close general similarity between the polyhaloid-derivatives of tetrethylphosphonium and those of trimethylsulphine and of tetramethylammonium, previously described. The tendency to form solid polyhaloid compounds is, however, more marked. Thus, for instance, a crystalline tetrethylphosphonium tribromide, PEt_4Br_3, was obtained, whereas the previously described tribromides were unstable liquids; also a solid, but unstable, more highly brominated bromide, which was shown by synthetic experiments to have the composition PEt_4Br_7. Chlorine acting on the chloride gives only one compound, the trichloride, PEt_4Cl_3; but with the iodide it forms the tetrachloride, PEt_4ICl_4, which is converted by alcohol into the dichloriodide, PEt_4ICl_2. Quantitative synthetic experiments were made to ascertain whether the sulphate really resembles the haloid compounds; from these it appears that it closely resembles the bromide in its behaviour towards bromine and the chloride in its behaviour towards chlorine, both in the nature and appearance of the products and in their composition. The solid brominated sulphate, $(PEt_4)_2SO_4{\cdot}Br_{12}$, yields the tribromide, PEt_4Br_3, when treated with alcohol. The most highly brominated derivative of the sulphate that could be obtained had the composition $(PEt_4)_2SO_4{\cdot}Br_{22}$; but it is doubtful whether this really represents a definite compound. The following table contains a list of the new substances, the methods of forming them, and their most marked properties. The first formula is queried because the experimental evidence does not suffice to establish it, though analogy renders it probable. The eighth formula is queried because of the doubt already expressed as to the definite nature of the substance to which it is assigned.

18. "*The Preparation of the Salts of Triethylsulphine, Tetrethylphosphonium, and Analogous Bases.*" By ORME MASSON, M.A., D.Sc. (Edin.), and J. B. KIRKLAND, University of Melbourne.

When sulphur is heated with ethyl iodide in sealed tubes at 180°, it entirely disappears and is converted into triethylsulphinetriiodide, $S+3EtI=SEt_3I_3$; on treating this triiodide under water with hydrogen sulphide it is converted into the iodide, from which the hydroxide, &c., may be prepared. The yield is nearly a theoretical one.

The same process is applicable to the preparation of selenine salts from selenium, and of tetraethylphosphonium salts from phosphorus—either the ordinary or the red modification. In the case of phosphorus, however, a mixture of two different polyiodides is obtained: $2P+7EtI=PEt_4I_3+PEt_3I_4$. The second of these is converted by the treatment with hydrogen sulphide and water into triethylphosphine oxide, so that only half of the phosphorus goes to form the phosphonium salt,—

$$PEt_4I_3+H_2S=PEt_4I+2HI+S;$$
$$PEt_3I_4+H_2S+H_2O=PEt_3O+4HI+S.$$

The yield obtained is very nearly theoretical.

The use of silver hydroxide may be obviated by adopting Hofmann's potash process in recovering tetrethylphosphonium iodide from the solution obtained after the hydrogen sulphide treatment. The solution is saturated with potash and warmed, when the iodide forms an oily layer on the surface, which is readily separated and purified. This method works well, and it also answers in the case of the sulphine preparation.

The researches of Carius and of Crafts and Silva on the preparation of triethylphosphine oxide from phosphorus and ethyl iodide are criticised in the light of the results of the present investigation.

No.	Substance.	Method of formation.	Temperature of formation.	Chief properties.
1.	PEt_4IBr_4 (?).	Br_2 on iodide.	Cold	Bright red crystal, solid, unstable.
2.	PEt_4IBr_2.	Alcohol on 1.	—	Orange crystals, stable.
3.	PEt_4ICl_4.	Cl_2 on iodide.	70°	Yellow crystal mass, unstable.
4.	PEt_4ICl_2.	Alcohol on 3.	—	Yellow crystals, stable.
5.	PEt_4Br_7.	Br_2 on bromide.	110°	Scarlet crystal mass, unstable.
6.	PEt_4Br_3.	Alcohol on 5 or 9.	—	Red crystals, stable.
7.	PEt_4Cl_3.	Cl_2 on chloride.	110°	Yellow crystal mass, unstable.
8.	$(PEt_4)_2SO_4Br_{22}$ (?).	Br_2 on sulphate.	Cold	Red liquid, unstable.
9.	$(PEt_4)_2SO_4Br_{12}$.	,, ,,	110°	Red solid, unstable.
10.	$(PEt_4)_2SO_4Cl_4$.	Cl_2 ,, ,,	130°	Yellow solid, unstable.

PHYSICAL SOCIETY.

Annual General Meeting, February 9, 1889.

Prof. Reinold, F.R.S., President, in the chair.

The Reports of the Council and Treasurer were read and adopted. From the former it appears that the number of members has only slightly increased during the year, due, it is supposed, to the advantages offered by the Society not being generally known, and a fly-leaf has been prepared, giving a short account of the Society's objects and procedure, copies of which may be obtained from the Secretaries.

During the past year Vol. I., Part I,, of "Physical Memoirs selected and translated from Foreign Sources" has been printed and issued to members, and translations of important memoirs by Fourier, Hittorf, and Volta are well advanced, and will be published shortly.

The Treasurer's report showed the financial position of the Society to be very satisfactory.

Owing to the lamented death of Prof. Clausius, a vacancy has occurred in the list of Honorary Members, to fill which Prof. R. W. Bunsen was nominated by the Council and duly elected.

The following gentlemen were elected to form the new Council:—

President—Prof. A. W. Reinold, M.A., F.R.S.

Vice-Presidents—Dr. E. Atkinson; Prof. W. E. Ayrton, F.R.S.; Shelford Bidwell, M.A., LL.B., F.R.S.; The Right Hon Lord Rayleigh, M.A., D.C.L., Sec.R.S.

Secretaries—Walter Baily, M.A.; Prof. J. Perry, F.R.S.

Treasurer—Prof. A. W. Rücker, M.A., F.R.S.

Demonstrator—C. Vernon Boys, F.R.S.

Other Members of Council—Hon. R. Abercromby; T. H. Blakesley, M.A., M.Inst.C.E.; W. H. Coffin; Conrad W. Cooke; Prof. O. Lodge, D.Sc., F.R.S.; Prof. W. Ramsay, Ph.D., F.R.S.; W. N. Shaw, M.A.; Prof. S. P. Thompson, D.Sc.; H. Tomlinson, B.A.; G. M. Whipple, D.Sc.

Cordial votes of thanks were passed:—1st, To the Lords of the Committee of Council on Education for the Use of the rooms and apparatus of the Normal School of Science; 2nd, To the Council and Officers of the Society for their services during the past year; and 3rd, To the Auditors, Mr. Inwards and Prof. Minchin, for examining the accounts.

In returning thanks for the Council and Officers, the President attributed the great success of their meetings to the indefatigable zeal displayed by the Hon. Secretaries.

The meeting was then resolved into an Ordinary Science Meeting, at which Mr. James Wimshurst and Mr. Percy W. Sellon were elected Members.

Prof. A. S. Herschel, D.C.L., F.R.S., read a paper on "*Physico-Geometrical Models*," and exhibited a collection of geometrical figure models illustrating elementary forms of crystallographical and chemical form constructions.

The subject, he said, had suggested itself to him as an important one for study some five years ago, from the possibility which he then discovered of effecting a four-limbed mechanical cycle, similar to a thermo-dynamic cycle, with a conically revolving pendulum, the mathematical conditions of whose motion involved the logarithm of the circle radius of the knobs' revolution as a quantity equivalent to entropy in the thermal cycle. The mechanical cycle may be effected as follows:—Suppose the pendulum knob to be revolving at velocity V_1 and radius r_1; imagine the controlling force to decrease, so that the radius varies from r_1 to r_2, the velocity remaining constant at V_1; then increase the controlling force to its original value and simultaneously impart velocity to the knob to keep the radius constant at r_2, the final velocity being V_2. Next, further increase the controlling force so as to cause the radius to decrease to r_1 at velocity V_2, and finally, decrease the controlling force to its initial value, simultaneously retarding the knob till the velocity is V_1 at radius r_1. The nett energy concerned in the operations was given as $W=(V_1^2-V_2^2)\phi$, where $\phi=\log.\frac{r_1}{r_2}$, and the cycle affords an illustration of transformation of gyratory motion into energy of reverberatory push along the axis. The logarithm, ϕ, is also measured by the area of a hyperbolic sector, and is connected (as was shown) with a sector of the circle which a lamp's conical beam would inscribe upon a square glass screen or plate dividing a long room of square cross-section into two parts. The conical beam, prolonged through the glass, then traces, on the walls beyond, hyperbolas, whose sectors from their summits are related to the circles' corresponding sectors by a well-known hyperbolocyclic trigonometrical connection. From this mode of constructing the connection, and from a discordance which it shows at the asymptote extremities with Euclid's definition of parallel straight lines, the author concludes that cubic space cannot be continuous in its structure, but must be in a physically constructive sense, like material particles indestructively atomic or molecular. The models showed modes of constructing cubic space in various ways, chiefly by means of tetrahedra, octahedra, and dodecahedra, the common element of form in these being also shown to be the right-angled tetrahedron or "biquoin" obtained by dividing a cube into six equal parts by three planes through its diagonals.

A model of Sir W. Thomson's soap foam figure and some wooden models representing Haüy's polyhedral atoms and their combinations were exhibited to illustrate the structural view thus taken of geometry, and chemical figure models of the ring of tetrahedral carbon molecules in benzene, and of the asymmetric groups of similar atoms in active and inactive tartaric acid were shown.

CORRESPONDENCE.

ACTION OF FERROUS SULPHATE ON SOILS.

To the Editor of the Chemical News.

Sir,—Formerly, the action of nitrate of soda on the soil was imperfectly understood—whether due to the nitric acid present in the nitrate or to the soda. No tyro in agricultural chemistry would now dream of attributing it to the action of the soda. No more would, I feel convinced, the recent experimenters on ferrous sulphate attribute, as they all seem to me to have done, the action of this substance to its base alone, if they instituted comparative experiments with (1) sulphuric acid (highly dilute), (2) gypsum, (3) salt-cake, (4) sulphate of alumina, (5) sulphate of iron, using equivalents of sulphuric acid in each.

Has green vitriol any tendency to absorb ammonia from the atmosphere, or has the compound to which it is resolved in the soil any such tendency?

The result of the action of sulphuric acid in the form of sulphate of alumina upon the soil should be interesting, as alumina seems only to be present in the ash of the Lycopods. So far as I have followed these experiments the great bulk of them seem to have been upon sulphur-loving plants.

I should be glad if some one who has more time and opportunity than I have would undertake the experiments which I have indicated.—I am, &c.,

J. G. McIntosh.

THE FATAL EXPLOSION OF A GAS CYLINDER AT DUBLIN.

To the Editor of the Chemical News.

Sir,—The recommendation to make the couplings of different sizes would not prevent the man in charge of the compressing pumps from accidentally putting coal-gas into the oxygen compressor, or *vice versa*, and then re-filling a returned half-empty bottle with the wrong gas. What the public require is perfect security, even if the gases have been accidentally supplied mixed. Bearing in mind that the most energetic combustion is at once arrested by contact with a sufficient quantity of cold metal, I believe that all risk of explosion would be avoided by attaching a spiral worm of fine copper tubing to the lower portion of the valve, so as to project into the bottle, through which worm the gases would have to pass before reaching the jet. If one coil was found insufficient, two, or even three coils could be used, one inside the other, without materially reducing the capacity of even the smallest sized bottle.

A Hemmings' safety jet, permanently fixed behind the valve and in the bottle, would, of course, have the same effect, but would, I fear, reduce the pressure at the burner too considerably to admit of its use.—I am, &c.,

Clement J. Leaper.

Technical Schools, Kevin Street,
Dublin.

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. cviii., No. 4, January 28, 1889.

Reactions of Hydrogen Peroxide with Chromic Acid.—M. Berthelot.—If hydrogen peroxide is brought in contact with chromic acid in presence of a powerful mineral acid, such as sulphuric or hydrochloric acid used in excess, there is first produced the blue colouration of perchromic acid, followed by a slow escape of oxygen. The chromic acid is converted into chromic sulphate. Feebler acids, such as acetic and phosphoric, produce, with chromic acid and oxygenated water, a purple or violet colouration, due to a mixture of perchromic acid and of a brown compound. With more feeble acids, such as boric and hydrocyanic acids, the liquid merely turns brown. With pure potassium dichromate oxygenated water is decomposed to an indefinite extent. After the liquid, which at first turns brown, has resumed its original colour, on the addition of a fresh dose of oxygenated water the brown colour reappears. In twenty-four hours one equivalent of potassium dichromate has thus been found to decompose 40 equivalents of oxygenated water. At the end of the experiment the solution of dichromate retains its original composition, and contains no trace either of perchromic acid or of chromium oxide.

Butylic Ethers, Mixed and Properly So-called.—E. Reboul.—The author describes di-isobutylic ether, a secondary isobutylic ether, a tertiary isobutylic ether and di-secondary butylic ether, and the secondary-tertiary and ditertiary butylic ethers.

On the Gadolinium of M. de Marignac.—Lecoq de Boisbaudran.—This paper is a critique on certain researches of Mr. Crookes.—The author quotes certain passages quite correctly in English in a footnote, but modifies them very seriously in the body of his paper, imputing to Mr. Crookes assertions which he has never made, as anyone may see who takes the trouble to compare the footnote with M. de Boisbaudran's paraphrase and comments.

New Solvents for Prussian Blue; Easy Preparation of Ordinary Soluble Prussian Blue and of Pure Prussian Blue Soluble in Water.—Common Prussian blue and Turnbull's blue, when duly purified, appear identical. Ordinary Prussian blue may be rendered soluble by digestion for some days, or by boiling with a solution of potassium ferrocyanide or, preferably, ferricyanide. It may be at once prepared by adding gradually a hot solution of 70 parts crystalline ferrous sulphate to the boiling solution of 110 parts potassium ferricyanide, boiling for two hours and filtering, washing with pure water, and stopping when the washings run through deeply blue. Soluble blue gives, with metallic salts, a series of definite blue compounds. Molybdic acid and ammonium molybdate and tungstate dissolve Prussian blue readily.

Relations between Solubilities and Melting-Points. — A. Etard.— This paper requires the accompanying diagram.

Determination of Organic Nitrogen by Kjeldahl's Method.—C. Viollette.—On determining the nitrogen in maize-cake by this method and by those of Will-Varrentrapp and Dumas, the author obtains results closely agreeing, that by the soda-lime process being the lowest by 0·12 per cent. The Kjeldahl process does not economise time.

Compounds of Aniline with Chloric and Perchloric Acids.— Ch. Girard and L. L'Hote.—Aniline chlorate and perchlorate may be prepared by the direct action of the acids upon aniline, or the chlorate may be obtained by double decomposition. "Ordinary" nitric acid and hydrochloric acid react upon aniline chlorate without ignition, giving coloured products which the authors are studying.

Lime Combined in Soils.—Paul de Mondesir.—Most soils contain a noteworthy proportion of lime not in the state of carbonate, but capable of being removed by cold dilute acids.

No. 5, February 4, 1889.

Certain Reactions of Mercury Ammonium Chlorides.—M. André —The precipitation of the two bodies above mentioned, effected in the cold, yields a series of compounds which are sometimes very complicated, and which are frequently mixtures in various proportions of Kane's mercuriammonium chloride or chloramidide (NH_2HgCl), and of dimercuriammonium chloride. This complexity depends on the action of an excess of water upon the chloramidide.

Separation of Zinc and Nickel.— H. Baubigny.—(See p. 88).

The Formation-heat of Aniline Bichromate.—Ch. Girard and L. L'Hote.

Alcoholic Combinations of Sodium Glycol-alcoholate.— M. De Forcrand.— These two thermochemical papers do not admit of useful abstraction.

The Acetonic Function of Nitro-camphor; its Hydrochloration and its Polymerisation.—P. Cazeneuve.— The author describes reactions showing the acetonic function of nitro-camphor. He then explains the formation of nitro-camphor hydrochlorate, its decomposition by alcoholised water yielding a hydrate and subsequently a polymer with a phenolic function.

Determination of Organic Nitrogen by Kjeldahl's Process.—E. Aubin and M. Alla.—The authors, in reply to a paper by M. L'Hote (*Comptes Rendus*, Jan. 7, 1889), describe the manner in which they have carried out the process. They took 0·5 grm. of nitrogenous organic matter, 20 c.c. of pure sulphuric acid at 66°, and 0·5 grm. of mercury. The operation did not exceed ninety minutes, and the liquids obtained were clear and colourless. The authors conclude that Kjeldahl's method is trustworthy and accurate, the results being equal, if not superior, to those obtained with soda-lime. The organic matter is completely transformed during the operation, and all the nitrogen is recovered as ammonia. There is no loss of ammonia during the operation.

Journal fur Praktische Chemie.
Vol. xxxix., No. 1.

On Metallic Diamine Compounds.—S. M. Jorgensen.—The author has obtained and examined platinum and cobalt bases in which ethylene-diamine takes the place of ammonia, and finds then exceedingly stable. In this memoir he describes the salts of platino-ethylene-diamine, the ethylene-diamine-luteo-cobaltic and the dichloro-praseo-cobaltic salts.

Diazo- and Azo-compounds of the Fatty Series, No. IV.—Th. Curtius and R. Jay.—This paper, which treats of hydrazine, is too extensive for abstraction.

Researches from the Laboratory of the University of Freiburg.—These consist of a paper by Ad. Claus and J. Hirsch on Metakresol.

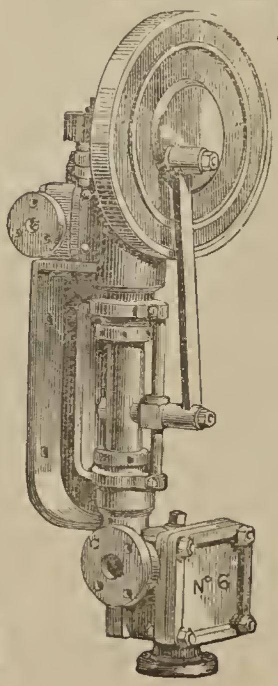
Journal de Pharmacie et de Chemie.
Vol. xix., No. 3.

The Presence of the Vapour of Benzene in Coal-Gas, and on its Determination.—M. Berthelot.—Already noticed.

Chemical Constitution of Spongine.—M. P. N. Zalocostas.—Spongine approximates in its constitution to the collagenous substances.

MEETINGS FOR THE WEEK

Monday, 25th.—Medical, 8.30.
Tuesday, 26th.—Institute of Civil Engineers, 8.
— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
— Society of Arts, 8. "English Bookbinding in the Reign of Henry VIII.," by W. H. J. Weale.
— Royal Medical and Chirurgical, 8.30.
Wednesday, 27th.—Society of Arts, 8. "The Irish Lace Industry," by Alan S. Cole.
Thursday, 28th.—Royal, 4.30.
— Royal Institution, 3. "The Venom of Serpents and Allied Poisons," by Sidney Martin, M.D.
— Institute of Electrical Engineers, 8.
Friday, March 1st.—Royal Institution, 9. "Leigh Hunt," by Edmund Gosse, M.A.
Saturday, 2nd.—Royal Institution, 3 "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.



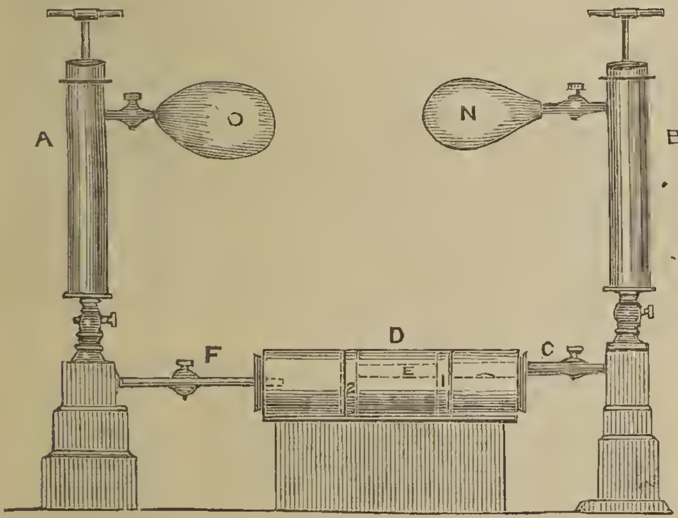
THE CHEMICAL NEWS.

Vol. LIX. No. 1527.

THE PARTIAL SEPARATION OF OXYGEN FROM THE ATMOSPHERE BY MEANS OF EXOSMOSE.

By H. N. WARREN, Research Analyst.

The diffusion or osmotic properties of a gas, when compared with another of opposed density, has been pointed out from an early date, perhaps one of the simplest means of observing the same being the swift passage of hydrogen gas when in admixture with one of greater density, through the pores of a moist membrane. So perfect, however, is this peculiar separation in the case of hydrogen when in admixture with an equal bulk of oxygen, the operation being performed in a caoutchouc bag kept weighted, that on examining the same after an hour's duration a sufficiency of hydrogen will be observed to have escaped, so as to totally destroy the explosive nature of the mixture. By taking advantage of the peculiarity of caoutchouc to condense gases upon its surface, an apparatus has been lately constructed, and intended for the parting or partial separation of oxygen gas from the atmosphere as explained by the accompanying figure. It is composed of two somewhat powerful exhausting syringes, A and B, the top extremity of each being provided with a cock, and connected to the same two small gas bags, the bottom, or further extremity of each syringe being connected with a porous pot, D, provided internally with two discs of compressed charcoal, and charged with a preparation of finely-divided caoutchouc, obtained by immersing the same, before using, in a solution of caoutchouc in naphtha. The outer wall of the porous cylinder is also provided with a tightly fitting jacket of very thin rubber, the pipe, E, in connection with the cork, C, being pierced with two small orifices, and terminating at the commencement of the second disc, and intended to remove the nitrogenous atmosphere remaining in the cylinder after the separation of the oxygen by means of the A syringe. The piston rod of the syringe, A, being now raised upwards, a vacuum is naturally produced within the porous cylinder, D, and being surrounded by the atmosphere, an inward pressure is at once experienced, the result being that the cylinder is partially filled with an atmosphere extremely rich in oxygen, and also with one in which nitrogen predominated largely, which, by working the piston on either side of the cylinder with due care, may be collected in their respective bags, namely, O and N, intended for the reception of the same. On submitting both portions of these separated gases to examination, that portion obtained from the syringe, A, was found to be sufficiently rich in oxygen to readily re-kindle a glowing splint, and even support the combustion of iron wire, results of several analyses proving an existence of 50 per cent of oxygen, while the nitrogenous atmosphere collected by the opposite cylinder readily extinguished a lighted match when introduced into the same. By a slight alteration in the arrangement of the apparatus a mixture of hydrogen and oxygen were separated so effectively as to produce only the minutest quantity of water when separately made to ignite. Carbonic anhydride and various other gases in admixture with one another were experimented upon with a like result.



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

COTTON-SEED OIL AND BEEF FAT IN LARD.

By J. A. WILSON.

Up to some time ago the positive detection, not to say the approximate determination, of cotton-seed oil and beef fat in lards was of a difficult character, but the discovery of certain optical and general tests has rendered this problem tolerably easy. Some time ago the author had reason to examine two samples of old cotton-seed oil, which had been in the laboratory thirteen and seventeen months respectively, and although the samples responded clearly to the general tests, on applying the silver test in the different forms prescribed, no reduction occurred alone or when mixed with genuine lard. Here then we have a serious objection to these silver tests, for the matter causing reduction of silver nitrate seems to be destroyed by keeping; hence a reaction with silver nitrate proves the presence of cotton oil, but no reaction does not prove the absence in lard.

Chemists having old samples of oil in their possession will render service by trying the silver nitrate reaction on the oils. It is to be remarked here that I tried the reaction on the fatty acids produced by saponification, with a negative result. By acting on the oil by sulphur chloride, small percentages of cotton oil can be detected.

Researches on this subject have been published by Mr. Warren. Some time ago the author made some experiments on the surface tension tests for oils. Pure dry melted lard, dropped on water of 100° F., does not extend or increase in size. Beef fat or mutton fat extends over the surface of the basin, breaking up into innumerable droplets, and is agitated by a rapid gyratory motion.

The author mixed pure lard with 10, 15, 20, and 25 per cent of beef fat, and allowed one drop to fall on water of 100° F. By noticing the degree of expansion and the time required, approximate determinations of the beef fat can be obtained. Mutton fat behaves similarly, and therefore cannot be distinguished. On repeating this with exactly the same lard eight months after, the drop behaved exactly like beef or mutton fat, this being most unfortunate. The only other test is the delicate test with iodo-mercuric chloride of Hubl. This method is one of the most delicate and best in the chemistry of oils and fats. The author's experience is most extensive, its results are exact and reliable. Somewhat discrepant statements exist, however, as to the iodinic absorption of cotton-seed oil and lard. Thus Pattinson (*Journal Society Chem. Industry*, No. 1, vol. viii.) gives from 57 to 63 per cent iodine absorbed by lard, and 105 to 116 per cent for cotton oil. The author has never found more than 60 per cent for lard and 110 per cent for cotton-seed oil. Again, Pattinson gives 41 per cent for beef fat, whilst my figures approach the average, 44 per cent. It is needless to say these different statements would cause grave errors in calculating the foreign fat in a sample of lard

It would be of great service if chemists would state their experience of this most excellent test. In my opinion no satisfactory statement of the amount of beef fat or stearin can be given in lard containing cotton-seed oil. The following table gives the maximum and minimum absorptions of iodine in the common oils I have found:—

Name of Oil or Fat.	Maximum Absorption. Per cent.	Minimum Absorption. Per cent.
Cotton-seed Oil	110·11	106·0
Linseed „	149·10	148·07
Rape Oil (Stettin)	102·76	100·43
Castor „	83·40	—
Palm „	52·40	51·01
Olive „	84·00	78·50
Neatsfoot „	70·70	70·00
Cocoanut „	9·35	8·97
Lard	60·00	57·10
Beef Fat	44·00	43·26
Mutton „	46·19	45·18
Bone „	49·58	46·27
Tallow	41·98	40·01

The Laboratory,
Tottington Mill, near Bury.

SEPARATION OF ALUMINIUM AND ZIRCONIUM.*

By I. THOMAS DAVIS, Jr.

While studying some of the iodine compounds of zirconium it was found that the iodate, when precipitated from neutral or very feebly acid solutions, gave filtrates in which no zirconium could be detected with ammonia. This apparent insolubility and the fact that aluminium iodate, according to Berzelius,† was deliquescent, suggested the possibility of separating these metals by means of an alkaline iodate. Solutions of aluminium refused to show the least signs of precipitation when treated in a manner similar to that by which complete precipitation had been obtained from zirconium salts. In order to examine the method quantitatively, a solution of zirconium chloride in hydrochloric acid was employed. This solution was prepared as follows:—

Zircon was decomposed with sodium carbonate and hydrate, the fusion boiled out repeatedly with water, and the residual sodium zirconate decomposed with sulphuric acid. This solution was evaporated carefully to dryness, and kept at a heat just below redness for half an hour. It was then dissolved in water, to which a little sulphuric acid had been added, and precipitated with ammonia. The resulting hydrate was dissolved in hydrochloric acid, and the zirconium precipitated several times with sodium thiosulphate to separate the last trace of iron. The zirconium was finally precipitated with ammonia, washed until the filtrate no longer reacted for chlorine, dissolved in hydrochloric acid, which was added in sufficient quantity to prevent the deposition of an oxychloride, and diluted to the proper strength. It contained in round numbers 5 per cent of hydrochloric acid by weight.

In order to standardise this solution the zirconium was precipitated with ammonia, using to a certain extent the same precautions which are to be observed when aluminium is precipitated in a similar manner, and Nos. (1) and (2) represent duplicate determinations.

Weight of solution.	ZrO_2 found.	ZrO_2 in 25 grms.
(1) 25·344 grms.	0·1696 grm.	0·1673 grm.
(2) 25·322 „	0·1686 „	0·1669 „

The average, 0·1671 grm., has been taken as representing the correct amount of the tetrachloride, $ZrCl_4$, in terms of the dioxide, ZrO_2, in 25 grms. of the solution.

Qualitative experiments seemed to point to the possibility of complete precipitation, as an oxyiodate, when the solution contained a moderate amount of free acid.

Weight of solution.	ZrO_2 used.	ZrO_2 found.	Error.
(3) 25·325	0·1693	0·1604	0·0089 −
(4) 25·297	0·1691	0·1576	0·0115 −

In (3) and (4) the acid was neutralised with sodium carbonate, and hydrochloric acid added in such quantity that the solutions contained 1 per cent by weight. Sodium iodate was then added in excess, and the solutions brought to a boil, and fifteen minutes afterwards filtered, washed with hot water until the filtrate and washings in each case amounted to about 400 c.c. They were dried and ignited together with the filters. During the ignition slight explosions took place, and once the lid of the crucible, which contained (4), was thrown off. At the same time it took prolonged ignition at the highest heat of the blast-lamp to arrive at constant weight, small quantities of iodine vapours being evolved. These vapours were due to sodium iodate retained by the precipitate, as the zirconium salt seems to part with its iodine at a heat below redness. Hence the idea of igniting this iodate or of precipitating zirconium from solutions containing much acid was abandoned.

Weight of solution.	ZrO_2 used.	ZrO_2 found.	Error.
(5) 20·300	0·1357	0·1380	0·0023 +
(6) 20·159	0·1347	0·1349	0·0002 +

In (5) and (6) the acid of the zirconium solution was neutralised with sodium carbonate, which was added until a permanent precipitate was formed. This was dissolved in the smallest possible quantity of dilute hydrochloric acid, sodium iodate added in excess, and the solutions boiled for fifteen minutes. Instead of filtering immediately, as in (3) and (4), it was thought safest to allow them to stand some time. They were therefore allowed to stand over night, then filtered, washed with hot water, dissolved in hydrochloric acid, of which it took a considerable amount, even while hot, precipitated with ammonia, ignited, and weighed. Unfortunately in (5) the washing was very imperfect, but in (6) and all subsequent experiments the washing was continued until the filtrates no longer gave a reaction for chlorine.

Weight of solution.	ZrO_2 used.	ZrO_2 found.	Error.
(7) 10·086	0·0674	0·0674	0
(8) 10·088	0·0674	0·0682	0·0008 +
(9) 20·263	0·1354	0·1352	0·0002 −
(10) 20·408	0·1364	0·1365	0·0001 +

(7), (8), (9), and (10) were carried on exactly like (5) and (6), with the exception that to (9) 5 grms. of sodium chloride were added, and to (10) 10 grms. Precipitation seems to be complete, and sodium chloride is without action on the iodate. In filtering the iodate, which is flocculent, it is safest to use Swedish paper, as the precipitate can be more readily washed off without loss than from some of the other papers used.

These experiments having turned out so satisfactorily, it was thought possible that complete precipitation might take place in solutions containing some free acid, but not nearly in such quantity as had been employed in (3) and (4). To determine this point, (11) and (12) were made.

Weight of solution.	ZrO_2 used.	ZrO_2 found.	Error.
(11) 30·337	0·2028	0·1996	0·0032 −
(12) 30·410	0·2032	0·2010	0·0022 −

The acid was neutralised as before and enough hydrochloric acid added to make the solution contain about 0·1 per cent of it. Aluminium chloride was also added in quantity about three times that of the zirconium chloride

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* *American Chemical Journal*, Vol. xi., No. 1.

† *Lehrb.*, ed. 1843—48, iii., 479.

present. The solution of aluminium chloride was prepared by precipitating pure potassium alum several times to separate all sulphuric acid, and the hydrate dissolved in hydrochloric acid. Its strength was only approximately known. It is evident that precipitation, even in the presence of this small amount of acid, is incomplete. However, no aluminium seems to have been thrown down. The solutions, then, previous to precipitation, must be nearly neutral. Therefore in (13—14) and (15—16) the precipitation was carried on as in (5) and (6).

Weight of solution.	ZrO_2 used.	ZrO_2 found.	Error.
(13) 10·097	0·0675	0·0673	0·0002 –
(14) 10·070	0·0673	0·0671	0·0002 –
(15) 49·490	0·3308	0·3302	0·0006 –
(16) 49·398	0·3302	0·33 01	0·0001 –

In (13) and (14) the quantity of aluminium was about three times that of the zirconium, while in (15) and (16) equal quantities were used. These numbers seem to be within the error of analysis. Therefore to separate these two metals I proceed as follows:—Their solution in hydrochloric acid is treated with sodium carbonate until a permanent precipitate is formed. This precipitate is dissolved in the smallest possible quantity of dilute hydrochloric acid, and sodium iodate added in excess. The solution is heated for about fifteen minutes. It is then allowed to stand twelve hours, filtered, washed down with boiling water, dissolved in hydrochloric acid, and finally precipitated with ammonia, ignited, and weighed. A convenient strength of solution is 100 m.grms. ZrO_2 in 100 c.c.

Three analyses of the zirconium salt proved it to be an oxyiodate of variable composition. Several attempts were made to separate iron, both in the ferrous and ferric state, but without success. This metal must be removed from the mixture of aluminium and zirconium previous to their treatment with sodium iodate.

OFFICIAL METHODS OF ANALYSIS
OF THE
ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

(Continued from p. 89).

Methods of Analyses of Dairy Products.

Butter.

Microscopic Examination.

Place a small portion of the fresh sample, taken from the inside of the mass, on a slide, add a drop of pure sweet-oil, cover with gentle pressure, and examine with a one-half to one-eighth inch objective for crystals of lard, &c.

Examine same specimen with polarised light and selenite plate without the use of oil.

Pure fresh butter will neither show crystals nor a particoloured field with selenite. Other fats, melted and cooled and mixed with butter, will usually present crystals and variegated colours with the selenite plate.

Specific Gravity.

Take a specific gravity flask, not graduated, the stopper of which carries a delicate thermometer, whose bulb occupies sensibly the centre of the flask. The thermometer should be first compared with a standard instrument.

Clean the picnometer with water, alcohol, and ether; dry, be careful to remove all the ether vapour, and weigh. Fill with distilled water, insert stopper, and place in vessel containing water which comes nearly to top of picnometer (without stopper); gradually raise the temperature of water in vessel containing flask until it is 40·5° to 41° C.

The moment the thermometer of the picnometer marks 40° remove the flask, dry carefully, cover capillary safety-tube, and set in balance or desiccator to cool. Weigh when temperature falls nearly to that of balance-room. Having determined the titre of the flask, it is to be carefully dried, filled with the melted and filtered fat at a temperature below 40°, and the weight of the fat determined at 40°, as directed above.

Melting-point.

Apparatus.—The apparatus consists of (1) an accurate thermometer, for reading easily tenths of a degree; (2) a less accurate thermometer for measuring the temperature of water in the large beaker glass; (3) a tall beaker glass, 35 c.m. high and 10 c.m. in diameter; (4) a test-tube 30 c.m. high and 3·5 c.m. in diameter; (5) a stand for supporting the apparatus; (6) some method of stirring the water in the beaker—for example, a blowing-bulb of rubber and a bent glass tube extending to near the bottom of the beaker ; (7) a mixture of alcohol and water of the same specific gravity as the fat to be examined.

Manipulation.—The discs of the fat are prepared as follows:—The melted and filtered fat is allowed to fall from a dropping tube from a height of 15 to 20 c.m. on to a smooth piece of ice floating in water. The discs thus formed are from 1 to 1½ c.m. in diameter, and weigh about 200 m.grms. By pressing the ice under the water the discs are made to float on the surface, whence they are easily removed with a steel spatula.

The mixture of alcohol and water is prepared by boiling distilled water and 95 per cent alcohol for ten minutes to remove the gases which they may hold in solution. While still hot the water is poured into the test-tube already described until it is nearly half full. The test-tube is then filled with the hot alcohol. It should be poured in gently down the side of the inclined tube to avoid too much mixing. If the tube is not filled until the water has cooled the mixture will contain so many air-bubbles as to be unfit for use. These bubbles will gather on the disc of fat as the temperature rises and finally force it to the top of the mixture.

The test-tube containing the alcohol and water is placed in a vessel containing cold water, and the whole cooled to below 10° C. The disc of fat is dropped into the tube from the spatula, and at once sinks until it reaches a part of the tube where the density of the alcohol-water is exactly equivalent to its own. Here it remains at rest and free from the action of any force save that inherent in its own molecules.

The delicate thermometer is placed in the test-tube and lowered until the bulb is just above the disc. In order to secure an even temperature in all parts of the alcohol mixture in the vicinity of the disc the thermometer is moved from time to time in a circularly pendulous manner. A tube prepared in this way will be suitable for use for several days; in fact, until the air-bubbles begin to attach themselves to the disc of fat. In no case did the two liquids become so thoroughly mixed as to lose the property of holding the disc at a fixed point, even when they were kept for several weeks.

In practice, owing to the absorption of air, it has been found necessary to prepare new solutions every third or fourth day.

The disc having been placed in position, the water in the beaker-glass is slowly heated and kept constantly stirred by means of the blowing apparatus already described.

When the temperature of the alcohol-water mixture rises to about 6° below the melting-point, the disc of fat begins to shrivel, and gradually rolls up into an irregular mass.

The thermometer is now lowered until the fat particle

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* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

is even with the centre of the bulb. The bulb of the thermometer should be small so as to indicate only the temperature of the mixture near the fat. A gentle rotary movement should be given to the thermometer bulb, which might be done with a kind of clockwork. The rise of temperature should be so regulated that the last 2° of increment require about ten minutes. The mass of fat gradually approaches the form of a sphere, and when it is sensibly so, the reading of the thermometer is to be made. As soon as the temperature is taken the test-tube is removed from the bath and placed again in the cooler. A second tube, containing alcohol and water, is at once placed in the bath. It is not necessary to cool the water in the bath. The test-tube (ice-water being used as a cooler) is of low enough temperature to cool the bath sufficiently. After the first determination, which should be only a trial, the temperature of the bath should be so regulated as to reach a maximum about 1·5° above the melting-point of the fat under examination.

Working thus with two tubes about three determinations can be made in an hour.

After the test-tube has been cooled the globule of fat is removed with a small spoon attached to a wire before another disc of fat is put in.

Volatile Acids.

Take about 2·5 grms. filtered fat in 200 c.c. flask, to be used in subsequent distillation; add 2 c.c. aqueous solution potassium hydrate containing 0·5 grm. KOH per c.c. Add 2 c.c. 95 per cent alcohol and heat on water-bath, with occasional agitation. Saponification is complete in a few minutes. Evaporate until alcohol is all driven off, using a current of air to remove alcoholic vapour. The flask is fitted with a delivery tube and condenser. The delivery tube is carried up about 8 inches before it is bent to enter the condenser, and a bulb is blown in it just below the elbow, and this is filled with broken glass or glass-wool.

The fatty acids are then set free with 20 c.c. of a solution of phosphoric acid, made by dissolving 200 grms. glacial phosphoric acid in water and making up to 1 litre. Enough water is added to make the volume of liquid in the flask 70 c.c. Distillation is continued until the distillate measures 50 c.c., which is titrated with N/10NaOH, using phenol-phthalein as indicator.

(Care should be taken to have the potash used free from carbonate. A potash containing carbonate saponifies a fat with great difficulty. In an instance where the saponification was taking place very slowly, the potash was found to contain 6·80 per cent CO_2, equal to 21·17 per cent K_2CO_3).

Soluble Acids.

The washings obtained in the process of estimating the insoluble acids, the description of which follows, are made up to one litre, and an aliquot part taken for titration with one-tenth N alkali, using phenol-phthalein as indicator.

METHOD FOR THE DETERMINATION OF SOLUBLE AND INSOLUBLE ACIDS.

Reagents.

1. A standard semi-normal hydrochloric acid solution, accurately prepared.

2. A standard decinormal soda solution, accurately prepared; each 1 c.c. contains 0·0040 grm. of NaOH, and neutralises 0·0088 grm. of butyric acid, $C_4H_8O_2$.

3. An approximately semi-normal alcoholic potash. Dissolve 40 grms. good stick potash in one litre of 95 per cent alcohol, redistilled. The solution must be clear and the KOH free from carbonates.

4. A 1 per cent solution of phenol-phthalein in 95 per cent alcohol.

Saponification is carried out in rubber-stoppered beer-bottles holding about 250 c.c.

About 5 grms. of the melted butter fat, filtered and freed from water and salt, are weighed out by means of a small pipette and beaker, which are re-weighed after the sample has been taken out and run into a saponification bottle; 50 c.c. of the semi-normal potash is added, the bottle closed and placed on the steam-bath until the contents are entirely saponified, facilitating the operation by occasional agitation. The alcoholic potash is measured always in the same pipette and uniformity further insured by always allowing it to drain the same length of time, viz., thirty seconds. Two or three blanks are also measured out at the same time and treated in the same way.

In from five to thirty minutes, according to the nature of the fat, the liquid will appear perfectly homogeneous, and when this is the case the saponification is complete, and the bottle may be removed and cooled. When sufficiently cool the stopper is removed and the contents of the flask rinsed with a little 95 per cent alcohol into an Erlenmeyer flask of about 250 c.c. capacity, which is placed on the steam-bath, together with the blanks, until the alcohol has evaporated.

Titrate the blanks with semi-normal HCl, using phenol-phthalein as an indicator. Then run into each of the flasks containing the fat acids 1 c.c. more semi-normal HCl than is required to neutralise the potash in the blanks. The flask is then connected with a condensing tube three feet long, made of small glass tubing, and placed on the steam-bath until the separated fatty acids form a clear stratum on the surface of the liquid. The flask and contents are then allowed to become thoroughly cold, ice water being used for cooling.

The fatty acids having quite solidified, the contents of the flask are filtered through a dry filter paper into a litre flask, care being taken not to break the cake. Two hundred to three hundred c.c. of hot water is next poured on the contents of the flask, the cork with its condenser tube re-inserted, and heated on the steam-bath until the cake of acids is thoroughly melted, the flask being occasionally agitated with a circular motion, so that none of its contents are brought on the cork. When the fatty acids have again separated as an oily layer the flask and its contents are cooled in ice water, and the liquid filtered through the same filter into the same litre flask. This treatment with hot water, followed by cooling and filtration of the wash water, is repeated three times, the washings being added to the first filtrate. The mixed washings and filtrate are next made up to 1 litre, and 100 c.c., in duplicate are taken and titrated with decinormal NaOH. The volume required is calculated to the whole liquid. The number so obtained represents the measure of decinormal NaOH neutralised by the soluble fatty acids of the butter fat taken, plus that corresponding to the excess of the standard acid used, viz., 1 c.c. The amount of soda employed for the neutralisation is to be diminished, for the 1 litre, by 5 c.c., corresponding to the excess of 1 c.c. ½ N acid.

This corrected volume, multiplied by the factor 0·0088, gives the butyric acid in the weight of butter fat employed. (See table).

The flask containing the cake of insoluble fat acids is inverted and allowed to drain and dry for twelve hours, together with the filter-paper through which its soluble fatty acids have been filtered. When dry the cake is broken up and transferred to a weighed glass evaporating dish. Remove from the dried filter-paper as much of the adhering fat acids as possible and add them to the contents of the dish. The funnel, with the filter-paper, is then placed in an Erlenmeyer flask, a hole is made in the bottom of the filter-paper, and it is thoroughly washed with absolute alcohol from a wash-bottle. The flask is rinsed with the washings from the filter-paper and pure alcohol, and these transferred to the evaporating dish. The dish is placed on the steam-bath and the alcohol driven off. It is then transferred to the air-bath and dried at 100° C. for two hours, taken out, cooled in a desiccator, and weighed. It is then again placed in the air-bath and

Table for the Calculation of Soluble Fatty Acids.

No. c.c. KOH sol.	Equiv. Grms.	N 10NaOH.	Equiv. Grms.	N/10NaOH.	Equiv. Grms.	N/10NaOH.	Equiv. Grms.
10	0·088	+0·25	0·0902	+0·50	0·0924	+0·75	0·0946
11	0·0968	0·25	0·0990	0·50	0·1012	0·75	0·1034
12	0·1056	0·25	0·1078	0·50	0·1100	0·75	0·1122
13	0·1144	0·25	0·1166	0·50	0·1188	0·75	0·1210
14	0·1232	0·25	0·1254	0·50	0·1276	0·75	0·1298
15	0·1320	0·25	0·1342	0·50	0·1364	0·75	0·1386
16	0·1408	0·25	0·1430	0·50	0·1452	0·75	0·1474
17	0·1496	0·25	0·1518	0·50	0·1540	0·75	0·1562
18	0·1584	0·25	0·1606	0·50	0·1628	0·75	0·1650
19	0·1672	0·25	0·1694	0·50	0·1716	0·75	0·1738
20	0·1760	0·25	0·1782	0·50	0·1804	0·75	0·1826
21	0·1848	0·25	0·1870	0·50	0·1892	0·75	0·1914
22	0·1936	0·25	0·1958	0·50	0·1980	0·75	0·2002
23	0·2024	0·25	0·2046	0·50	0·2068	0·75	0·2090
24	0·2112	0·25	0·2134	0·50	0·2156	9·75	0·2178
25	0·2200	0·25	0·2222	0·50	0·2244	0·75	0·2266
26	0·2288	0·25	0·2310	0·50	0·2332	0·75	0·2354
27	0·2376	0·25	0·2398	0·50	0·2420	0·75	0·2442
28	0·2464	0·25	0·2486	0·50	0·2508	0·75	0·2530
29	0·2552	0·25	0·2574	0·50	0·2596	0·75	0·2618
30	0·2640	0·25	0·2662	0·50	0·2684	0·75	0·2706

dried for another two hours, cooled as before, and weighed. If there is no considerable decrease in weight the first weight will do; otherwise, re-heat two hours and weigh. This gives the weight of insoluble fat acids in the quantity taken, from which the percentage is easily calculated.

The table gives the weight of the soluble fatty acids (butyric, &c.) for each quarter of a c.c. of decinormal alkali from 10 to 30.

Example:—

	Grms.
Weight fat taken	4·967
No. c.c. N/10 alkali used	25·50
Less 5 c.c. due to 1 c.c. N/2 acid	20·50
Weight soluble fat acids	0·1804
Per cent soluble fat acids	3·63

Saponification Equivalent.

About 2·5 grms. butter fat (filtered and free from water) are weighed into a patent rubber-stoppered bottle, and 25 c.c. approximately semi-normal alcoholic potash added. The exact amount taken is determined by weighing a small pipette with the beaker of fat, running the fat into the bottle from the pipette and weighing beaker and pipette again. The alcoholic potash is measured always in the same pipette, and uniformity further ensured by always allowing it to drain the same length of time (thirty seconds). The bottle is then placed in the steam-bath, together with a blank containing no fat. After saponification is complete and the bottles cooled, the contents are titrated with accurately semi-normal hydrochloric acid, using phenol-phthalein as an indicator. The number of c.c. of the acid used for the sample deducted from the number required for the blank gives the number of c.c. which combines with the fat, and the saponification equivalent is calculated by the following formula, in which W equals the weight of fat taken in m.grms. and N the number of c.c. which have combined with the fat.

$$\text{Sap. Equiv.} = \frac{2W}{N}.$$

If it is desirable to express the number of m.grms. of potash for each grm. of fat employed it can be done by dividing 5610 by the saponification equivalent and multiplying the quotient by ten.

Water.

Place about 2 grms. in flat-bottomed platinum dish two-thirds full of clean, dry sand and heat for two hours in air-bath at 105° C. (For alternate method of estimation of water, see later on).

Estimation of Salt.

Volumetric Method.—The amount of the butter, or butter substitute, to be taken is 5—10 grms.; weigh in a counterpoised beaker-glass. The butter (fresh from the refrigerator) is placed in portions of about 1 grm. at a time in the beaker, these portions being taken from different parts of the sample. By this means a reasonably fair sample of the whole is obtained.

The given quantity having been weighed out, it is removed from the pan.

Hot water is now added (about 20 c.c.) to the beaker containing the butter, and after it has melted the liquid is poured into the bulb of the separating apparatus. The stopper is now inserted and the contents shaken for a few moments.

After standing until the fat has all collected on top of the water, the stop-cock is opened, and the water, containing most of the salt, is allowed to run into an Erlenmeyer flask, being careful to let none of the fat globules pass.

Hot water is again added to the beaker and thence poured into the separatory apparatus, the bottle well shaken, and the foregoing process is repeated ten to fifteen times, using each time 10 to 20 c.c. of water.

The resulting washings contain all but a mere trace of the NaCl originally present in the butter.

Estimation of NaCl in Filtrate.—The chloride of sodium is now determined in the filtrate by a standard solution of $AgNO_3$, using a few drops of a saturated solution of potassium chromate as indicator.

Total Mineral Matter. (*Ash*) *and Curd.*

The methods of estimating curd depend on the principle of first drying a weighed portion of the butter, and afterwards extracting the fat with ether or petroleum. The residual mass is then weighed and the curd determined by loss on ignition. This process is carried on as follows:—

Five to ten grms. of butter fat are dried at 100° C. for a few hours in a porcelain dish. The dried fat, &c., is filtered through a Gooch crucible, the contents of the dish are all brought into the crucible and well washed with ether or light petroleum. The filter crucible is dried for two hours in air-bath and weighed. The curd is then determined by loss of weight on ignition.

The total mineral matter is represented by the residue left after ignition.

Curd and insoluble substances may be estimated somewhat more accurately as follows:—

Place the butter (5 to 10 grms.) in a Gooch crucible; set the crucible on a pad of blotting-paper in an air-bath (100° C.) for an hour, wash two or three times with ether or light petroleum. Dissolve the salt with hot water, dry at 100° C., and weigh. Any insoluble mineral matter and the ash of the curd is weighed with it in this method.

Casein.

Method of Babcock.—Ten grms. of the dried butter are treated with light petroleum until all fat is removed. The residue is then ignited with soda-lime or treated by the Kjeldahl method.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 21st, 1889.

Mr. William Crookes, F.R.S., President, in the Chair.

Mr. A. E. Tutton was formally admitted a Fellow of the Society.

It was announced that the following changes in the Council List were proposed by the Council:—

As *President*, Dr. W. J. Russell, F.R.S., *vice* Mr. Crookes, F.R.S.

As *Vice-Presidents*, Professor J. Emerson Reynolds, F.R.S., and Mr. R. Warington, F.R.S., *vice* Mr. Howard and Prof. Schorlemmer, F.R.S.

As *Treasurer*, Prof. Thorpe, F.R.S., *vice* Dr. Russell, F.R.S.

As *Members of Council*, Mr. Norman Collie, PhD., Professor John Ferguson, M.A., Mr. S. U. Pickering, M.A., and Mr. J. F. M. Page, *vice* Profs. Carnelley, P. F. Frankland, and Ramsay, F.R.S., and Mr. Friswell.

Messrs. R. H. Davies, R. J. Friswell, and S. Rideal were appointed by the meeting to audit the Treasurer's accounts.

Certificates were read for the first time in favour of Messrs. John Leigh Hoskyns-Abrahall, Norman Villa, Rusholme, Manchester; James Annal, 3, Reid Street, Dundee; Richard Douglas Bailey, City Brewery, Gloucester; Henry Richardson Hoyles, c/o Messrs. Treacher and Co., Bombay; Clement Joseph Leaper, 4, Chester Road, Ranelagh, Dublin; George T. Wilkinson Newsholme, 74, Market Place, Sheffield; Richard W. Roberts, 22, Calle Arturo Prat, Valparaiso, Chili; Thomas Alexander Shegog, 39, St. Mary's Road, Dublin; Henry Simmons, 9, Christ Church Terrace, Cheltenham; Patrick Alexander Weir, M.B., Ghazipur, N.W.P., India; Charles Wood, 5, Woodview, Bradford, Yorks.

The following were elected Fellows of the Society:— Messrs. P. Carmody, Edward Mitchell Chaplin, John W. Clayton, John Curragh, Philip Norman Evans, Robert Ferguson, M.A., David Ferrier, Conrad Gerling, Alfred Miall Hanson, John Joseph Hickey, William H. Jowett, William E. Lauer, George McCalman, Harry East Miller, Arthur F. Morgan, Henry Joshua Phillips, George Arthur Pingstone, Harry Hollis Robins, Stanley Southam, James Speakman, Thomas B. Stillman, George Sherbrooke Turpin, M.A., B.Sc., Thomas John Underhill.

The following papers were read:—

19. "*Note on the Decomposition of Potassic Chlorate by Heat in the presence of Manganic Peroxide.*"

Having observed the alteration in appearance that peroxide of manganese undergoes when heated with potassic chlorate, the author has made a number of experiments, using different kinds of oxide of manganese, determining the loss of weight that the mixture suffers when heated, and also the quantity of chlorine simultaneously generated. The heating was generally effected by the vapour of boiling mercury, at which temperature the potassic chlorate is not changed. The more finely divided the peroxide, the more rapid is the action and the more chlorine is evolved. When the evolution of chlorine is prevented by the addition of a small quantity of sodic or potassic carbonate, the decomposition of the chlorate proceeds very slowly, unless the temperature be raised much above that of boiling mercury. When potassic chlorate is fused with a minute quantity of peroxide of manganese, the residue is found to be pink on cooling, indicating the presence of a permanganate: and inasmuch as potassic permanganate is decomposed at a temperature of 275°, it is not improbable that the permanganate is decomposed by the heat as rapidly as it is produced into potassic manganate, manganic peroxide, and oxygen; the resulting potassic manganate is acted on by chlorine generated by the action of the peroxide on some fresh chlorate, forming potassic chloride, manganic peroxide, and oxygen, so that the peroxide is being continually reproduced. The quantity of chlorine evolved corresponds to only a very small proportion of the manganic peroxide present, so if the first action really takes place the chlorine must be absorbed and employed in converting the potassium into chloride.

Discussion.

Professor Thorpe, referring to the well-known fact that no perchlorate is formed in presence of manganese dioxide, asked how this was to be explained.

Mr. Williams stated that he had been unable to obtain the theoretical amount of oxygen from potassium chlorate by heating it *in vacuo*: a gas was given off which attacked mercury—presumably chlorine, and therefore it was probable that the residue contained potassium peroxide. On heating silver iodate *in vacuo* the theoretical amount of oxygen was obtained without difficulty.

Professor McLeod said that he was unable to account for the non-production of perchlorate in presence of manganese dioxide; as potassium perchlorate was not decomposed by heating with manganese dioxide, it probably was not even an ephemeral product. He had without difficulty obtained almost the theoretical amount of oxygen from chlorate. He did not think that the pink colour was due to ferrate as had been suggested, as he had found that iron oxide gave a somewhat different colour.

Professor Ramsay remarked that Stas, in his determination of the ratio of potassium chloride to oxygen in chlorate, had not found that peroxide was formed.

20. "*The Vapour-Density of Hydrogen Fluoride.*" By T. E. Thorpe, F.R.S., and F. J. Hambly.

Gaseous hydrogen fluoride, on being heated from a few degrees above the boiling point of the liquid, shows a rapid decrease in density, owing to the dissociation of H_xF_x molecules ultimately into HF molecules, the course of the dissociation being similar to that observed in the case of nitrogen peroxide and acetic acid. The authors have carefully studied the molecular breaking down of the vapour as it is effected by changes of temperature and pressure. It would appear that there is no evidence for the existence of a molecule corresponding to the formula H_2F_2. If it exists at all, it must be formed only during the process of transition of H_xF_x into x HF, and be such that it can persist under given circumstances only in the presence of definite proportions of molecules more or less complex than itself. The density at above 32° corresponds apparently with H_2F_2, but the curve gives no indication of any condition of statical equilibrium in the neighbourhood of this temperature such as would be manifest if such a molecule were capable of independent existence At temperatures below this point the density gradually increases in a perfectly regular manner until at 26·4°, the lowest temperature observed, the density becomes 1·773, equivalent to a molecular weight of 51·2 ($H_3F_3 = 60$); as it is heated the vapour behaves like a mixture of a complex molecule H_xF_x, or of H_xF_x and H_yF_y molecules, with a gradually increasing number of molecules of HF, the process of dissociation being perfectly continuous until the temperature increases to about 60°, when the density becomes approximately normal, *i.e.*, corresponds to a vapour consisting wholly of HF molecules.

As in the case of nitrogen peroxide, dissociation takes place with increasing rapidity as the temperature increases until it attains a maximum when about 50 per cent of the heavier molecules have been decomposed, after which the increase becomes gradually smaller, at first slowly, then rapidly. The curves showing the mean increase resemble in fact that given by Naumann (*Thermochemie*, 1882) as representing the increase in the rate of dissociation of nitrogen peroxide, but with this very marked difference, that the mean increase for 1° C. in the case of hydrogen fluoride is at its maximum nearly three times as great as that of nitrogen peroxide.

The authors have studied the effect of pressure on the course of the dissociation by attenuating a given volume of the gas maintained at the constant temperature of 32°, at which point the vapour is supposed to consist wholly of H_2F_2 molecules. It is seen that the slightest alteration of pressure at this temperature at once disturbs the ultimate proportion of the complex to the simpler molecules in the gaseous mixture—a fact which again points to the non-existence of a stable molecule corresponding to H_2F_2. The reduction of the actual pressure may be effected not on by direct attenuation but by mixing the vapour with a neutral gas. Experiments made by the addition of dry air showed that the intervention of the air particles has no effect on the extent of the ultimate decomposition of the complex hydrogen fluoride molecules corresponding to a particular diminution of pressure. The presence of the air may alter the rate of the dissociation, but it has no appreciable influence on its maximum amount. Lastly, they see in the fact that their values for the density at *circa* 32°, under ordinary atmospheric pressure, agree almost exactly with those obtained by Mallet, a proof that the nature of the vessel or the character of its surface exert no appreciable effect on the extent of the dissociative change, Mallet's experiments having been made in glass coated with paraffin, whereas those of the authors were made in a vessel of platinum. This point is of importance in view of Konowalow's experiments on the effect of surface in influencing the rate and extent of dissociation.

Discussion.

Professor **Ramsay** said that Professor Thorpe, in speaking of the analogy of the results obtained in the case of hydrogen fluoride with those of the Brothers Natanson for nitric peroxide, had pointed out that these latter afforded insufficient proof of the higher limiting value of n in the formula N_nO_{2n}; and that this limiting value was also unknown in the case of acetic acid, of which the vapour-density also increased with fall of temperature. Now there were three separate lines of argument leading to a knowledge of the higher limiting formulæ of these bodies which had been pointed out by himself and Dr. Young, and of which the data were to be found in papers published in the *Philosophical Transactions*, in the *Philosophical Magazine*, and in the *Chemical Society's Transactions*. The first of these has reference to the alteration of density of the saturated vapour with fall of temperature and corresponding fall of pressure. It is argued that the density of the vapour of a substance must necessarily, at any given temperature, be higher when the vapour is on the point of condensation than when it is unsaturated. Hence, if it can be proved that the density of the saturated vapour of bodies like nitric peroxide and acetic acid shows no signs of increasing beyond those required for the respective formulæ N_2O_4 and $C_4H_8O_4$, such formulæ must denote the limit of complexity of the molecules, in the gaseous state at least. To ascertain such a limit, Dr. Young and the speaker constructed from the Natansons' data for the relations of volume, pressure, and temperature of nitric peroxide, and their own data for the vapour-pressure of that body, isothermal curves in which pressures formed ordinates and vapour-densities abscissæ. The terminal points of such curves are characterised by rapid increase of density without rise of pressure, and, in fact, denote that the substance is no longer in the gaseous state, the vapour-pressure of the liquid having been reached. The densities of the saturated vapour therefore will correspond with the angles of union of the isothermal curves with horizontal straight lines representing condensation to liquid under vapour-pressures constant for each temperature. By joining with each other such angles of union for each temperature a curve is obtained expressing the densities of the *saturated* vapour in relation to pressure. It is evident from inspection of such a curve for acetic acid, shown in a plate in the Society's *Transactions* (1886, 806), that the line of zero-pressure would be cut at the density 60, corresponding to the formula $C_4H_8O_4$; a similar curve can be constructed from the Natansons' results and Ramsay and Young's determinations of the vapour-pressures of nitric peroxide, and this intersects the line of zero-pressure at a point corresponding to the vapour-density 92, equivalent to the formula N_2O_4.

The second argument is as follows:—Representing the relations of temperature and pressure of a "perfect" gas for any given constant volume, $p = c \cdot t$, where c is a constant and t absolute temperature. This is the equation to a straight line; such a line is termed an *isochoric line* or *isochor*, its point of origin for a perfect gas is absolute zero of pressure and temperature. If a different volume be chosen, the slope of the line is different. Now it is clear that if a given volume of gas contains $2n$ mols., pressure will rise with rise of temperature at twice the rate that it would if the given volume of gas contained n molecules. Constructing for nitric peroxide and for acetic acid on the assumption that they are perfect gases diagrams showing the relations of pressure and temperature for the formulæ NO_2 and $C_2H_4O_2$, at such volumes that 1 grm. occupies, say 1000 c.c. in each case, the resulting straight lines will manifestly differ in slope from those corresponding to the respective formulæ N_2O_4 and $C_2H_8O_4$, the pressure in the latter case not rising so rapidly with rise of temperature, owing to the smaller number of molecules in that volume. But we know that the actual behaviour of these bodies is not that of perfect gases. The line representing the relations of pressure and temperature should, at high temperatures, when the substances exist in the molecular state NO_2 and $C_2H_4O_2$, nearly coincide with the theoretical line for these molecular states; and at low pressures and temperatures with the line denoting the molecular condition N_2O_4 and $C_4H_8O_4$. The data of actual experiments show that such is the case. The S-shaped isochoric curve trends so that it is probable that it would become tangential with that expressing the behaviour of molecules of the higher formulæ, showing no signs of cutting it, as it must needs do, were still more complex molecules capable of existence.

The third line of argument is derived from the application of Raoult's method to a solution of nitric peroxide in acetic acid; the results obtained by the speaker show that even with very varying proportions of peroxide the molecular weight corresponds closely with the formula N_2O_4.

In conclusion, the speaker suggested that it was very desirable that the authors should, if possible, obtain data for a greater number of isothermals than the two which they had already constructed, so as to afford means for determining the true complexity of the molecule; and also that such results should be checked by the application of Raoult's method, dissolving the hydrogen fluoride in glacial acetic acid.

Professor Thorpe said that it was impossible to apply Raoult's method, on account of the violence of the action which took place on adding hydrogen fluoride to acetic acid.

21. "*Contributions to the Chemistry of Lignification; the Constitution of the Jute Fibre Substance.*" By C. F. Cross and E. J. Bevan.

The authors describe the results of fuller study of the ligno-celluloses (compare *Chem. Soc. Trans.*, 1882, 90; 1883, 18). The substance of the jute fibre may be empirically represented by the formula $C_{12}H_{18}O_9$, and although an aggregate, its properties and composition are sufficiently constant to warrant its being regarded as a chemical unit. It is to a certain extent attacked and dissolved by hydrolytic agents, but the insoluble residues possess the composition and properties of the original; hydrolytic agents which are at the same time oxidising agents, *e.g.*, dilute nitric acid, however, cause its resolution into insoluble cellulose and soluble non-cellulosic acid products. On treatment with a mixture of concentrated nitric and sulphuric acid, it is converted into explosive nitrates, ultimately into what appears to be the tetranitrate, $C_{12}H_{14}O_5(NO_3)_4$.

The characteristic action of chlorine, whereby ligno-cellulose is resolved into cellulose and a yellow chlorinated derivative, has been studied by a special method and apparatus, and it is shown that interaction takes place according to the equation—

$$C_{456}H_{702}O_{342}+24Cl_2= 6C_{19}H_{17}Cl_4O_9+57C_6H_{10}O_5+3H_2O+24HCl.$$

Previous observations showed the probable presence in the chlorinated fibre of mairo-gallol.

A comparison of the composition of the latter with that of the chlorinated derivative, however, indicates that it is associated with another substance having approximately the formula $C_{137}H_{169}O_{59}$.

Moreover, the chlorinated derivative has been found to contain a constituent yielding, on hydrolysis, furfural and acetic acid. These compounds are also readily yielded by the original ligno-cellulose, and the quantities obtained confirm the empirical formula deduced as above from the statistical comparison with mairo-gallol.

The non-cellulosic constituent therefore appears to be composed of (*a*) a group, $C_{18}H_{18}O_{10}$—a ketone transitional to a quinone, capable of combining directly with chlorine to form mairogallol; (*b*) a furfural group, $C_5H_4O_2$, in combination by condensation with *a* and with (*c*) a group yielding acetic acid. These are associated in the approximate molecular proportions of (*a*) 2, (*b*) 6, (*c*) 5 = $C_{76}H_{80}O_{37}$.

From the examination of various types of lignified tissues and fibres, the authors conclude that the composition of the ligno-celluloses in the earlier stages of growth approximates to that of jute; but that in the true woods, in which the carbon percentage is higher and the properties of which differ sensibly from those of the first named —condensation has proceeded further.

22. "*The Atomic Weight of Chromium.*" By S. G. Rawson, B.Sc.

The author has determined the equivalent of chromium by converting a known weight of carefully purified ammonium bichromate into chromic oxide: the chromate was first reduced by means of alcohol and muriatic acid, an excess of ammonia solution was then added to precipitate the chromium as hydroxide, the water was removed by evaporation, and after drying the residue at 140°, the ammonium salt was expelled by ignition in a muffle. All the operations were carried out in one and the same platinum dish; full details are given in the paper. The results obtained are given in the Table.

Weight of $(NH_4)_2Cr_2O_7$ (corrected).	Weight of Cr_2O_3 (corrected).	Ratio of Cr : H.
1·01275	0·61134	52·130
1·081806	0·65266	52·010
1·29430	0·78090	52·020
1·13966	0·68799	52·129
0·98778	0·59595	52·016
1·14319	0·68987	52·059
General mean		52·061
Maximum difference.. ..		0·120

At the next meeting on March 7th there will be a ballot for the election of Fellows, and the following papers will be read:—

"The Constitution of Certain Naphthalene Derivatives." By Dr. Armstrong and Mr. Wynne.

"The Decomposition of Carbon Bisulphide by Shock." By Professor Thorpe.

NOTICES OF BOOKS.

Chemical Lecture Notes. By P. T. Austen, Ph.D., F.C.S. New York: J. Wiley and Sons.

This book, the author informs us, is not a text-book, but a collection of notes and observations. Some of these observations, especially the glorification of "high" explosives, to be met with in a chapter on "The Chemical Factor in Human Progress," may make us shake our head in doubt, and must at any rate be handed over for appreciation to political, economical, and moral organs. But others, especially the introductory sections, are most valuable. From these sections we are glad to find that in the great war between education and examination Dr. Austen is on our side. He says to the student:—"As your faculties are of use and can be depended on only so far as they have been properly trained and directed, I must satisfy myself that you observe correctly. . . . . You must be on a continual watch that nothing escapes you, and indeed, that your faculties do not deceive you. Whoever causes the mind of pupils to take the necessary action *teaches* the pupils. The teacher is not one who *tells*, but who sets the learner's mind to work. The true method of education is to show you a road by which you cannot help arriving at results for yourselves. The true teacher makes himself unnecessary to the pupil as soon as possible." The road here marked out alike for teacher and student is utterly unlike that followed by the "coach" and for the youth who is preparing for an examination. Dr. Austen further earnestly recommends Herbert Spencer's work on "Education" and Prof. Galloway's "Education, Scientific and Technical."

There is much in this little book which may be most profitably studied.

CORRESPONDENCE.

ACTION OF FERROUS SULPHATE ON SOILS.

To the Editor of the Chemical News.

Sir,—Mr. J. G. McIntosh (Chemical News, vol. lix., p. 96) will find in the *Journal of the Chemical Society*, 1886, pp. 114—120, that ferrous sulphate *does* absorb ammonia from the soil, &c.

I am afraid he has not read the papers published in the *Journal of the Chemical Society*, 1882—87, with sufficient care, or he would have found that iron sulphate is not only a *direct*, but an *indirect* plant-food.

Concerning Mr. McIntosh's idea of instituting a series of comparative experiments with various sulphates; if he turns to the pages of *La Sucrerie Indigène et Coloniale*, vol. xxxi., pp. 571—576, he will find that M. Muntz (Professor at the Institut National Agronomique, Paris) says:—"With *any* sulphate there is an increase of 13·54 per cent, but with *iron* sulphate the increase is 30·2 per cent." M. Muntz also obtained an *increase* of 9 6 per cent of chlorophyll in those crops grown with the *iron* manure.

Iron, according to Professor Sachs, is "absolutely necessary for the formation of chlorophyll;" therefore for starch, fat, and woody substances generally. Although our soils contain a certain amount of *iron*, it is not always in the most suitable form for root-absorption, and it may be that many farm crops (which only live a few months) suffer from a want of "this life-giving substance." The weak acids secreted by the rootlets is most likely insufficient to dissolve the requisite amount of iron (from the soil) for a healthy growth.

I think it would be well for Mr. McIntosh to remember that *iron* is an important plant-food, while, on the other hand, *soda* is not a plant-food. I may also remind him that Mr. Yoshida (*Journal of the Chemical Society*, 1887, p. 748) proved the existence of *alumina* in the ashes of the pea, bean, rice, wheat, and cereals generally.—I am, &c.,

"X."

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. cviii., No. 6, February 11, 1889.

On the Loss of Gaseous Nitrogen during the Decomposition of Organic Matter.—Th. Schlœsing.—The author considers that ammonia is, with nitric acid, the last stage of combination at which the nitrogen of any organic matter may arrive during its decomposition. The ammonia produced in his experiments corresponds to the nitrogenous matters which have ultimately lost all their nitrogen. Consequently, the gaseous nitrogen escaping must be compared with the ammoniacal nitrogen to find the proportion of this gaseous nitrogen lost in the course of the decomposition of the nitrogenous substances. Under the conditions of the author's experiments these losses have been minute. These results seem to clash with those which M. Reiset has obtained, but the author experiments on the destruction of the organic matter, whilst M. Reiset has studied meat and farmyard manure only during the first stage of decomposition. It is quite possible that the loss of nitrogen takes place especially in this stage.

Certain Reactions of the Mercury-ammonium Chlorides.—G. André.—The author studies the decomposing action of water upon the chloramidide with the view of fixing the conditions under which dimercuriammonium is transformed into chloramidide in contact with sal-ammoniac.

On Amorphous Bismuth.—F. Hérard.—Pure crystalline bismuth is heated to full redness in a current of nitrogen; greenish vapours rise up and condense upon the cooler portions as a greyish dust. This dust, if examined under the microscope, appears in the form of minute globes united in links. Such gases as hydrogen and carbon monoxide cannot be used in place of nitrogen in its preparation. The minute sub-division of amorphous bismuth renders it more susceptible to reagents than is crystalline bismuth.

On Titanium Peroxide.—Lucien Lévy.—The author assigns to this oxide the formula TiO_3. It is not an acid in the strict sense of the word.

Syntheses Effected by Means of Cyano-succinic Ether.—L. Barthe.—The author gives an account of methyl-cyanosuccinic ether, of the analogous ethyl compound, of ethylethenyl-tricarbonic ether, and propyl-cyanosuccinic ether.

Action of Bromine upon Aconitic Acid and Carballylic Acid.—E. Guinochet.—From both these acids the author obtains the same tribromo-compound.

On a Nitrophenol isomeric with Nitro-camphor α.—P. Cazeneuve.—The compound obtained has the same percentage composition as nitro-camphor. It is white, and crystallises in long needles with 1 mol. of water of hydration. It is soluble in water, alcohol, ether, and chloroform.

Moniteur Scientifique, Quesneville.
January, 1889.

Determination of Phosphoric Acid in Basic Slags.—Dr. M. A. von Reiss (*Zeitschrift angewandte Chemie*).—Among the many methods of dissolving the slag the author prefers the use of hydrochloric acid without separation of the silica. If this separation is necessary in any case he attacks the sample with sulphuric acid at 66° B. The method of analysis which best combines accuracy and dispatch is, he considers, the direct precipitation of the phosphoric acid with magnesia mixture in presence of citric acid. Laubheimer treats the phosphoric solution (freed from silica) containing from 1 to 2 decigrms. of phosphoric acid with 20 c.c. of citric liquid (500 grms. citric acid in 1 litre) and 50 c.c. of ammonia, sp. gr. 0·92. He cools and adds 20 c.c. of magnesia mixture, stirring with a glass rod until the liquid is rendered opaque by the precipitate. The author modifies this process as follows:—He moistens 10 grms. of slag with a little water, adds 50 c.c. of strongest hydrochloric acid, and heats the covered capsule to a boil for some minutes. He removes it from the fire, adds cautiously 50 c.c. of strongest sulphuric acid, and heats until white vapours appear. He then cools for fifteen minutes, takes up in 100 c.c. of water and heats, whilst stirring, until the liquid turns green. If too strong a heat is applied there appears a red precipitate of an iron salt containing phosphoric acid, which does not re-dissolve. The whole is poured into a flask of 500 c.c., and when cold the volume is made up to the mark. Account must be taken of the space taken up by the insoluble precipitate, about 4 c.c. He then adds 4 c.c. of water over and above the 400 c.c., and filters. Of the filtrate he takes 32 c.c. and treats with 10 c.c. of the citric solution and 25 c.c. of ammonia at sp. gr. 0·92. After cooling he adds 25 c.c. of magnesia mixture and stirs. If no immediate turbidity is produced a little more ammonia is carefully added. When the precipitate forms he adds 20 c.c. more ammonia, stirs for a minute, and filters after about ten minutes. The precipitate in its filter is dried and ignited in a porcelain crucible, which is placed first at the mouth of the muffle until the filter is entirely incinerated, and it is then exposed to a bright red heat for an hour.

Determination of Sulphur in Iron.—C. Meinecke (*Zeitschrift angewandte Chemie*).—The author treats 5 grms. of iron, or more if necessary, in a flask with 50 grms. of ammonium copper chloride, 250 c.c. of hot water, and 10 to 15 c.c. of hydrochloric acid. He keeps the whole near the boiling-point until the deposit of copper is re-dissolved, which generally takes place in a quarter of an hour. It is then thrown upon an asbestos filter, washed with hot water acidulated with a little hydrochloric acid, and washed. The contents of the funnel are then transferred into a flask with the smallest possible quantity of water, a few crystals of potassium chlorate are added, about 5 c.c. nitric acid (sp. gr. 1·4), and 10 c.c. hydrochloric acid (sp. gr. 1·19). It is evaporated to dryness in the sand-bath, re-dissolved in a little hydrochloric acid, digesting in heat so as to be sure of having expelled all the nitric acid, and filtered. In the filtrate the sulphuric acid is determined with barium chloride in the usual manner.

The Avoidance of Tared Filters for Weighing Certain Precipitates.— L. L. de Koninck.— Already noticed.

Determination of Paraffin, Ceresine, or Mineral Oils in Fatty Bodies or Waxes.—F. M. Horn (*Zeitschrift ang. Chemie*).—The author weighs 5 to 6 grms. of the sample in a porcelain dish of 6 to 10 c.m. in diameter, adds 2 to 3 grms. solid caustic potash, 80 c.c. of strong alcohol, and heats in the water-bath whilst stirring. The dried soap formed is passed into a cornet of filter-paper and extracted with chloroform in a suitable apparatus. The chloroformic solution is placed in a tared glass capsule, dried in the water-bath, and then heated for two hours in the stove to 105° to 110°, let cool in the desiccator, and weighed. To determine paraffin in waxes, Horn treats 5 to 6 grms. as above. The mixture of myricic alcohol and paraffin is boiled with acetic anhydride, the myricic alcohol is etherified and dissolves in the acetic acid, whilst the paraffin collects in drops on the surface. The whole is filtered through very compact paper and repeatedly washed first with acetic anhydride and then with hot water. Lastly, the filter is dried at 100° in a precipitating glass, the paraffin is re-dissolved in petroleum ether or chloroform, the solution placed in a tared capsule, evaporated, and the residue is weighed.

Determination of Glycerin in Commercial Glycerins.—R. Benedikt and M. Cantor (*Zeitschrift angewandte Chemie*).—The authors base their process on the principle that glycerin, if boiled with acetic anhydride, is transformed quantitatively into triacetine. If it is then dissolved in water and the free acetic acid is neutralised with caustic soda, we may determine the quantity of dissolved triacetine by saponifying with an excess of standard soda and determining the excess of this reagent by titrating with normal acid. The requisites are:—(1) Hydrochloric acid, hemi-normal or tetra-normal. (2) Dilute soda-lye at 20 grms. caustic per litre. (3) Caustic soda-lye at $\frac{1}{10}$. From 1 to 1·5 grm. of the sample is pladed in a flask holding about 100 c.c., and having a long neck; 7 to 8 grms. of acetic anhydride and 3 grms. anhydrous sodium acetate are added. After boiling for ninety minutes with an ascending condenser it is let cool, 50 c.c. of water are added, and the mixture is again heated to a boil, still using the condenser. When all is dissolved it is filtered into a flask holding 400 to 600 c.c. The filter is washed, and when cold, phenolphthalein is added and the liquid is exactly neutralised with the dilute alkali, stopping before a full red colour is reached. Next, 25 c.c. of the strong alkali are added, taking care to empty the pipette each time exactly in the same manner. The liquid is boiled for thirty minutes, and then the residual free alkali is titrated with normal acid.

Vapour-density of Hydrofluoric Acid.—T. E. Thorpe, F.R.S., and F. J. Hambly.—From the *Journal of the Chemical Society*.

Qualitative Analysis of Colours Fixed upon Woollen Cloth.—Gaston Dommergue.—This paper does not admit of abstraction.

Reclamation of Priority Concerning the Process of M. l'Abbé Godefroy on the "Disinfection" of Alcoholic Phlegms of Hydrogenisation.—Laurent Naudin.—The only notice we can take of this tedious controversy is to protest against the abuse of the word "disinfection," in which M. Naudin indulges.

Results of the Most Recent Analyses of Quinine.—M. Lentz.—From the *Zeitschrift für Analytische Chemie*.

Determination of Carbonic Acid in Atmospheric Air.—G. Lunge and A. Zeckendorf (*Zeit. ang. Chemie*).—The authors make use of an apparatus called a minimeter for forcing the air into a flask of baryta-water.

Industrial Society of Mulhouse, Chemical Section, October 10, 1888.—The chief business of the meeting was the opening of two "sealed papers" which had been deposited by M. St. de Kostanecki, one on a new colouring-matter, nitroso-phenyl-azoresorcine, and the other on the diazo colouring-matters of resorcine.

Meeting of Nov. 14, 1888.

C. Kopp presented a memoir on starch and its derivatives, with especial notice of a product called "universal gum," obtained by treating starch with sulphurous acid under pressure, and at a high temperature.

M. Prud'homme sent in a paper on a spontaneous transformation of dinitro-resorcine.

February, 1889.

Studies on Drying Oils and on Methods for the Analysis of Fatty Bodies.—K. Hasura (*Zeitschrift ang. Chemie*).—This paper does not admit of useful abstraction.

Determination of Salicylic Acid in Beer and Wine (*Zeitschrift angewandte Chemie*).—Rœse founds a process on the following facts:—Salicylic acid dissolves almost entirely in a mixture of equal parts of ether and petroleum ether. Except acetic and carbonic acids, none of the normal acids of beer or wine dissolve in this mixture. On agitating the ethereal liquid with an equal volume of water the acetic acid is eliminated almost entirely. On concentrating the ethereal mixture by evaporation, no ponderable quantity of salicylic acid is lost. The salicylic acid in an aqueous solution may be accurately determined by titration with normal alkali. In the discussion which followed the reading of the author's paper it was shown that salicylic acid present in beer does not disappear in time spontaneously.

New Process for Producing Ammonium Chloride.—A. French.—From the *Journal of the Society of Chemical Industry*.

Manufacture of Aluminium by the Castner Process.

Chinese Treatment of Cobalt Ores.—T. I. Bowler.

The Reductive Action of Hydrogen in Presence of Platinum.—Stephen Cooke.—These three papers are from the Chemical News.

Manufacture of Borax from Boro-natro-calcite.—Dr. Fr. Witting (*Zeit. angewandte Chemie*).—The process consists of the four following stages:—Boiling the mineral with an excess of soda-ash, for half of which bicarbonate may be advantageously substituted; treatment of the mud in a filter-press; crystallisation and treatment of the liquors.

Delta-metal.—Analyses of alloys sold under this name, in which tin ranged from 0 to 19·41 per cent, zinc from 14 to 42, and lead from 0·72 to 6·10. Copper varies from 54 to 60.

"Household Lye" intended as a Substitute for Soap and Soda.—A recent fraud, containing 68 per cent of silica, clay, lime, and magnesia. It is sold by a Heidelberg firm under the name of "ammonine," and is said to contain neither acid nor alkali, but to consist of sulphuretted hydrogen (!) condensed and crystallised. It is said not only to bleach linen, but to destroy vermin, bacteria, &c.

An Associate of Indigo.—M. Bieret.—The author asserts that indo-phenol can be added to an indigo-vat with great economy.

Determination of Sulphur in Coal.—R. Brullé.—The author, instead of a platinum capsule, effects the combustion in a long platinum boat, 0·30 metre in length by 0·015 in width and depth. A ledge along each side allows the cover to slide longitudinally from end to end, so as always to be over the part which is being heated.

Determination of Invert-Sugar by Means of Cupro-alkaline Solutions.—F. G. Weichmann.—From the *School of Mines Quarterly*.

Determination of Higher Homologous Acids in Artificial Salicylic Acid.—E. E. Ewell and A. B. Prescott.—From the *Pharmaceutical Journal and Transactions*.

MISCELLANEOUS.

The Newly Discovered Aluminous Compounds.—In the note which appeared on the first page of the CHEMICAL NEWS for the 15th instant we accidentally omitted to state that the new double fluoride was obtained by Dr. Hampe, and that the discovery was first published in the *Chemiker Zeitung* (Goethen).

Patent Laws.—Under the title of "The True Position of Patentees," Mr. H. Moy Thomas has published, through Messrs. Simpkin, Marshall, and Co., a little book in which the patent laws and regulations at home, abroad, and in the colonies and dependencies are explained for the information of English inventors.

Determination of Chlorides in Urine.—Brignone (*Annali di Chimica*).—The author prefers a process first devised by Mohr. The sample is evaporated to dryness, incinerated with an addition of permangananate, and the solution in water is titrated with permanganate.

The Loss of Nitrogen during the Decomposition of Organic Matter.—Th. Schlœsing.—The author finds that this question has not been fully decided by the researches of Reiset, of Lawes and Gilbert, and of Kœnig and Morgan. He therefore institutes new experiments which are here described and figured. His results will be given on a subsequent occasion.—*Comptes Rendus*, Vol. cviii., No. 5.

Determination of Caoutchouc in Plants.—G. Kassner (*Archiv. der Pharmacie*).—The plants, dried and powdered, are exhausted with benzene, petroleum ether, or carbon disulphide. The extract is evaporated to dryness and treated with boiling alcohol. The insoluble residue is freed from fats, waxes, and chlorophyll by heating with alcoholic potassa and repeated washing with hot dilute alcohol. The pure caoutchouc thus obtained is an elastic mass, still having a slightly dark colour, and is perfectly soluble in carbon disulphide and chloroform.

An Abridged Method for Determining Potassium in Ashes, Minerals, &c.—M. Kretzschmar (*Chemiker Zeitung*).—Supposing that from 0·5 to 1 grm. of the substance is sufficient for the determination of the potassa, 5 grms. are placed in an Erlenmeyer flask, if possible, in a hydrochloric solution. Any ferrous oxide present is peroxidised by means of a few drops of nitric acid, the sulphuric acid is precipitated at a boil by means of barium chloride, and the liquid, while still hot, is supersaturated with ammonia and ammonium carbonate. The liquid, along with the precipitate, disregarding any traces adhering to the sides of the flask, is transferred to a porcelain capsule, evaporated to dryness on the water-bath, and the whole dried at 110°, stirring twice or thrice. After adding a few drops of ammonia it is redissolved in hot water. The precipitate takes the form of a not very bulky insoluble powder, which can be easily washed. It is made up to 500 c.c., of which from 50 to 100 c.c. are taken for the determination. If the quantity of the magnesia present is trifling, the measured quantity of the liquid is evaporated down at once in a platinum capsule, and after the ammoniacal salts have been expelled and the residue dissolved the potassa is determined. If a considerable quantity of magnesia is present a very tedious washing of the potassium platino-chloride is necessary, on account of the sparing solubility of the magnesium platino-chloride. It is therefore more advantageous to evaporate down the measured quantity of the filtrate with an excess of oxalic acid, and, after faintly igniting the residue and filtering off the magnesia, the filtrate is used for determining the potassa.

Detection and Determination of Small Quantities of Chromic Oxide.—E. Donath and Rud. Jeller.—The solution, containing small quantities of chromic oxide along with an excess of ferric oxide, alumina, manganous oxide, and possibly alkaline earths, is allowed to flow into a hot solution of sodium carbonate mixed with permanganate. After a short ebullition the excess of permanganate is reduced by the addition of a few drops of alcohol and filtered. Ferric oxide, alumina, manganese, and the alkaline earths are precipitated, whilst the chrome remains in solution in the state of chromic acid in the filtrate, which will have a yellowish colour if the quantity of chrome is at all considerable. If the colour is not perceptible and the liquid appears colourless the filtrate is slightly concentrated, acidulated with dilute hydrochloric or sulphuric acid, and a drop of it is applied to a fragment of starch which has been previously moistened with a fresh prepared solution of potassium iodide. The appearance of a violet colour betrays the presence of chromic acid. If the filtrate was perceptibly yellow it gives the well-known iodine reaction on acidulation with hydrochloric acid and addition of potassium iodide and a little carbon disulphide. For the quantitative determination of very small quantities of chrome the authors proceed quite in the same manner, but the solution is dropped slowly from a pipette into the hot alkaline solution of permanganate, and the liquid is heated for ten minutes. The filtrate, after acidulation with hydrochloric acid and the addition of a little alcohol, is heated, and chromium sesquioxide is precipitated in the usual manner with ammonium sulphide.—*Zeitschrift fur Analytische Chemie*, vol. xxviii., Part 1.

Bad Manners in Business.—Under this title Dr. Krause, the editor of the *Chemiker Zeitung*, protests against certain bad customs in correspondence which have lately become prevalent, and which serve for the especial annoyance of editors. The first is the common practice of abridging the names of places, so that the recipient of a letter can only guess its origin. Along with this sin comes that of illegible signature. A third abuse is that some persons, in remitting small sums of money, take it upon themselves to deduct postage and sometimes the cost of post-office orders or postal orders. Next follows the abuse of sending remittances in foreign stamps, which the recipient cannot cash without much trouble. This transgression is rarely practised in Britain. Some correspondents do not prepay their communications sufficiently, and thus put the receiver to needless expense. Dr. Krause further complains of the practice of drying letters, MS., &c., with sand, instead of with blotting-paper. Another abuse mentioned is writing letters in copying-ink and not copying them. Matter intended for the press should, in our opinion, not be written with copying-ink at all. The characters are almost invariably blurred, and the compositor works less rapidly and with less certainty than if ordinary ink had been used. Finally our contemporary adds the recommendation that every one should have his address printed on his envelopes. One addition we must venture to make, that is the recommendation that Germans in all communications outside their own country should use the so-called Latin script as employed in the rest of the civilised world. A foreigner may be able to read, write, and speak the German language with ease and correctness, but to decipher a memoir written in German characters proves often a very heavy tax upon his time and patience.

MEETINGS FOR THE WEEK

Monday, March 4th.—Medical 8.30.
— Society of Arts, 8. Cantor Lectures. "The Decoration and Illustration of Books," by Walter Crane.
— Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 8. "Cider," by Messrs. Higgins and Heron. Discussion—"In what Direction is State Aid Needed to Assist Technical Education in Chemistry."
Tuesday, 5th.—Institute of Civil Engineers, 8.
— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
— Pathological, 8.30.
— Sanitary Institute, 8. "General History, Principles, and Methods," by Dr. B. W. Richardson, F.R.S.
Wednesday, 6th.—Society of Arts, 8. "Arc Lamps and their Mechanism," by Prof. Silvanus P. Thompson.
— Geological, 8.
Thursday, 7th.—Royal, 4.30.
— Royal Institution, 3. "The Venom of Serpents and Allied Poisons," by Sidney Martin, M.D.
— Royal Society Club, 6.30.
— Chemical, 8. "Constitution of certain Naphthalene Derivatives," by Dr. Armstrong and Mr. Wynne. "The Decomposition of Carbon Disulphide by Shock," by Prof. Thorpe.
Friday, 8th.—Royal Institution, 9. "The Discharge of a Leyden Jar," by Prof. O. Lodge.
— Medical, 8.30. (Anniversary).
— Quekett Club, 8.
— Astronomical, 8.
— Society of Arts, 8. "Present Condition and Prospects of Indian Agriculture," by Prof. Robert Wallace.
Saturday, 9th.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.
— Physical, 3. "On the Magneto-optic Notation by Transient Currents with reference to the Time required for the Production of the Effect;" "On an Electrostatic Field Produced by Varying Magnetic Induction;" "On some Experiments Allied to those of Hertz;" "On the Velocity of Electric Pulses along a Pair of Isolated Wires;" "Sundry Laboratory Notes;" by Prof. O. J. Lodge, F.R.S.

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OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

(Continued from p. 104).

METHODS FOR MILK ANALYSIS.

Estimation of Water.

FROM a weighing-bottle take 5 c.c. milk, put in a weighed thin glass dish or dish lined with tinfoil one-third full of powdered asbestos; dry for two hours at 100° C. The temperature obtained in a boiling water-bath does not reach 100° C. The milk should be dried in an air-bath, the temperature of which is carefully controlled.

Alternate Method of Estimating Water.

Evaporate 1 to 2 grms. of milk in shallow watch-glass or platinum dish on the water-bath for thirty minutes. Dry for an hour at 100° C. and weigh.

Estimation of Casein.

Take 5 grms. of milk, digest in Kjeldahl apparatus with 20 c.c. H_2SO_4, and estimate ammonia in the usual way.

Alternate Method of Estimation of Casein.

Rub up in a mortar the thin disc containing the dried residue from the above process or remove the foil containing it and transfer to soda-lime combustion tube in the usual way.

The mortar and pestle must be well cleaned with the soda-lime, and these cleanings placed in the tube.

Or the dish or tinfoil and its contents may be transferred to a digestion flask and the casein estimated by the method of Kjeldahl.

Estimation of Fat.

Method of Adams.—The kind of paper and the method of using it first proposed by Adams are as follows:—

As for material, the only extra article is some stout white blotting-paper, known in the trade as "white demy blotting, mill 428," weighing 38 pounds per ream. This should be in unfolded sheets, machine-cut into strips 2½ inches wide, and 22 inches long; each sheet in this manner cuts into seven strips.

I have tried other papers but none have answered so well as this; it is very porous and just thick enough. Each of these strips is carefully rolled into a helical coil, for which purpose I use a little machine, made by myself, consisting of a stout double wire, cranked twice at right angles, and mounted in a simple frame. One end of the strip being thrust between the two wires, the handle is turned and the coil made with great facility. This may be done, for the nonce, on a glass rod, the size of a cedar pencil. Two points have to be carefully attended to; the paper must not be broken, and the coil must be somewhat loose, the finished diameter being a little under an inch. I am in the habit of rolling up a considerable number at a time and placing each within a brass ring as it is rolled, inscribing on one corner with a lead-pencil its own proper number.

These coils are next thoroughly dried, and I need hardly say the accuracy of the process depends upon this drying. This can be satisfactorily done in an ordinary air-bath at 100° C., providing the bath be heated properly and the paper kept in it long enough. I found the common way of heating the thin bottom of the bath with a single jet not to answer. My bath is placed upon a stout iron surface, which is heated by a large ring of jets; in this way the heat is evenly distributed over the whole of the bottom of the bath, and the papers, which are put in a cage frame of tinned iron-wire 5 by 2½ inches and divided into eight partitions, get evenly and completely dried, if allowed to remain in the bath all night, and weighed in a weighing-tube next morning, and their weights having been registered according to their numbers, stored away ready for use, as follows:—

The milk to be examined is shaken, and with a pipette 5 c.c. are discharged into a small beaker 2 inches high by 1¼ inches in diameter, of a capacity of about 30 c.c., weighing about 12 grms. This charged beaker is first weighed and then a paper coil gently thrust into the milk very nearly to the bottom. In a few minutes the paper sucks up nearly the whole of the milk. The paper is then carefully withdrawn by the dry extremity of the coil and gently reversed and stood, dry end downwards, on a clean sheet of glass. With a little dexterity all but the last fraction of a drop can be removed from the beaker and got on the paper. The beaker is again weighed and the milk taken got by difference. It is of importance to take up the whole of the milk from the beaker, as I am disposed to consider the paper has a selective action, removing the watery constituents of the milk by preference over the fat.

The charged paper is next placed in the water-oven on the glass plate, milk-end upwards, and rough-dried. Mismanagement may possibly cause a drop to pass down through the coil on to the glass. This accident ought never to occur; but if it does it is revealed in a moment by inspection of the surface of the glass, and the experiment is thereby lost.

In about an hour it is rough-dried and in a suitable condition for the extraction of the fat.

The method of Adams has been thoroughly tried by the English chemists and has received the approval of the English Society of Public Analysts. It gives uniformly about 0·2 per cent more fat in normal milk than the ordinary gravimetric methods.

The following modifications of the process may be used:—

The blotting-paper is replaced by thick filtering-paper cut into strips two feet long and 2·5 inches wide. These are thoroughly extracted by ether or petroleum or alcohol.

One end of the strip of paper being held horizontally by a clamp or by an assistant, 5 c.c. milk is run out by a pipette from a weighing-bottle along the middle of the strip of filtering-paper, being careful not to let the milk get too near the ends of the paper, and to secure an even distribution of it over the whole length of the slip. The pipette is replaced in the weighing-bottle and the whole re-weighed, and thus the quantity of milk taken is accurately determined. The strip of paper is now hung up over a sand-bath in an enclosed space, high enough to receive it, where the air has a temperature of 100° C. (*circa*). In two or three minutes the paper is thoroughly dry. It is at once, while still hot, rolled into a coil, and placed, before cooling, in the extraction apparatus already described.

The fat is dissolved by ether or petroleum, collected in a weighed flask, and after thorough drying, weighed.

The fat after extraction may also be estimated volumetrically, as described in the method of Morse.

From data which have been collected, it appears that the estimation of the fat in milk by the lactocrite is strictly comparable with the results of the Adams method. Those who have this instrument, therefore, can use it instead of the method given.

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* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 1888.

Alternate Method of Estimating the Fat in Milk.

Method of Morse, Piggot, and Burton.—This method consists in the dehydration of the milk by means of anhydrous sulphate of copper; the extraction of the fat by means of the low-boiling products of petroleum; the saponification of the butter by means of an excess of a standard solution of potassium hydroxide in alcohol; and the determination of the excess of the alkali by means of a solution of hydrochloric acid. The following apparatus and reagents are required:—

1. A porcelain mortar and pestle.
2. An extraction tube, 14 or 15 m.m. in diameter, 220 m.m. in length, with funnel-shaped top. A straight chloride of calcium tube may be used for this.
3. A 200 c.c. Erlenmeyer flask, strong enough to be used with a filter-pump.
4. A suitable stand for holding the flask and extraction-tube.
5. Ten c.c. pipettes.
6. Weighing-glasses with ground-glass stoppers.
7. A low-boiling gasoline, distilling between 30° and 0° C.
8. Dehydrated sulphate of copper.
9. Semi-normal solution of potash in 95 per cent alcohol.
10. A semi-normal solution of hydrochloric acid.

Manipulation.—Place about 20 grms. of the anhydrous copper sulphate, roughly measured in a copper spoon of the size to hold about that amount, in a porcelain mortar; make a cavity in the centre of the mass with the pestle. Allow 10 c.c. of the milk to run on to the copper sulphate, being careful that none of it touches the sides of the mortar. When the milk is nearly dry, grind the mass up with a little clean sand, transfer to the extraction-tube, gently pressing it down in the tube by means of a glass rod. The lower portion of the extraction-tube to be packed with clean cotton-wool. The fat is extracted in the following way:—15 c.c. of benzine are poured over the material in the extraction-tube and drawn down, with the aid of the filter-pump, until the whole of the mass to be extracted has become wet with the liquid, when the connection with the pump is closed; after about five minutes another portion of 15 c.c. of benzine is poured into the tube and the whole of the liquid slowly drawn through with aid of the pump into the flask. Usually one extraction of this kind is sufficient to withdraw the whole of the butter, but for the sake of greater accuracy the process may be repeated two or three times.

Titration.—The benzine may be evaporated and the residual butter fat saponified with about 25 c.c. of the approximately semi-normal potash. The residual alkali is determined by means of the semi-normal hydrochloric acid, using phenol-phthalein as indicator. The difference between the amount required in this process and the amount necessary to neutralise the quantity of alkali taken gives the amount of alkali required for the saponification. The number of m.grms. of potash required for one grm. of the fat is taken at 230. The fat may also be accurately titrated without evaporating the benzine.

Alternate Method of Estimating Water and Fat in Milk.

Method of Babcock.—In the bottom of a perforated test-tube is placed a clump of clean cotton; the tube is then filled three-quarters full of ignited asbestos, lightly packed, and a plug of cotton inserted over it. The tube and contents are weighed and the plug of cotton carefully removed and 5 grms. of milk from a weighed pipette run into it, and the plug of cotton replaced. The tube connected at its lower end by a rubber tube and adapter with a filter-pump is placed in a drying-oven of 100° C., and a slow current of dry air drawn through it until the water is completely expelled, which in no case requires more than two hours.

The tube containing the solids from the above operation is placed in an extraction apparatus and exhausted with ether in the usual way.

Alternate Method of Estimating Water and Fat.

Method of Professor Macfarlane.—A glass tube 4 to 5 c.c. in length and 2 c.m. in diameter, open at one end, drawn out to a tube 5 m.m in diameter at the other end, is two-thirds filled with asbestos fibre, such as is used in manufacturing packing. It is dried in the water-bath for several hours, cooled in the desiccator, and weighed. Ten c.c. of the milk is then added from a pipette, which is completely absorbed by the asbestos. It is then weighed, the additional weight of the milk representing the amount taken. The tube, along with many others, is placed in a water-bath with constant level and dried for ten or twelve hours (during the night) at a temperature of 90°. Next morning the tubes are cooled in the desiccator and weighed, the loss in weight being the moisture. The tubes are then placed in the Soxhlet extraction apparatus and exhausted with petroleum ether for four hours. They are then removed and dried in a steam-bath, cooled in desiccator, and weighed. The loss represents the butter fat.

The Estimation of Sugar.

The reagents, apparatus, and manipulation necessary to give the most reliable results in milk-sugar estimation are as follows:—

Reagents.—1. *Basic Plumbic Acetate*, specific gravity 1·97. Boil a saturated solution of sugar of lead with an excess of litharge, and make it of the strength indicated above. One c.c. of this will precipitate the albumens in 50 to 60 c.c. of milk.

2. *Acid Mercuric Nitrate.*—Dissolve mercury in double its weight of nitric acid, specific gravity 1·42. Add to the solution an equal volume of water. One c.c. of this reagent is sufficient for the quantity of milk mentioned above. Larger quantities can be used without affecting the results of polarisation.

3. *Mercuric Iodide with Acetic Acid.*—KI 33·2 grms., $HgCl_2$ 13·5 grms., H,C_2H_3O 20 c.c., H_2O 64 c.c.

Apparatus.—(1). Pipettes marked at 59·5, 60, and 60·5 c.c. (2). Sugar flasks marked at 102·4 c.c. (3). Filters, observation tubes, and polariscope. (4). Specific gravity spindle and cylinder. (5). Thermometers.

Manipulation.—(1). The room and milk should be kept at a constant temperature. It is not important that the temperature should be any given degree. The work can be carried on equally well at 15° C., 20° C., or 25° C. The slight variations in rotary power within the above limits will not affect the results for analytical purposes. The temperature selected should be the one which is most easily kept constant.

(2). The specific gravity of the milk is determined. For general work this is done by a delicate specific gravity spindle. Where greater accuracy is required, use specific gravity flask.

(3). If the specific gravity be 1·026, or nearly so, measure out 60·5 c.c. into the sugar flask. Add 1 c.c. of mercuric nitrate solution, or 30 c.c. mercuric iodide solution, and fill to 102·4 c.c. mark. The precipitated albumen occupies a volume of about 2·44 c.c. Hence the milk solution is really 100 c.c. If the specific gravity is 1·030, use 60 c.c. of milk. If specific gravity is 1·034, use 59·5 c.c. of milk.

(4). Fill up to mark in 102·4 c.c. flask, shake well, filter, and polarise.

Notes.—In the above method of analysis the specific rotatory power of milk-sugar is taken at 52·5, and the weight of it in 100 c.c. solution to read 100 degrees in the cane-sugar scale at 20·56 grms. This is for instruments requiring 16·19 grms. sucrose to produce a rotation of 100 sugar degrees. It will be easy to calculate the number for milk-sugar, whatever instrument is employed.

Since the quantity of milk taken is three times 20·56 grms., the polariscopic readings divided by 3 give at once the percentage of milk-sugar when a 200 m.m. tube is used.

If a 400 m.m. tube is employed, divide reading by 6; if a 500 m.m. tube is used divide by 7·5.

Since it requires but little more time, it is advisable to make the analysis in duplicate and take four readings for each tube. By following this method gross errors of observation are detected and avoided.

By using a flask graduated at 102·4 for 60 c.c. no correction for volume of precipitated caseine need be made. In no case is it necessary to heat the sample before polarising.

In the above method no account is taken of the fat which is retained on the filter with the caseine. It is worth while to enquire if a correction similar to that made for the albumenoids should not also be made for the fat? (See *ante*, Vieth's Investigation of this subject from *Analyst*, xiii., 63).

Estimation of Ash.

Evaporate to dryness in a weighed platinum dish 20 c.c. of milk from a weighing-bottle, to which 6 c.c. of HNO_3 has been added, and burn in muffle at low red heat until ash is free from carbon.

(To be continued).

ANALYSES OF WATERS OF THE YELLOWSTONE NATIONAL PARK,

With an Account of the Methods of Analysis Employed.*

By FRANK AUSTIN GOOCH
and JAMES EDWARD WHITFIELD.

Introduction.

The series of waters—forty-three in all—of which it is the purpose of this paper to give some account comprises typical representatives of the geysers, hot springs, mud springs, cold springs, and surface waters found within the limits of the Yellowstone Park. It embraces collections made during the field seasons from 1883 to 1886 under the direction of Mr. Arnold Hague, geologist in charge of the Yellowstone Park Division, and submitted to us for analysis. In our account we have to deal simply with the results of analysis and with the analytical processes we have used—with the latter on the ground that some knowledge of the methods employed in the examination and of the quantities of material at our disposal is essential to a correct understanding of the meaning and value of the analyses themselves. Discussions of the broader chemical aspects of the problems which are involved in a thorough consideration of the relations of these waters, of correlative matters of geological interest, and of the physical phenomena belong properly to others.

The difficulties in the way collecting and transporting large quantities of water in a region comparatively inaccessible were such that the number of large samples, for the more complete analyses, was restricted to a half-dozen; but, though at the beginning of the examination it was supposed that a partial analysis, such as might be made with smaller amounts of material, must suffice, it happened, fortunately, that the development of certain methods as the work progressed has so far extended the reach of the analyses of the smaller samples that from them it is possible to deduce results of fair accuracy, and, if such elements be left out of consideration as are shown by the more elaborate analysis to be present either not at all or only as traces in closely comparable waters, nearly as comprehensive results as those drawn from the examination of the larger samples.

Operations in the Field.

The examination of the waters was necessarily confined in the field to a very few points. Note was made of the *clearness* or *turbidity*, the *reaction* to litmus and turmeric, the *temperature*, and the presence or absence of *hydrogen sulphide*. The tests for the last were the sense of smell and the action of the water upon a polished silver blade.

The operations of collecting and preparing the samples for transportation were carried out as simply as possible. The water was bottled in boxed demijohns when it was possible, and otherwise in beer bottles. In every case great care was taken to clean the receptacle thoroughly and rinse before bottling with some of the water to be examined. In the greater number of cases the waters were so marvellously clear that filtration was entirely superfluous. When, however, the need and opportunity occurred the waters were filtered previous to bottling. All samples were corked tightly and sealed hermetically.

The size of the sample varied from a half litre to one hundred litres, according to the purpose for which it was taken; but the great bulk of the largest samples was, in every case excepting one, reduced greatly by the evaporation of the main portion of the sample previous to bottling. In the one exceptional case the sample was taken for the specific purpose of examining it as to its contents in the heavy metals, and was kept for subsequent reduction in porcelain in the laboratory, in order that the danger of contamination by the tin or copper of the tin-lined still which was employed to effect the reduction in the field might be precluded. No attempt was made to fix with more than a rough approximation the quantities of water evaporated. The concentrated waters, with the rinsings of the still in the natural water of the charge (such portions of the residue as adhered to the walls of the vessel having been dislodged as completely as possible by gentle friction with a rubber or the ball of the finger), were carefully bottled and sealed, and the determination of the degree of concentration was left to be effected in the laboratory in a manner to be described later. A portion of the water represented by the concentrated sample was always reserved in the natural condition for examination.

For the determination of hydrogen sulphide special samples of from 600 c.m.³ to 700 c.m.³ were generally taken, and to each, if the water did not carry free sulphur, was added before corking and sealing a small amount of lead acetate in crystals. Doubtless it might have been well to fix the hydrogen sulphide similarly in the case of waters carrying free sulphur, having first separated this by filtration; but on the few occasions when that need arose the means of removing the sulphur were not at hand. In these cases, therefore, the samples were simply bottled and sealed with care, and kept for examination in the laboratory.

Nearly all the waters examined were hot when the samples were taken and not surcharged with carbonic acid. It was considered unnecessary, therefore, under the circumstances, to take a special sample for the determination of the carbonic acid and treat it in the field so as to fix that gas in insoluble form, but for this estimation reliance was placed upon the general sample which, as has been said, was corked and sealed with great care.

Operations in the Laboratory.

The operations in the laboratory comprised the determination of the specific gravity of the waters and, in the concentrated samples at hand, the estimation of the substances given in Table (see next page).

In analyses for which the natural water alone was available those substances only were sought which are marked in the table with an asterisk (*).

The determination of what is known as the *total residue*, the amount of solid matter left upon evaporating a known amount of water, is usually regarded as desirable, if for no other reason than to serve as a control of the summation of the determinations of the individual constituents; but the complexity of these waters and the relations of the combined salts are such that it is not possible to

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* *Bulletin of the United States Geological Survey*, No. 47.

*Silicic acid.
Titanic acid.
*Sulphuric acid.
Sulphurous acid.
*Carbonic acid.
Nitric acid.
Nitrous acid.
Phosphoric acid.
*Boric acid.
*Chlorine.
Bromine.
Iodine.
Fluorine.
*Sulphur.
*Hydrogen sulphide.
Copper.
Lead.
*Arsenic.
Antimony.
*Iron.
*Aluminum.
Manganese.
Barium.
Strontium.
*Calcium.
*Magnesium.
Cæsium.
Rubidium.
*Potassium.
*Sodium.
*Lithium.
*Ammonia.
*Albumenoid ammonia.

arrive at the same end in two successive treatments by evaporation and desiccation of the residue. The action of free silica, which is an abundant constituent of the waters, is to set free during the process carbonic acid from the carbonates and boric acid from the borates; to magnify the tendency of the chlorides of calcium, magnesium, and lithium to exchange chlorine for oxygen, and, if the temperatures be pushed sufficiently high, to dehydrate the silica and to volatilise sulphuric acid. Furthermore, the extent of such action is variable and indeterminate. There is obvious reason, therefore, for the difficulty which we experienced in obtaining residues of constant composition; and similar obstacles, as we found practically, oppose the attempt to reduce the residue to a definite condition by evaporation and ignition with sulphuric acid in excess. By means of no device which occurred to us (and several lines of experimentation which need not be mentioned here were followed) were we able to apply, in any form, this general method of control. The proof of the accuracy of our analytical work rests, therefore, upon the agreement of duplicate determinations.

For convenience in the matter of arrangement, we describe first those methods of analysis which were applied to waters in the natural condition; and the account of the treatment of concentrated waters follows. Methods for the determination of certain substances are described under both heads. For when the entire work was done upon the natural water the mode of examination was sometimes made, of necessity, by processes different from those which were applied in the examination of concentrated water; and under reversed conditions the converse was true. In some of the earlier analyses methods were employed which later experience taught us might be advantageously replaced by processes which were developed subsequently. In the account of the methods employed all of these are placed under the proper head; and in the statement of analyses mention is made when there might be doubt of the particular method adopted.

Treatment of Natural Waters.

Specific Gravity.—The figures which stand for the specific gravity of a water represent the weight of any volume of the water under consideration at 15·5° C. compared with the weight of the same volume of distilled water at the same temperature. The determinations were nearly all made with a Geissler bottle, fitted with a ground tubular stopper and cap, and a thermometer. In a few of the earlier determinations a bulb-apparatus similar in general principle, but wanting the immersed thermometer, was employed. The temperature of the water in the bottle was taken immediately after the final adjustment of volume, and the latter was effected instantly and without handling after the filled bottle had been permitted to stand a few moments to bring about an equal distribution of temperature. When the bulb-apparatus was employed the temperature of the water was taken before filling the bulb and after weighing, and the mean of the two readings was assumed to be the temperature of the water at the time when the volume was adjusted. The weight shown by the balance was taken as the weight of the water which would fill the apparatus at the temperature noted. The weight of the same volume of the water at 15·5° C. was calculated from the weight observed, upon the assumption that the coefficient of expansion of the water under examination was the same as that of pure water. The rates of the value thus found to the value found by a similar treatment of pure water is a specific gravity at 15·5° C. It is obvious that, in order that the assumption of the identity of the coefficients of expansion of the water under examination and of pure water may be the occasion of the least error, the observed temperature must be as near 15·5° C. as may be; and that the temperature of the balance-room should be not far from the same, in order that errors which may arise from changes of temperature in the water during the manipulation and from the establishment of air-currents in the balance-case may be less liable to occur. So far as we were able these sources of inaccuracy were guarded against, but the conditions under which the work was performed necessitated the application of corrections rather greater than we should wish. The figures which represent the specific gravity in the statement of the analyses are probably not accurate beyond the fourth decimal place.

Hydrogen Sulphide and Free Sulphur.—Hydrogen sulphide in waters which did not carry free sulphur was determined in the special sample to which lead acetate had been added in crystals at the time of bottling. Before breaking the seal of the bottle a scratch was made upon the neck on the line of the meniscus of the water within, and the volume of the sample—usually about 600 $c.m.^3$—was determined subsequently with sufficient accuracy (the amount of hydrogen sulphide present being always trifling) by finding the volume of water necessary to fill the bottle to the mark. The precipitate which had been formed in the bottle by the addition of lead acetate was left undisturbed at first, and the supernatant liquid decanted as completely as possible. Then the precipitate was easily removed, and for the most part dissolved by means of a little sodium hydrate in solution, and the solution and remaining precipitate were added to the water previously decanted. At this point the lead sulphide showed itself, if any was present, and was collected without difficulty by filtering the alkaline liquid in which it floated through a felt of asbestos in a perforated crucible, in the manner described by one of us previously.* The felt and the adherent precipitate were transferred to a beaker, treated with potassium chlorate and hydrochloric acid to oxidise the sulphide, and the sulphuric acid thus formed was determined by precipitation as barium sulphate. From waters carrying free sulphur that element was separated by filtration. The residue, after washing sufficiently to remove the sulphates, was treated with hydrochloric acid and potassium chlorate, and the resulting sulphuric acid was determined as barium sulphate. The filtrate from the sulphur contained the hydrogen sulphide, if it was present in the sample, and this was removed by lead acetate and estimated in the manner described above.

Sulphurous Acid.—The test for sulphurous acid was made in the case of a few waters which did not carry more than a trace of hydric sulphide by titrating 200 $c.m.^3$ of the water, acidified with sulphuric acid, with a standardised solution of potassium permanganate. In none of these was a reducing action found greater than was attributable to the action of the hydrogen sulphide and arsenic (assumed to be in the condition of arsenious acid) known to be present.

Sulphuric Acid.—The sulphuric acid was precipitated from a known weight of water, after acidifying distinctly with hydrochloric acid and heating to boiling by means of barium chloride. After cooling and settling, usually after twelve hours, the supernatant liquid was decanted as com-

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* *Am. Chem. Jour.*, vol. i, 1879. p. 317.

pletely as possible from the precipitate and passed through an asbestos felt in a perforated crucible. The precipitate remaining in the beaker was boiled with a small portion of strong hydrochloric acid, and the latter was removed by evaporation on the water-bath. Treatment with hot acidulated water left the precipitate as pure as barium sulphate may be, and ready for collection upon the same felt through which the supernatant liquid had been poured. Thorough washing, ignition, and weighing completed the operation.

Nitric and Nitrous Acids.—In examining the waters as regards their contents in nitric and in nitrous acids a modification of the indigo method was followed. The action of these acids upon indigo is known not only to be variable with the conditions of dilution, temperature, and the proportion of sulphuric acid added, but also to be dependent upon the order in which the solution of indigo, the sulphuric acid, and the nitrous or nitric acid are intermixed. On this account great care was taken to secure uniformity of treatment of the standard solutions and the water under the test. For preliminary testing a portion of water was reduced by evaporation to a volume of 50 c.m.^{3} cooled to the temperature of the air, introduced into an Erlenmeyer flask, and mixed with an equal volume of strong sulphuric acid. To the mixture the solution of indigo was added until a distinct tinge of green became visible. In this manner the amount of the solution of indigo from which a given amount of the water under test would discharge the colour became known approximately. For the exact test the portion of water, after evaporation and cooling, was brought to a volume which was less than 50 c.m.^{3} by an amount equivalent to the volume of the solution of indigo used in the preliminary test. To the portion thus prepared were added 50 c.m.^{3} of strong sulphuric acid at once, and the solution of indigo as rapidly as the catching of the exact point at which the tinge of green appeared would permit. At the instant of colouration the flask with its contents was placed in a bath of paraffin heated to 140° C. The volume of the solution of indigo which had been added was noted, and if at the end of five minutes' heating in the bath the tinge of colour was still visible, this volume was taken as the measure of the nitrates and nitrites in the water. If, on the other hand, the colour vanished during the heating, it was reproduced by the addition of more indigo, and the digestion in the bath at 140° C. was prolonged during another interval of five minutes.

This mode of treatment was repeated until the colouration was permanent during the interval of digestion. The total volume of the solution of indigo employed was recorded, and its value in terms of nitric acid determined in the manner to be described.

As Warington has shown,[*] the oxidising power of nitric acid upon indigo decreases as the dilution of the solution in which the action takes place increases. It is plain, therefore, that in order that the exact value of the volume of the indigo solution employed in the test may be known, the amount of nitric acid needed to discharge the colour from an equal amount of the same solution under the conditions of the test must be determined. To effect this determination we made use of a solution of potassium nitrate of known strength, and found by experiment the amount of it which, mixed with 50 c.m.^{3} of strong sulphuric acid, with water enough to bring the final volume to 100 c.m.^{3}, and with the amount of the solution of indigo employed in the test, was just adequate to discharge all colour excepting the faint characteristic tinge which must remain unchanged after five minutes' heating. The oxidising power of the nitrates and nitrites in the water is exactly measured by the amount of nitric acid in the quantity of the standard nitrate solution which is required to produce the end-reaction. The solution of potassium nitrate which we used contained 0·0001 g. to 1 c.m.^{3} The mode of manipulation which we adopted keeps the proportion of strong sulphuric acid added to the mixture (excepting the preliminary tests) always the same, and consequently the heat generated in the reaction is the same always. The order in which the reagents are brought together is the same in all cases, and sources of inaccuracy due to the variability of the action of nitric acid with the degree of dilution are eliminated.

(To be continued).

ON THE
TRUE FORMULA FOR PERMANGANATES.[*]

By CHARLES M. BRADBURY, of Virginia.

Introductory Note.

The material obtained by fusing alkali and peroxide o manganese together, which was investigated by Scheele about 1740, and named by him "mineral chameleon," had, as is well known, been observed nearly a hundred years before by Glauber. Up to the early part of the present century, however, but little was known as to its chemical constitution. In 1817 Chevillot and Edwards examined this subject with considerable care,[†] and concluded that mineral chameleon contained a peculiar acid of manganese, but they did not assign to this proposed acid any formula, nor did they recognise the fact (afterwards ascertained by Forchammer) that they were dealing with two acids of manganese instead of one. The first reliable quantitative analyses of these acids were made in 1832 by Mitscherlich,[‡] who assigned to them the respective formulæ that (if we translate from the old to the new chemistry) have been nearly always accepted until very recently. His conclusions have not, however, been unchallenged. Schönbein in 1848 endeavoured to show that permanganates are properly compounds of manganese dioxide with a tetroxide of the base;[§] and in 1859 Phipson denied the existence of permanganic acid, while allowing that of manganic.[||]

Chemical literature from 1832 to 1835 inclusive contains many discussions on the permanganates; they are again frequently noticed from 1851 to 1856; and from 1859, when their usefulness as disinfectants was pointed out, they have continued to attract attention and to increase in variety of application.

Since the establishment of the new system of chemical nomenclature, and until quite recently, permanganic acid has been almost universally regarded as dibasic, so that the permanganates have been represented as $\overset{\mathrm{I}}{R}_2Mn_2O_8$ or $\overset{\mathrm{I}}{R}Mn_2O_8$. Some of the newest treatises[¶] have, however, substituted for this expression one indicating just half its molecular weight, *i.e.*, $\overset{\mathrm{I}}{R}MnO_4$ or $\overset{\mathrm{I}}{R}(MnO_4)_2$, without giving any reason for so doing. It was to determine, if possible, whether this change was justified by the facts in the case, that the present inquiry was undertaken.

Is Permanganic Acid Dibasic.

In searching for the correct answer to this question it will be well to examine in the first place the facts that seem to favour the affirmative.

Let us take, for the sake of convenience, potassium permanganate as a type of the entire class. Then, so far as the manner of writing the formula is concerned, it may

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[*] *Jour. Chem. Soc.*, London, 1879, p. 578.

[*] Dissertation presented to the Faculty of the University of Virginia in application for the degree of Doctor of Philosophy. *Thesis*:—Permanganic acid is monobasic, and the permanganates are represented by the general formula $\overset{n}{R}(MnO_4)n$.

[†] *Ann. de Chim. et de Phys.* (2), iv., 287; also viii., 237.

[‡] *Ann. der Chem. und Pharm.*, ii., 10.

[§] L. Gmelin, *Handbook of Chemistry*, tr. by H. Watts, iv., 213.

[||] *Comptes Rendus*, l., 694.

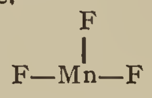
[¶] See, for example, Richter's *Inorganic Chemistry* (Dr. E. F Smith's trans.), 1883; *Principles of Chemistry*, M. M. Pattison Muir, 1884; *Treatise on Chemistry*, Roscoe and Schorlemmer, 1886 be remarked that under the old system of atomic weights no simpler formula than the one we now write, $K_2Mn_2O_8$, was possible; for K_2O was KO, and permanganate of potash was $KOMn_2O_7$,[*] or, according to Berzelius, $KOMnO_7$. But inasmuch as the adoption of the new system has resulted in halving the formulæ of many compounds, *e.g.*, nitric acid, which before were in a precisely similar condition, this fact, taken alone, has no greater weight than attaches to the mere priority of the dibasic formula, which is scarcely worthy of mention.

In the second place, however, there is what seems to be a very good reason indeed for retaining the formula $K_2Mn_2O_8$, namely, that manganese undoubtedly deports itself in many cases as an artiad[†] element, and hence to write potassium permanganate $KMnO_4$ is to violate Gerhardt's law of even numbers. Without giving to this law greater credence than is proper, the fact that it holds in most cases is hardly deniable. Unless good reasons can be shown for disregarding it, it should be observed in this instance.

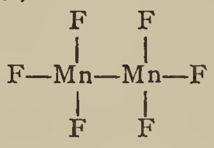
A few examples of the even valence of manganese will help to show the weight of the evidence in favour of the formula $K_2Mn_2O_8$.

The manganous and manganic chlorides both display this even valence; so do the fluoride.

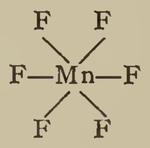
(1) F—Mn—F

(2) 

$$\begin{array}{c}\text{F}\\ |\\ \text{F—Mn—F}\end{array}$$

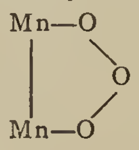
(3) 

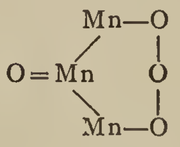
$$\begin{array}{c}\text{F}\quad\ \ \text{F}\\ |\qquad |\\ \text{F—Mn—Mn—F}\\ |\qquad |\\ \text{F}\quad\ \ \text{F}\end{array}$$

(4) 

The oxides best known are MnO, Mn_2O_3, Mn_3O_4, and MnO_2, which may be written respectively—

(1) Mn=O

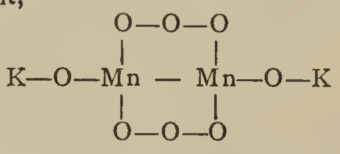
(2) 

(3) 

(4) O=Mn=O

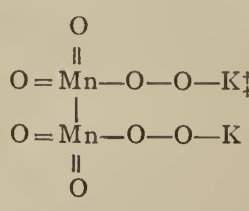
According to the law that quantivalence always varies, if at all, by *pairs* of equivalents, such evidence as the above would seem to prove conclusively that manganese is artiad in all of its compounds.

It is evident that by retaining the molecular formula $K_2Mn_2O_8$ not only is Gerhardt's law satisfied, but it becomes easy enouth to write structural formulæ of probable correctness. For example, supposing manganese to be tetravalent,



$$\begin{array}{c}\text{O—O—O}\\ |\qquad\quad |\\ \text{K—O—Mn — Mn—O—K}\\ |\qquad\quad |\\ \text{O—O—O}\end{array}$$

or, as is more usual, making it hexavalent,



$$\begin{array}{l}\quad\ \ \text{O}\\ \quad\ \ \|\\ \text{O=Mn—O—O—K}^{\ddagger}\\ \quad\ \ |\\ \text{O=Mn—O—O—K}\\ \quad\ \ \|\\ \quad\ \ \text{O}\end{array}$$

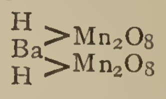
So far as I have been able to discover, the facts just stated—namely, the even valence of manganese taken in connection with Gerhardt's law, and the impossibility, in view of this even valence, of writing a graphic formula corresponding to $KMnO_4$—have determined the retention of the molecular formula $K_2Mn_2O_8$ so long after other apparently double formulæ have been simplified. It is clear that with the nitrates, chlorates, perchlorates, &c., neither of the reasons exist for retaining the double formula that seem to make that course necessary with the permanganates; for the nitrogen and chlorine of these salts, and the elements that bear similar relations to others whose molecular weights have been divided by two since the introduction of the new system, are perissad.

If, then, the dibasic formula corresponds so well with known facts, why should it be called into question, much less rejected? A general answer to this may be found without much difficulty. Stated briefly, it may be divided into two propositions: First, there has been up to the present time *no positive evidence* of dibasicity in permanganic acid in the shape of acid or double salts. Second, there are theoretical considerations, partly of recent development, that permit and, indeed, require the use of the monobasic formula. In other words, at least one of the two laws that indicate so positively the correctness of the old formula must, in the light of later research, be accepted in a modified sense only.

With regard to the first proposition, it is clear that it could hardly be true of a really dibasic acid as well known as permanganic. That in all the experimental study of the permanganates that has been made in the past,[*] this particular question could, by an accidental coincidence, have been entirely overlooked is highly improbable. In fact, there is one acid permanganate—that of barium—spoken of in one of the older treatises,[†] but, as will be shown, this fact increases the improbability just alluded to. If even this one acid permanganate could be proved to exist, further discussion as to the basicity of the acid would be unreasonable; but the whole account of it is indefinite, improbable, and contradictory, and recent works do not speak of it at all.

It appears that, according to some observers, if aqueous permanganic acid (obtained by treating a solution of barium permanganate with sulphuric acid) be evaporated at a gentle heat till quite concentrated, it deposits on cooling "dark carmine-red needles, which yield 8·411 per cent of water." This is certainly singular, to say the least, when compared with the admitted fact that a similar solution evaporated over oil of vitriol merely deposits hydrated peroxide of manganese. But without denying that such crystals have been obtained, the question as to what they were is an open one, for Fromherz regarded them, not as acid barium permanganate, but as crystallised permanganic acid. Mitscherlich and Wöhler are said to have inclined to the opinion that they were acid barium permanganate. It does not appear, however, from the account given that any analysis of the crystals had been made, and it is difficult to see how, after enough sulphuric acid had been added to precipitate all the barium and the solution decanted, enough barium could still remain in solution to form an essential constituent of "dark carmine-red needles," or of anything else at all noticeable.

Besides this, the percentage of water given is about three times as much as acid barium permanganate would contain. For assuming that the acid is dibasic and acid barium permanganate possible, it must be,—



$$\begin{array}{l}\text{H}\\ \text{Ba}>Mn_2O_8\\ \text{H}>Mn_2O_8\end{array}$$

or $H_2Ba(Mn_2O_8)_2$, the molecular weight of which is 615. It could yield only one molecule of water, and $\frac{18}{615}=0·029$.

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[*] See, for instance, analysis by Machuca (*Comp. Rend.*, li., 140).

[†] With regard to the whole subject of quantivalence, I have endeavoured to follow what seem to be the prevailing ideas, as exemplified in Odling's article, "Metals, atomic weights and classification of," in "Watts' Dictionary."

[‡] From "Watts' Dict.," 1st Supp., 236.

[*] See, for instance, an account by Gorgeu (*Comptes Rendus*, l., 610) of a "manganate and permanganate," (?) $Mn_2O_7K_2O.2MnO_3K_2O$.

[†] Gmelin's *Handbook*, iv., 210.

That the excess could be water of crystallisation is unlikely, whether the substance be compared with other acid salts or with other permanganates; nor is any allusion made to the excess, nor any explanation offered. Finally, attempts to make this "acid barium permanganate" met with no success. Of this more will be said in another place.

The assertion that the dibasic formula has not been supported by *experimental* evidence is, then, justifiable. It will now be shown that the *theoretical* defences of this formula must give way to known facts.

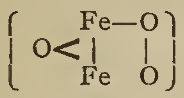
It will suffice for my present purpose to speak of the statement that is the very keystone of the supports of the double formula; namely, that manganese is an artiad element. The evidence in favour of this conclusion is too strong to be set aside without exceedingly good reasons. There is no doubt that in general this element has an even number of atomicities.

If, however, it can be proven that there are exceptions to the rule—that the statement in question, while generally true, is not rigidly so—the *possibility* of the monobasic formula for permanganates will be established.

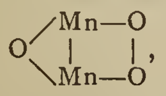
As a matter of fact, while manganese is most frequently of even valence, it can nevertheless exist in a state that (unless the meaning of "valence" be modified, as some have proposed) can only be described as one of uneven or perissad valence. There is ample evidence to prove that the law that quantivalence always varies by twos, while it very generally holds good, does not always do so. The fact that mercury appears to be both monad and dyad is well known; nitrogen also is frequently recognised as peris-artiad. That tungsten does not conform to the law is evident from the list of chlorides of that metal,

$$WCl_2,\ WCl_4,\ WCl_5,\ WCl_6.$$

The same is true of vanadium, which forms the series of chlorides VCl_2, VCl_3, VCl_4, and the oxides V_2O, V_2O_2, V_2O_3, V_2O_4, V_2O_5.* According to Odling,† iron, which is dyad in ferrous oxide ($Fe{=}O$), is triad in the ferric oxide—



and similar differences exist in the salts of the allied metals nickel, copper, cobalt, and manganese. This would make graphic formula for Mn_2O_3,—



nstead of that given above. Without accepting even Odling's views with regard to the iron metals (including manganese) as decisive, no reasonable doubt remains that either there are genuine exceptions to the law under discussion, or the meaning of "valence" must be restricted so as to exclude some of the phenomena usually designated by that word. In the present instance it can make no difference which alternative is chosen; it will be sufficient to show that manganese is as much an exception to the law as any other element.

As evidence to this effect, it is fair to mention the fact that some eminent authorities, as Odling, have come to this conclusion by observing the analogy (1) between aluminic and ferric and (2) between ferric and manganic oxides.

Again, although the supposed heptachloride of manganese of Dumas turned out to be an oxychloride, the formula MnO_2Cl_2, assigned to it by H. Rose,‡ in which the manganese is perhaps most naturally regarded as hexad, had been changed by Roscoe§ to MnO_3Cl, and no structural formula can be written corresponding to this, without making the manganese heptad, or at least a perissad of some sort.*

These reasons for regarding manganese as peris-artiad may not be conclusive, but are worthy of attention. Strong and direct evidence may be obtained, however, by a consideration of the *periodic relations* of the element.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

February 23, 1889.

Prof. REINOLD, F.R.S., President, in the chair.

MR. M. H. KILGOUR was elected a Member of the Society.

Dr. J. W. WAGHORNE read a "*Note on the Measurement of Electrical Resistance,*" showing that two resistances may be compared by joining them in series with a battery, and observing the deflections of a galvanometer connected successively with their terminals. The resistances are proportional to the currents which pass through the galvanometer in the two cases, provided they are large compared with that of the battery, or are not very different from each other. By using a rocking key the method is rendered expeditious, and the galvanometer resistance need not be known.

"*On a New Polarimeter,*" by Prof. S. P. THOMPSON, D.Sc.

The author gave a *resumé* of the ordinary methods of determining the position of the plane of polarisation, pointing out their advantages and disadvantages, and exhibited his new polarimeter, in which two black glass mirrors placed at a small angle (about 2½ degrees), are used to polarise the light in two different planes. By using a modified Nicol as analyser the plane can be determined to one-tenth of a degree, when the substance examined does not absorb much light; but for dark coloured liquids, the author prefers to use one of his "twin prisms," described before the British Association in 1887 as polariser, in which the planes of polarisation are 90° apart. A method of dividing a polarised beam into two parts inclined at a variable angle, by means of a combination of quarter wave plates of mica, was described, in which the two halves of the field are similarly coloured.

Mr. GLAZEBROOK considered Poynting's glass cell with different thicknesses of active solution, a very convenient means of obtaining two beams polarised at a small angle, as by altering the strength of the solution the angle may be varied at will.

Prof. THOMPSON also read a note "*On the Formation of a Cross in Certain Crystal Structures.*"

Several specimens (including benzoic acid, stalactite, Eno's salt, &c.) which exhibit a radial structure and show a cross when examined by polarised light, were thrown upon the screen, and the fact that the cross remains stationary when the specimens are rotated, demonstrated. Similar effects were produced by mica sectors arranged radially, thus showing the stationary cross to be caused by the light not being analysed in those directions.

"*On Electrical Measurement.*" By Prof. W. E. AYRTON, F.R.S., and Prof. J. PERRY, F.R.S.

In a paper "On Winding Voltmeters," read before the Society in 1885, the authors showed, on the assumption that the thickness of insulating covering on wires was proportional to their diameter, that instruments wound with copper wire gave a less heating error than similar

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* Roscoe and Schorlemmer, "Treatise," II, ii., 293, 283.

† "Watts' Dict." III, 595 sq.

‡ "Watts, Dict.," 1st Supp., 246.

§ R. and S., "Treatise," II, ii., 22.

* According to Lossen's system (Muir's *Principles of Chemistry*) this statement does not hold good but according to most authorities it does.

ones wound with German silver. Since then platinoid has been introduced and the electrical constants of phosphor-bronze determined. Further, a remarkably simple relation between the volts corresponding to a given deflection on a given type of instrument, and the resistance per unit lengths of the wire used in winding it, has been suggested by Mr. Crawley. Suppose F = number of ampére turns required to produce the deflection, P and U the half area of section and volume of the coil respectively, and d and D the diameters of the bare and covered wires. Then—

$$A = \frac{F}{n}, \quad n = \frac{P}{D^2}, \quad r = \frac{4l\rho}{\pi d^2}, \text{ and } l = \frac{U}{D^2};$$

from these we get—

$$V = Ar = \frac{FU}{P} \cdot \frac{4\rho}{\pi d^2} = K \cdot \frac{4\rho}{\pi d^2} \text{ (say}$$

where K is a constant depending on the type of instrument. Since $\frac{4\rho}{\pi d^2}$ is the resistance per unit length, *the volts required to produce a given deflection are proportional to the resistance per unit length of the wire used, whatever be the material of the wire or thickness of the insulation.* Taking this into account and using a more accurate value for the thickness of the covering, it is shown that the four metals above referred to arrange themselves in the following order of merit when used for high-reading voltmeters; platinoid, phosphor-bronze, German silver, copper, and for comparatively low reading instruments, the last two change places.

As a standard ammeter of great range, a circuit containing a Depretz D'Arsonval galvanometer is shunted by a wide sheet of thin platinoid, and by altering the resistance in the galvanometer circuit the sensibility may be varied in known proportions. An instrument on this plan has been arranged to measure any current from 0·1 to 800 ampéres to ¼ per cent, and the same galvanometer in series with various resistance coils is used as a standard voltmeter of practically unlimited range. Whilst arranging these standards it has been found that the deflections are not generally proportional to the currents, and the discrepancy traced to the centre of gravity of the swinging coil not being in the line of suspension. By replacing the bottom torsion wire by a long thin spring the defect may be remedied. As relating to calibration curves of intruments, it was mentioned that in "Siemens's Dynamometer," the "square law" is not correct, probably owing to distortion of the spring.

Referring to "Hot Wire Voltmeters," in which the sag of a wire heated by a current is measured by a magnifying spring, the authors remark that in their original paper on the subject they neglected the change of length due to change of stress in the wire, and subsequently their assistant, Mr. Bourne, found that maximum sensibility was never coexistent with minimum sag. The sag which gives maximum sensibility depends on the initial stress in the wire; and by altering the initial sag the instruments may be compensated for changes of temperature of the room. In the present paper the mathematical treatment is more rigorous, and the results are in accordance with experiment. A voltmeter intended for use with "electric welders," which deflects about 300 degrees for 2 volts (direct or alternating), and is graduated to 1-100th of a volt, was exhibited, and used to measure the resistance of a storage cell.

Dr. Thompson suggested that the want of proportionality of D'Arsonval's galvanometers might be due to lateral displacement of the coil caused by the current in the torsion wires crossing a magnetic field, but from experiments with pivotted coils the authors thought this improbable.

Prof. Rücker read a "*Note on the Dimension of Electromagnetic Units*," by Prof. G. S. Fitzgerald, F.R.S., which suggests that specific inductive capacity and permeability be *assumed* to be of dimensions $[\frac{T}{L}]$ (slowness); if this be done the dimensions of quantities expressed in electrostatic and electromagnetic measure become identical. The author also states that it seems most likely that inductive capacities are related to the reciprocal of the square root of the mean energy of turbulence of the ether.

Prof. Rücker remarked that in his recent paper on the subject he considered it important to retain K and μ as secondary fundamental units, and Mr. Blakesley did not concur with Prof. Fitzgerald's suggestion.

A photograph of Crystal Models by Mr. R. T. Anderson, Belfast, was exhibited at the meeting.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, March 4, 1889.

Sir James Crichton Browne, M.D., F.R.S., Vice-President, in the Chair.

John Cope Butterfield, F.C.S., Charles Cave, Mrs. E. S. Dewick, Miss K. D. Doulton, Joseph Gordon Gordon, Mrs. Sibble Heap, Miss Mona Kemp, Lieutenant Nathaniel J. Lyon, Alfred Nobel, Richard Douglas Powell, M.D., F.R.C.P., Thomas James Reeves, B.A., F.Z.S., Mrs. W. Chandler Roberts-Austen, Mrs. H. Sutton, George Edward Whitton, M.B., Ernest H. Winstone, M.A., and Mrs. M. A. E. Wright 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.

OBITUARY.

JOHN WILLIAMS, F.C.S., F.I.C.

We much regret having to put on record the death of Mr. John Williams, F.C.S., F.I.C., which took place at his residence, 63, Warwick Gardens, S.W., on Sunday, March 3rd, within a few days of the completion of his 65th year.

The deceased gentleman was the son of John Williams, who formerly filled the position of Secretary to the Royal Astronomical Society and was connected with other learned Societies.

Mr. Williams was born in London on March 9th, 1824, and was for many years assistant to the late Mr. Morson. Subsequently he was for nearly forty years partner with Mr. King Hopkin, in the firm of Hopkin and Williams.

For seventeen years he was a member of the Council of the Pharmaceutical Society of Great Britain, during three years of which he acted as Treasurer, and for three more years he filled the office of President. Mr. Williams was at one time a contributor to the Chemical News, to which he supplied, among others, a paper on the "Preparation of Urea" (vol. xvi., p. 299), and one on the "Milligrade Graduation of Thermometers" (vol. xxxi., p. 214).

Signal Lights for Ships and Lighthouses.—A. Jaksch.—The author proposes the following mixture for distress signals:—Barium nitrate, 30 parts; magnesium powder, 20 parts; flower of sulphur, 4; and beef tallow, 7 parts. The tallow is added in a melted state, and the mixture is sifted. This mass filled into strong zinc boxes 10 c.m. in height and 8 in diameter. It gives for 20 seconds a light of 20,000 candles, visible in clear air at the distance of 100 kilometres. If the mixture is used for rockets the tallow is omitted.—*Chemiker Zeitung.*

NOTICES OF BOOKS.

Calalogue of Chemical and Physical Apparatus and Chemicals. Manufactured and Imported by Philip Harris and Co., Limited, Bull Ring, Birmingham.

The appearance of the catalogue before us is a plain proof that the need and the demand for chemical and physical apparatus and reagents is vastly greater than it was the case a quarter of a century ago. A peculiarity of Messrs. Harris's catalogue is that chemical appliances and those for the different departments of physics are not placed under separate headings, but all follow in the same alphabetical series. This arrangememt is, on the whole, convenient, since various physical apparatus are used in chemical research, and the experimentalist is thus saved the trouble of referring to separate lists for the articles which he may require. The assortment of electrical apparatus here included is very extensive. There are dynamos, batteries, accumulators, voltmeters, ammeters, friction-machines, Wimshurst's influence machines, and those of Holtz, Carré, &c. The apparatus for the production and application of heat are very numerous, including the well-known devices of Fletcher; the Hofmann, Glaser, and Erlenmeyer furnaces for organic analysis, assay furnaces, &c.

Optical instruments are not wanting; there are microscopes, polariscopes, spectroscopes, and photometers. Among chemical apparatus, properly speaking, we notice the profusion of appliances for gas analysis, both scientific and technical. We must call especial attention to the improved and very complete set for testing the illuminating power and purity of coal-gas.

Crucibles and capsules of iridio-platinum, of pure nickel, platinised nickel, copper, and silver are here mentioned.

The list of chemicals is fairly complete, and includes some rare preparations, such as yttrium oxide.

As an appendage to the catalogue, we find the lists of apparatus which the Science and Art Department require for the study of different subjects. It is curious and typically "departmental" to find diagrams showing the anatomy and physiology of the honey bee, placed not under "Animal Physiology," but under "Principles of Agriculture." For this, however, Messrs. Harris are in no wise responsible.

The illustrations are numerous and well executed, and, saving certain printing faults, the whole catalogue is admirably got up.

CORRESPONDENCE.

WARNING TO CHEMISTS.

To the Editor of the Chemical News.

Sir,—With reference to the letters which have appeared under the above heading in your issues of 13th and 20th January, and 23rd November, 1888, it may be of interest to others besides the writer to know that an individual, who has been identified under various names, is now on remand at Bow Street, and will be brought up again on Wednesday morning next.—I am, &c.,

F.I.C.

London, March 6th, 1889.

SOLUBILITY OF BRASS.

To the Editor of the Chemical News.

Sir,—I must apologise for having overlooked Mr. Blount's letter on this subject in the Chemical News (vol. lix., p. 47). He points out that my statement in the *Trans. Chem. Soc.*, 1889, p. 18, that brass dissolves in weak sulphuric acid is incorrect; and, no doubt, he is right. I used the term "brass" where I should have used "certain alloys of copper and zinc." This error does not, of course, affect the validity of my explanation of the thermal results of the action, and even if no action of the sort takes place, all that can be said is that there is nothing to explain.

My authority for the action will be found in Berthelot's *Méc. Chim.*, ii., 461.—I am, &c.,

Spencer Pickering.

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. cviii., No. 7, February 18, 1889.

On the Egyptian or Vestorian Blue.—F. Fouqué.—This very fine blue pigment, which ceased to be manufactured from the time of the fall of the Roman Empire, is a double copper-calcium silicate containing silica 63·7 per cent, lime 14·3, copper oxide 21·3, and ferric oxide 0·6. No trace of alkalies is found. It may be boiled without decomposition in sulphuric acid; ammonium hydrosulphate does not blacken it, and lime only attacks it in heat. Hydrofluoric acid is its only easy solvent. It is produced at a bright red heat, but it becomes altered if this temperature is decidedly exceeded. Vitruvius gives the following account of its preparation:—Sand and natron are ground together as fine as flour, mixed with copper filings, and the whole is made into a paste with a little water. This paste is moulded into balls which are let dry and finally heated in an earthen pot set in a furnace, so that the mass enters into fusion and turns to a blue colour. M. Fouqué finds this process successful, but there is no occasion for the sodium carbonate, potassium sulphate forming a better flux. The mass is then ground up, purified with hydrochloric acid, and finally by means of Daniell Klein's dense liquor. Magnesia cannot be used in place of lime, which is not mentioned in the formula quoted from Vitruvius. The beauty and the permanence of this pigment, which is affected neither by air, moisture, light, nor most chemical agents, the ease of its preparation, and the low price at which it can be manufactured, render it desirable that it should again come into use.

Reagents for the Mercaptan Function.—G. Denigès.—Isatin, which is already employed in a sulphuric solution to detect thiophene, is also an excellent reagent for the mercaptan function. If we mix a few c.c. of pure sulphuric acid with a small quantity of a one per cent solution of isatin in sulphuric acid and add traces of free mercaptan, or better, dissolved in a little alcohol, a fine green colour is produced, which is obtainable neither with ethyl sulphide, nor sulphurous gas, nor with hydrogen sulphide. To augment the sensitiveness of this reaction we steep the end of a glass rod, terminating in a ball in the sulphuric solution of isatin, and move it about in the atmosphere of the vessel containing mercaptan; the green colour appears very quickly even with very minute traces of mercaptan. Or, after the rod has been thus exposed for a time to the action of the mercaptan vapours its end may be plunged into a little sulphuric acid, which takes up the colouring-matter, and by repeating the operation a certain number of times the acid takes an intense colour. The presence of mercaptan may thus be detected when mixed with other volatile products without any previous separation. The green colouration is produced with the methylic, ethylic, propylic, primary butylic, isobutylic and amylic mercaptans, whilst the corresponding sulphides have no action upon the sulphuric solution of the reagent. The aldehyds and the higher alcohols destroy or mask the colour due to the mercaptans. In this case we may use sodium nitroprusside for their detection. The substance in question, in aqueous suspension or solution, is treated with a few drops of soda or potassa lye, shaken for a few moments, diluted with water, and the nitroprusside is added. A red-violet colour is obtained, which is not due to the production of alkaline sulphides, for no precipitate of lead sulphide is obtained on adding dilute mercaptan to an alkaline solution of lead oxide; but it is owing to the sodium or potassium derivative of the mercaptan used. If the liquid examined contains at the same time sulphuretted hydrogen or sulphides it is well to use, instead of the potassa or soda-lye, an alkaline solution of lead oxide, and then to add the nitroprusside. The black precipitate of lead sulphide thus formed does not prevent the appearance of the red colour if a mercaptan is present. The alcohol sulphides and sulphurous gas have no action upon the nitroprusside in presence of alkalies.

Preparation and Properties of Propyl and Isopropyl Fluorides.—M. Melsans.—Propyl fluoride is a gas of an ethereal odour, less pleasant than that of methyl and ethyl fluorides. It burns with a luminous flame, giving off hydrofluoric acid. At −2 under ordinary atmospheric pressure it is liquefied, forming a colourless, very movable liquid, which does not act upon glass. Its density at 20° is 2·161, theory demanding 2·175. It is very soluble in the alcohols, benzene, ether, the alcoholic iodides, and dissolves at 16° in one volume of water. The isopropyl fluoride has a more pungent odour. It burns like the propyl compound. Its density at 15° is 2·171, the theoretical value being 2·175. It is rather more soluble than the propyl fluoride, 1 vol. of water taking up 1·5 vols. of the fluoride.

On Sorbite and on its Presence in Fruits of the Family of Rosaceæ.—MM. Vincent and Delachanal.—This compound, first obtained from the fruits of the service, has since been detected in pears, apples, medlars, the fruits of the "burning bush," and in cider from Bretagne. Sorbite does not give a crystalline compound with ethylic aldehyd in presence of sulphuric acid, which distinguishes it from mannite. Contrary to what has been asserted, sorbite acts upon polarised light. It is lævo-rotatory, and its specific power is −1·73 for the ray D at the temperature of 15°.

Experimental Researches on the Degree of Affinity of Various Animal Tissues for Sulphur.—M. J. de Roy-Pailhade.—Equal weights of the different tissues of one and the same animal convert unequal quantities of sulphur into hydrogen sulphide. The descending order of tissues, established by their affinity for sulphur, is the same as the descending order established by their affinity for oxygen.

Bulletin de la Société Chimique de Paris.
Vol. li., No. 3.

Small Analytical Notes.— C. de la Harpe and F. Reverdin.

Detection of Carbon Monoxide in the Air.—The presence of this gas may be ascertained by passing the air, previously filtered, through glass-wool or cotton, over pure dry iodic acid, heated to 150°, and then into starch dissolved in distilled water. The carbon monoxide passes into the state of dioxide, a corresponding quantity of iodine is set at liberty, and the solution of starch is coloured blue. The operation is most conveniently conducted by putting the iodic acid into a small fractionation flask, the delivery tube of which has been bent down so as to plunge into a small bottle containing the solution of starch. The flask is set in an oil-bath and air is let arrive in a moderate current at the bottom of the apparatus. Other reductive bodies, such, *e.g.*, as sulphuretted hydrogen, must first be removed by known methods.

Modification of Bunsen's Apparatus for Determining Manganese and Chromates.—The apparatus is here described and figured.

On the Experiments of M. Genvresse. — Ivan Ossipoff.— The author points out the results which he obtained fifteen months ago concerning the influence of temperature on the successive chlorination of acetylacetic ether.

On a Diquinolic Base.—A. Colson.—This base has the composition $C_{22}H_{18}N_2O_3$. It is soluble in six parts of dilute hydrochloric acid and in ten parts of alcohol at 92 per cent. It melts at 71·5°. It is deposited from its ethereal solution in long flattened needles, highly double refractory, which extinguish polarised light in the direction of their length, and appear to be uniaxial and positive.

Action of Sodium upon Ethyl Cyanide. Synthesis of the Pyrrolic Derivatives.—M. Hanriot and L. Bouveault.— This memoir does not admit of useful abstraction.

On a New Ptomaine, and on a Method of Analysing Alkaloids.—A. M. Delezinier.—The apparatus is very complex, and cannot be described without the aid of the accompanying figure. The ptomaine, $C_{32}H_{31}N$, is an oily liquid, almost colourless, very sparingly soluble in water, but soluble in all proportions in alcohol, ether, toluene, and benzene. It is extremely oxidisable, and forms very deliquescent salts.

On a New Acid of Tin.—W. Spring.—The author has obtained a compound corresponding to the formula $H_2Sn_2O_7$. It belongs to the same type as disulphuric and dichromic acid, and connects tin with sulphur and its analogues. To obtain it the author takes a saturated solution of stannous chloride in water containing enough hydrochloric acid to prevent precipitation, and treats it at the ordinary temperature with an excess of pure barium peroxide. The turbid liquid thus obtained does not become clear on standing, and contains the compound of tin in the colloidal state. The barium chloride is eliminated by dialysis, and when it ceases to pass through the contents of the dialyser are evaporated on the water-bath and yield a white mass.

Journal de Pharmacie et de Chemie.
Vol. xix., No. 4.

Conversion of Terpilene into a Menthene.—M. Bouchardat and J. Lafont.—The authors have effected this change by the prolonged action of aqueous hydriodic acid. Natural menthol ought to be attached lo the terpilene series, and it has relations of terpilenol or terpilene monohydrate, similar to those which connect the allylic and propylic alcohols.

Direct Determination of the Oxygen and Nitrogen Gases Dissolved in Natural Waters.—A. Lalien.—The author's method turns on the use of the apparatus here figured and described.

On a New Alkaloid: Imperialine.—Dr. Ch. Fragner.—The base in question is extracted from the bulbs of *Coronaria Imperialis*, and has the composition $C_{35}H_{60}NO_4$. It forms small colourless prisms, very sparingly soluble in water, sparingly soluble in ether, benzene, amylic alcohol, and petroleum ether, but very soluble in hot alcohol and chloroform. It is lævorotatory.

Alteration of the Aqueous Solutions of the Morphine Salts and their Transformation in the Organism.—Dr. Alph. Lamal (*Bulletin de l'Acad. de Belg.*).—These solutions do not alter if protected from light and from atmospheric dust. If exposed to these agents there may be formed an amorphous substance (morphetine?) and crystals of oxymorphine. Apomorphine does not appear to be formed. Morphine circulating in the blood and the tissues is transformed into oxymorphine, which latter substance should be sought for in toxicological investigations.

Influence of Diet upon the Melting-point and the Chemical Composition of Butter.—Ad. Mayer (*Landw. Versuch. Station*).—The volatile fatty acids rise and fall with the density of the butter fat. The melting-point of butter-fat is not in relation either with the density or the proportion of the volatile fatty acids, and depends upon the quantity of oleine rather than upon that of butyrine, caproine, &c. The total of the volatile fatty acids, and consequently its density, varies even for one and the same cow within much wider limits than it has been hitherto thought. It depends on the period of lactation, and falls as it is more advanced. Beet-root, grass, and green clover are most favourable; then follows hay, and lastly ensilage.

Detection of Alcohol in Essential Oils.—H. Hager (*Pharm. Zeitung*).—The author agitates the sample in question with glycerin, which removes the alcohol totally.

Adulteration of Vanilline.—Em. B. (*Gehe's Handelsbericht*).—The presence of benzoic acid may be detected by means of the microscope, as vanilline crystallises in needles and benzoic acid in minute laminæ.

Presence of Tyrotoxine in Ices and in Poisonous Milk.— Dr. C. Vaughan (*Archiv. f. Hyg.*).— The substance of this paper has been already noticed.

A New Reagent for Glucose.—L. Crismes (*Pharm. Zeitung*).—This reagent is safranine, the solutions of which are reduced and rendered colourless by glucose.

Revue Universelle des Mines et de la Metallurgie.
September, 1888.

Volumetric Method of Determining Manganese.—A. Ghilian.—The hydrochloric solution of the substance containing the manganese in the manganous state diluted with boiling water is poured into an Erlenmeyer flask holding from 900 to 1000 c.c. and mixed with an excess of zinc oxide suspended in water. The liquid is made up to 500 to 600 c.c. by means of boiling water and the standard solution of permanganate is slowly dropped in from a Mohr's burette, agitating after each division, and causing the oxides to settle by slanting the flask. The colour of the clear supernatant liquid shows the precise moment when it is coloured by an excess of permanganate. From the volume of permanganate employed the proportion of manganese is calculated. In the treatment of irons, steels, Bessemer metal, and ores whose proportion of manganese does not exceed 3 to 4 per cent the author uses a solution containing 4 grms. permanganate per litre, the value of which is 0·000213 per $\frac{1}{10}$ c.c. (*i.e.*, for one division of the burette). A solution of double the strength is employed for the determination of spiegels, ferro-manganeses, and rich ores. Its value is 0·000426. Twenty-five such assays may be executed in half-an-hour. The zinc oxide employed ought to be the kind obtained by precipitation. During the operation the liquids should be kept at about 80°.

October, 1888.

Studies on the Raw Materials and the Products of Siderurgy.—Dr. C. Meinecke (*Zeitschrift fur angewandte Chemie*).—The first chapter of this series treats of the precipitation of manganese as sulphide. The author finds that this process is free from inconvenience if we obtain the green anhydrous manganous sulphide, which is granular in texture, deposits rapidly, and can be collected on a filter and quickly washed with a small quantity of water; it shows no tendency to give a turbid filtrate. To obtain the sulphide in this condition the author proceeds as follows:—The boiling manganous solution is treated with a large excess of ammonia, and without stopping the ebullition or attending to the precipitate, if one is formed, a decided excess of ammonium sulphide is added. The ebullition is still kept up for a few minutes, and the liquid is then let settle and filtered when it has become clear. Traces of the green sulphide which remain in the filtrate may be recovered by expelling the ammonia by evaporation, decomposing the residual ammonium sulphide by a little hydrochloric acid, filtering off the deposit of sulphur, concentrating the filtrate, and precipitating the manganese with bromine and ammonia.

Removal of Fused Masses from Platinum Crucibles.—Professor L. L. de Koninck.—This process is devised for the extraction of fused masses obtained in consequence of disaggregations by alkaline carbonates, sulphates, &c. When the fusion is complete the author immerses vertically in the centre of the melted mass, the spiral extremity of a strong platinum wire, 0·5 m.m. in thickness and 8 to 10 c.m. in length, with a loop at its upper end. The wire is kept in this position until the mass solidifies. When completely cold the crucible is suspended by means of a second platinum wire, hooked to the former and attached to a glass hook supported a few millimetres above a triangle of platinum or of pipe-stems. The crucible is then rapidly heated by means of a strong lamp, and as soon as the outside layer of matter in contact with the matter enters into fusion, the crucible falls down upon the triangle and the mass which remains solid is suspended on the wire. This wire is immediately seized with the forceps with one hand and lifted away from the crucible, whilst with the other hand the lamp is removed.

MISCELLANEOUS.

Examination of Alcohol.—H. Bornträger.—A specimen of the alcohol is diluted with much water, observing if oily drops collect on the surface. If this is the case the spirit is tested for acetal with sulphuric acid and potash-lye (odour of acroleine) and for amylic alcohol with strong hydrochloric acid and aniline oil. A second sample is tested for aldehyd with potassium iodide and a solution of acid sodium-magenta sulphite. If no drops appear on the surface, test as above for aldehyd, dilute a further portion with two parts of water, shake up with chloroform, separate, let evaporate at a gentle heat, and test any residue for acetal and amylic alcohol as above.—*Zeitsch. f. Anal. Chemie*, Vol. xxviii., Part 1.

Coloured Reactions of Strychnine.— Flückiger (*Pharm. Zeitung*) refers the colours which strychnine produces with sulphuric acid and oxidising agents (lead peroxide, potassium chromate, ammonium vanadiate, ceri-cerous oxide, potassium ferricyanide, and permanganates) to the formation of one and the same lilac or violet product, which is very unstable. A permanent and certain colour is obtained with the following solution:—0·01 grm. potassium dichromate is dissolved in 5 c.c. of water and mixed with 15 grms. (8 15 c.c.) sulphuric acid of sp. gr. 1·84 at 15°. When cold the reagent is ready for use. A solid body to be tested for strychnine is moistened with a single drop of this liquid, or the powdered solid is scattered upon the liquid on a porcelain slab, or a saturated solution of the strychnine salt is let flow slowly over the acid, shaking very gently so as to obtain a distinct zone. Certain substances, such as brucine, give a fine red colour with the chromiferous sulphuric acid, and mask the reaction of strychnine. In case of a mixture of brucine and strychnine which does not at once give the strychnine reaction, the substance is placed upon a small moistened filter and chlorine-water is dropped upon it as long as a red colour is thus produced. Dichlorbrucine is thus formed as an amorphous, easily soluble body, which passes rapidly into solution. The undissolved alkaloidal residue gives the reaction of pure strychnine.

Reactions of Alkaloids.—Fr. Kundrát recommends as a reagent a solution of ammonium vanadiate in strong sulphuric acid, 0·1 grm. in 10 c.c. acid. It is applied in the same manner as Frœhde's mixture. It gives with aconitine a light coffee-brown; with atropine, a red, passing into yellowish red and finally into yellow; apomorphine, a dark violet blue, then dirty green, and by degrees red-brown to light brown; brucine, intense blood-red, gradually fading to the original colour; cinchonine, an insignificant orange, slowly turning greenish; cocaine, orange; codeine, greenish brown, gradually darkening, finally brown; colchicine, green, then brownish green, and finally coffee-colour; coniïne, intense green, gradually becoming browner; digitaline, intense dark brown with a reddish cast, finally a quite dark brown; quinidine, an unimportant bluish green; quinine, faint orange, then bluish green, and lastly greenish brown; caffeine, no reaction; morphine, brown, like digitaline; narceine, brown, passing into dirty blue violet with a brownish cast, then gradually becoming reddish brown; narcotine, intense blood-red with a carmine cast; nicotine, slightly darker, the original colour soon returning; papaverine, violet with a brownish cast (similar to the veratrine reaction) becoming gradually bluish green, and lastly orange yellow; picrotoxine, slightly darker, fragments of the dry substance are coloured an intense orange; pilocarpine, light orange; piperine, intense red-brown to black-brown, fragments of the dry base touched with the reagent turn black; physostigmine, greenish yellow, then crimson, lastly yellowish brown; salicylic acid, brownish green, gradually darkening; antifebrine, crimson, then brown; antipyrine, intense green-blue, turning more to a blue; kairine, dirty rose colour, then dirty light brown, and finally dirty greenish brown; santonine, no action; solanine, coffee brown, the drop becoming crimson at the edge, yellow within and dirty green at the centre; after about two hours the drop becomes a dark blue gelatinous mass; strychnine, violet blue, turning to red violet, carmine red, and lastly a splendid a fire red. If dry strychnine is touched with the reagent it takes a fine violet blue; veratrine, red-brown, then dark violet red.—*Chemiker Zeitung.*

MEETINGS FOR THE WEEK

Monday, 11th.—Medical 8.30.
—— Society of Arts, 8. Cantor Lectures. "The Decoration and Illustration of Books," by Walter Crane.
Tuesday, 12th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin —II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Royal Medical and Chirurgical, 8.30.
—— Sanitary Institute, 8. "Water Supply, Drinking Water, Pollution of Water," by Dr. Louis Parkes.
Wednesday, 13th.—Society of Arts, 8. "Aluminium and its Manufacture by the Deville-Castner Process," by William Anderson, M.Inst.C.E.
—— Pharmaceutical, 8.
—— Microscopical, 8.
Thursday, 14th.—Royal, 4.30.
—— Royal Institution, 3. "The Venom of Serpents and Allied Poisons," by Sidney Martin, M.D.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
Friday, 15th.—Royal Institution, 9. "Beacon Lights and Fog Signals," by Sir James N. Douglass, F.R.S.
—— Sanitary Institute, 8. "Ventilation, Measurement of Cubic Space, &c.," by Sir Douglas Galton, F.R.S.
Saturday, 16th.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.

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ON THE

TRUE FORMULA FOR PERMANGANATES.[*]

By CHARLES M. BRADBURY, of Virginia.

(Continued from p. 117).

THE periodic system of the elements has been brought to a stage of development which places it, at least as to its main facts, in the realm of accepted truth; and it may be appealed to for the decision of many doubtful questions with great confidence in the answers given by it. Now the atomic weight of manganese is well established; and according to the Periodic Law, *i.e.*, that the chemical properties of the elements are a periodic function of their atomic weights, manganese is forced, by virtue of its atomic weight, into the group of *heptad elements*, at the same time preserving its close relationship with the metals of the iron group. This may be seen by reference to a scheme or table of the periodic system. Even this bare fact would be conclusive, unless manganese could be shown to be an exception to the periodic law. Moreover, the relationship of manganese to the halogens may be received as not by any means incredible; for the behaviour of the elements in general, when viewed in the light of this system, indicates that under the influence of varying valence elements which are commonly far from alike may develop strong similarity. We may take, as examples of this variation in character of the same element, the marked differences between the *ous* and the *ic* compounds of iron, chromium, copper, and other metals, and between the acid and basic oxides; and the evident tendency of the metals in their higher oxides to assume functions identical with those of acidic elements.

An obvious objection to the verdict of the periodic system is that it seems to leave no room for the perfectly well-established dyad, tetrad, and hexad valence of manganese in many of its compounds, but declares it simply heptad. As to this, similar objections hold with many elements. The answer for all is found either in Prof. Muir's definition of valence:[*] "The valency of an elementary atom is a number which tells the *maximum number* of monovalent atoms (*i.e.*, atoms of H, F, Cl, Br, I, or Tl), with which the given element combines to form a molecule," or, perhaps better, in the distinction made by Prof. Richter[†] between hydrogen valence and halogen or oxygen valence; or, finally, what amounts to the same thing, in the difference between true valence and the "index of affinity,"[‡] deduced from consideration of the highest oxides. The first of these explanations is simple and, I believe, applicable in every case, but it seems likely that the others must also be reckoned with in interpreting the indications of the periodic system. However this may be, it is clear that we may either limit the meaning of "valence," as Muir does, in which case no room remains for any law whatever about variable valences, or we may use Richter's or Meyer's distinction between "hydrogen" or "real valence," subject to the law of variation by twos only, and "oxygen or halogen valence," or "index of affinity." In either case the impossibility of supposing that manganese can display an odd number of atomicities can no longer be alleged.

If, then, we assume that the valence of the manganese in permanganates is identical with that displayed in the highest oxide, Mn_2O_7 (this being, like that of the halogens in their highest oxides, heptad[§]), the chief objections to the formula $\overset{\text{I}}{R}MnO_4$—that it violates the law of even numbers, and that it does not correspond to any structural formula—disappear at once. If we represent manganese heptoxide as—

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[*] Dissertation presented to the Faculty of the University of Virginia in application for the degree of Doctor of Philosophy. *Thesis*:—Permanganic acid is monobasic, and the permanganates are represented by the general formula $\overset{n}{R}(MnO_4)n$.

[*] "Principles of Chemistry," 122.

[†] "Inorganic Chemistry," 164.

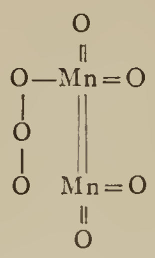
[‡] Lothar Meyer. See R. and S., II., ii., 511.

[§] R. and S., II., ii., 512.

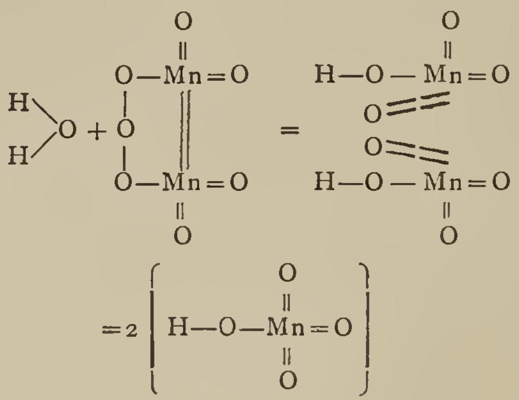
THE PERIODIC SYSTEM.

The following table is from Richter's "Inorganic Chemistry," except that the atomic weight of titanium (48) has been supplied from Roscoe and Schorlemmer's "Treatise."

		I. Group.	II. Group.	III. Group.	IV. Group.	V. Group.	VI. Group.	VII. Group.	VIII. Group.		
H Compounds.		—	—	—	MH_4	MH_3	MH_2	MH			M_2H
Highest salt-forming oxides.		M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	MO_3	MO_2	MO
Periods.	Series.	H 1									
1st	1st	Li 7	Be 9	B 11	C 12	N 14	O 16	Fl 19			
2nd	2nd	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35			
3rd	3rd	K 39	Ca 40	Sc 45	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 58	Ni 58
	4th	Cu 63	Zn 65	Ga 70	— 73	As 75	Se 79	Br 80			
4th	5th	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	— 100	Ru 104	Rh 104	Pd 106
	6th	Ag 108	Cd 112	In 113	Sn 118	Sb 122	Te 126	I 127			
5th	7th	Cs 132	Ba 137	La 139	Ce 140 Di 144	—	—	—	—	—	—
	8th	—	—	—	—	—	—	—			
	9th	—	—	Yb 173	—	Ta 182	W 184	—	Os 193	Ir 193	Pt 196
	10th	Au 197	Hg 200	Tl 204	Pb 206	Bi 210	—	—			
		—	—	—	Th 234	—	M 240	—			



(which suggests that loose union, which really exists, of a portion of the oxygen), then, upon contact with water,



or $H_2O + Mn_2O_7 = 2HMnO_4$, and similarly for K_2O, Na_2O, &c.

(To be continued).

MAGNETIC VISCOSITY.

By THOMAS T. P. BRUCE WARREN.

When experimenting on the magnetic permeability of oils and other liquids I found that if a magnetic substance, like soft iron, be covered by different liquids not only was its susceptibility modified by the permeability of the intervening medium, but distinct evidence was obtained in every case of a molecular stress being produced in the medium, and which indicated itself by a decided tendency of a balanced magnet to stick, as it were, when it was allowed to remain a short time over the soft iron.

The explanation seems to be that the maximum effect of a magnet on soft iron depends on the rapidity with which the medium accommodates itself to the constrained condition necessary for the soft iron to take its greatest degree of magnetisation.

As time is an element of importance in attaining a full maximum magnetisation from any magnet of a certain intensity, it is not unreasonable to suppose that when a *non*-magnetic medium has been so constrained by the lines of force passing through it that the molecular stress, which is also favourable to an increased magnetisation of the soft iron, will retain the magnet with a slight but decided extra force. I propose to call this extra force, which is due to molecular stress, *viscosity*.

Viscosity is more probably a function of permeability. We have the magnet acting across the medium to the soft iron, and conversely, the soft iron reacting through the same medium to the magnet, until the molecular arrangement of the medium accommodates itself to a maximum.

If a galvanometer needle, suspended in the usual way, be forcibly deflected by a current, it is found that the needle regains its fiducial position very slowly; this has been attributed to a crushing effect on the fibres. This effect has been called viscosity. I do not think it is entirely due to mechanical causes. The term as used in this communication is applied to a very similar phenomenon.

The experimental arrangement was as follows:—A balanced horseshoe magnet was suspended from one of the arms of a balance. Immediately under the magnet was placed a shallow specimen glass (salvers) with the usual flat glass cover. The cover prevented the magnet being wetted with the liquid, and allowed the attraction to be balanced through a uniform depth of liquid. The soft iron rested on the bottom of the glass.

When the magnet was allowed to rest on the cover for a short time, it required an increased weight being placed in the other pan to pull the magnet off, than when the magnet was momentarily in the same position, or only for so long as to restore equilibrium in the balance.

I propose giving some experimental results on a future occasion, and to point out its importance as an adjunct to analytical research.

PHOTOGRAPHIC MAP OF THE NORMAL SOLAR SPECTRUM.

(Second Series).

Made by Professor H. A. ROWLAND.

A new and greatly improved edition of this map, extending from the extreme ultra violet down to and including B to wave length 6950, is now ready. The old map, published in 1886, was made by means of a grating ruled on the old dividing engine, which was originally intended for only small gratings, and at a time when Professor Rowland's knowledge of photography was limited. Furthermore, it was not printed in a sufficiently careful manner, and the negatives, which were originally none too good, soon became broken or defaced, so that many of the prints, especially the later ones, were not satisfactory.

The whole work has now been gone over again. A new dividing engine to rule large gratings has been constructed and has proved to be superior in every way to the old one, although the old one is almost equal to it for small size gratings. It has been placed in the vault of the new physical laboratory, where an almost constant temperature is maintained. Several concave gratings of 6 inches diameter and 21½ feet radius have been ruled with 10,000 or 20,000 lines to the inch, giving definition hitherto undreamed of. These have been mounted in the best possible manner. The laboratory contains rooms for developing, making emulsions and dry plates, complete enlarging apparatus, and, indeed, every facility for photographic work on the spectrum of the sun, and a large steam engine, a variety of dynamos, continuous and alternating current, with Ruhmkorff coils of all kinds, one of which latter will melt down iron wire larger than $\frac{1}{18}$ inch diameter in the secondary circuit, give means of future investigation on the spectrum of the elements. Professor Rowland has devoted years to the making of dry plates, simple and orthochromatic, and is thus better prepared than before for the work of making the map. He has also revised his list of standard wave lengths and extended them into the ultra violet, and has placed the scale upon the photographs with greater care than before. The printing is carried on in Baltimore, where it is under the immediate supervision of Professor Rowland.

The negatives have been made on thick French plate-glass and the prints are much more artistic than the old ones. The definition is not only much finer throughout, but the prints are much more uniform and have fewer spots.

The process of making this map is the same as that used for the old one, and is based on the property of the concave grating as discovered by Professor Rowland: this property is that the spectrum, as photographed in any given order, is normal and of the same scale throughout. The focus remains automatically adjusted, so that one has only to move the instrument to the part of the spectrum required, absorb the overlying spectra, and put in the photographic plate. The negatives enlarged have been selected from many hundreds taken from different gratings, though three gratings were finally selected for the work. The negatives from any given order of spectrum are measured from one standard line to another on a dividing engine, so that the constant of the dividing engine is known. The scale is then made by ruling on a piece of French plate-glass having a coating of blackened collodio-chloride. The negatives are then clamped to the scale firmly, after being adjusted into position by the standards. They are then put in the enlarging apparatus and the whole enlarged from 2½ to possibly 4 times, so as to make the scale of the map about three times that of Angström's map. The positives thus made are then figured, and negatives made from them by contact.

In the negatives so far examined the scale has been placed within less than $\frac{1}{20}$ Angström division or $\frac{1}{100000}$ wave length of its true position.

As to the definition, much is lost in the enlargement, not so much from want of definition in the enlarging lens, a 25 × 21 inch Dallmeyer rapid rectilinear, as from the radical defect of phogographic processes: for when one brings out the fine doubles in which the streak of light in the centre is very faint, he loses many of the fainter lines. The original negatives show E, and even finer lines like that at wave lengths 5276·1 and 5914·3 plainly double, but there is little hope of showing this on the map.

The atmospheric line just outside of one of the D lines also nearly merges into it, although in the original negative it is widely sundered from it.

However, there are few instruments which will show more of the spectrum than can be found on the map, even below the D line where cyanine and chlorophyll plates had to be used, for the first line in B is shown widely triple. Above, and including the D line, the definition rapidly improves, and a low power magnifier must be used to bring out the full definition. However, from wave lengths 5300 to 3800 the superiority over the old edition is not so marked as above and below this. In the ultra violet above H there is an immense improvement in the new, both in definition and in the quality of the photograph.

As to comparison with other maps of the spectrum made by measurement and drawing, it may be said that no comparison is possible. The photograph is the work of the sunlight itself and the user of this map has the solar spectrum itself, before him, and not a distorted drawing full of errors of wave length and of intensity. The superiority is so great that there is no possibility for comparison.

The following is a list of the plates, each 3 × 2 feet, containing two strips of the spectrum.

a	includes from wave length	?	to 3350
b	,, ,, ,, ,,	3270	,, 3730
c	,, ,, ,, ,,	3670	,, 4130
d	,, ,, ,, ,,	4050	,, 4550
e	,, ,, ,, ,,	4450	,, 4950
f	,, ,, ,, ,,	4850	,, 5350
g	,, ,, ,, ,,	5250	,, 5750
h	,, ,, ,, ,,	5650	,, 6150
i	,, ,, ,, ,,	6050	,, 6550
	,, ,, ,, ,,	6450	,, 6950

Negatives b, c, d, e, f, g, h, i, j, are now ready, although that for i is too irregular to be entirely satisfactory and it may be replaced. The plate a to the extremity of the solar spectrum will be attempted this summer, but may cause much trouble and delay, and will be sold as an extra plate. The prints are on heavy albumen paper mounted on cloth.

The cost of printing has been so much increased that the prices for this new series will be greater than for the old one, but scarcely more than covers the cost of the printing.

The plates will be delivered in Baltimore or New York or will be sent by express or mail, securely packed, at the charge and risk of the purchaser, at the following net prices:—

Set of nine plates, wave length 3270 to 6950, 18 00 dols.
Single plates, ... 2 50 ,,

Should any extra plates continuing the spectrum in either direction be published, subscribers can have them at 2.00 dols. each.

Subscribers to the old edition will have the preference in the delivery of the new one and a reduction of 10 per cent in the price. The three plates h, i, j, to complete their set, will be furnished for 6.00 dols. They are advised to take g also, as the old map of that region was bad. The four, g, h, i, j, will be furnished to them for 8.00 dols.

Extra Plates.

Two plates, each 3 × 2 feet, suitable for framing and hanging on the wall, have been made of the B and D lines. The latter are 3 inches apart, and the former has an extent of about 24 inches. Enlargements of some of the carbon bands from the arc electric light have also been made. They show the wonderful structure of these bands, each containing many hundred lines, each one of which is a close double or, in some cases, a triple. These plates will be sold for 2.25 dols. unmounted, or 2.50 dols. mounted on cloth.

No plate will be given away or sent in exchange.

Remittances may be made by draft or money order. All subscriptions and orders should be sent and remittances made to the

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Baltimore, Md., February, 1889.

ANALYSES OF WATERS OF THE YELLOWSTONE NATIONAL PARK,

With an Account of the Methods of Analysis Employed.*

(Continued from p. 115).

By FRANK AUSTIN GOOCH
and JAMES EDWARD WHITFIELD.

Carbonic Acid.—The greater number of the waters with which we have had to deal were hot when the sample was taken, and not surcharged with carbonic acid. In view of the circumstances under which the waters were collected it was thought that a portion of the general sample, which was carefully sealed, might be made to serve the purpose of determining the carbonic acid contained in the water, instead of portions taken specially for that end and treated in the field with a mixture of ammonia and calcium chloride to fix the carbonic acid gas. Accordingly, dependence was placed upon the large general sample for this estimation. The presence of free silica in the waters, and the complexity of composition, place so great an obstacle in the way of determining the *free carbonic acid* that the attempt to make the estimation was not undertaken. The method which we adopted for the determination of the *total carbonic acid* is that well-known process which rests upon the boiling of the acidified liquid, and the absorption and weighing of the gas evolved. The apparatus which we employed, differing somewhat from that in ordinary use for this purpose, is shown in Fig. 1. It consisted eseentially of a flask in which to boil the water, a cooler to return the condensed steam to the flask, a U-tube filled with anhydrous cupric sulphate to intercept traces of hydrochloric acid, which might escape condensation in the cooler, a second U-tube charged with calcium chloride to dry the gas, potash bulbs to retain the carbonic acid, and two tubes filled with calcium chloride, one of which was to retain the moisture carried over from the potash bulbs and was weighed with them, the other serving to protect the weighed tube from the action of the external

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* *Bulletin of the United States Geological Survey*, No. 47.

air. Through the rubber stopper of the flask passed the tube of a separating funnel, the end of a condensing tube, and a tube which connected the interior of the flask with the system of bottles and scrubbing tower, which furnished at will and under slight pressure a supply of dry air free from carbonic acid.

Before beginning the operation of determining the carbonic acid in a water, the atmospheric air was expelled from the apparatus and replaced by pure air free from carbonic acid. The stop-cock in the funnel tube and the connection with the aspirator having been closed, the water started through the cooler, and the joint broken between the potash bulbs and the drying tube immediately preceding it, a few c.c. of distilled water were put into the flask and boiled. The steam generated drove the air from the flask, and that remaining in the tubes was swept forward by pure air admitted from the aspirator. The outer opening of the tube at the end of the line was closed, the source of heat removed, and the flask allowed to fill with air from the aspirator. The whole apparatus having been filled thus with air free from carbonic acid, the water to be examined—we found 200 g. to be a convenient amount—was introduced into the flask through the funnel tube and followed by a little boiled water and a sufficiency of sulphuric acid, care being taken to exclude the outer air during the operation. The connection between the line of drying tubes and the absorption bulbs was re-established, the liquid in the flask was brought to the boiling-point, and to secure constant and quiet ebullition as well as to aid in transferring the carbonic acid from the flask to the absorption bulbs, a current of pure air was sent slowly through the boiling liquid, which covered the end of the aspirating tube and that of the funnel tube. At the end of half an hour the burner was removed from under the flask and the apparatus was permitted to cool during another half hour, the current of air being kept in motion through it. The difference between the weights of the potash bulbs, with the drying tube which accompanies them, before and after the operation, was taken to be the weight of carbonic acid absorbed, and the *total carbonic acid* of the portion of water examined.

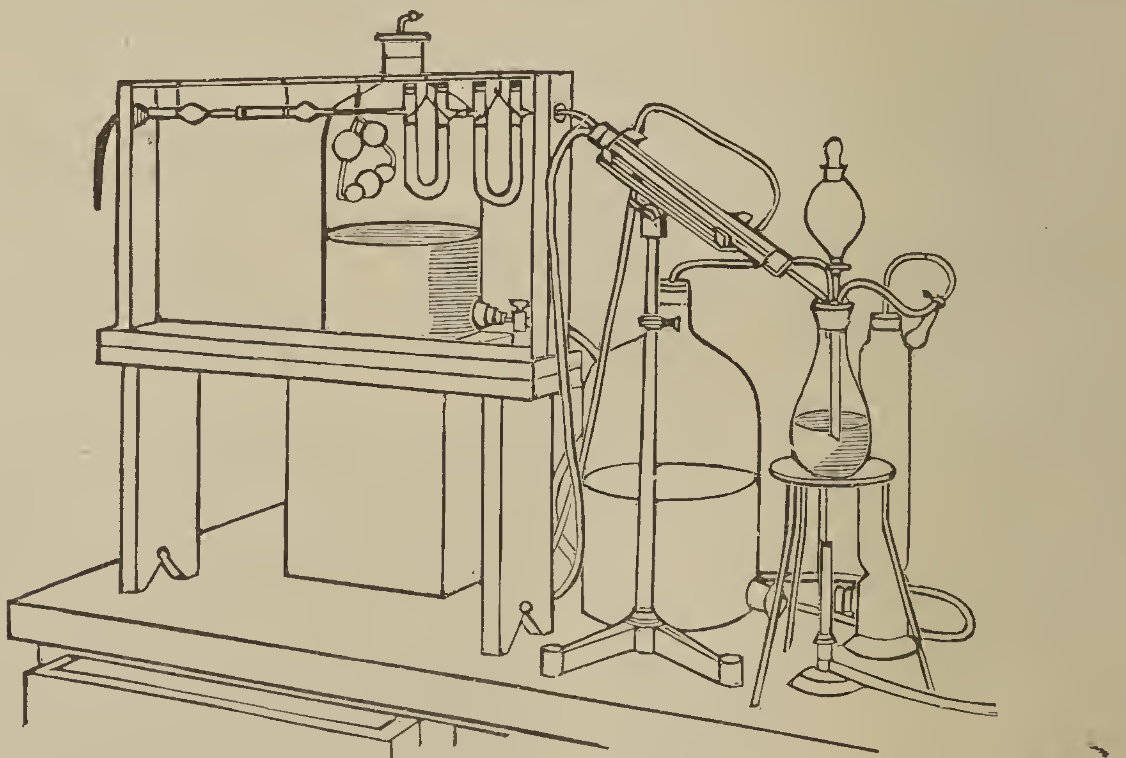

Fig. 1.—Apparatus for the Estimation of Carbonic Acid.

When the water under examination contained hydrogen sulphide, a little cupric sulphate was introduced before acidifying into the portion which was serve for the determination of carbonic acid.

Arsenious Acid and Boric Acid.—To the portion taken for analysis—usually 500 g.—hydrochloric acid was added in distinct excess, the temperature of the liquid was raised to 70° C., and the source of heat having been removed, hydrogen sulphide gas was introduced in a gentle current for several hours. The precipitation of the arsenious sulphide began at once, but the action of the precipitant was continued to insure completeness. The precipitate was collected upon an asbestos felt, washed, and dissolved in fuming nitric acid. The solution in nitric acid was evaporated to dryness, the residue was dissolved in hydrochloric acid, and from this solution, made strongly ammoniacal, but kept small in volume, the arsenic was precipitated by the addition of the magnesium chloride mixture and brisk agitation. The precipitated ammonium-magnesium arsenate was allowed twelve hours in which to settle, and was then transferred by means of the mother liquor without the use of other liquid to a perforated crucible carrying an asbestos felt, washed thoroughly with the mixture of one part of ammonia to three of water, usually employed for this purpose, but with the sparing use of the washing material which this mode of filtration permits, dried carefully, ignited gently at first, and at a low red heat afterwards, in an atmosphere of oxygen

The great faults of this process, originally Levol's, have been the solubility of the precipitate in the mother liquor, and more especially in the ammoniacal wash water, and the difficulty in drying or igniting the precipitate collected on paper. These sources of inaccuracy vanish, however, so completely with the use of the asbestos filter, and due care in keeping the volume of mother liquor and the washings small, that the filtrate, freed from ammonia, acidified and charged with hydrogen sulphide, fails to yield arsenious sulphide. As a test for the presence of arsenic, the method has enjoyed an excellent reputation, and in the form in which we have made use of it we believe it to be exact.

The filtrate from the precipitate of arsenious sulphide, containing all the boric acid, was nearly freed from hydrogen sulphide by the transmission of air, and the chlorine, with residual traces of hydrogen sulphide, was removed by treatment with silver nitrate and filtration.

The filtrate from the precipitated sulphide and chloride was treated with sodium hydrate in quantity, a little more than sufficient to precipitate the excess of silver as completely as may be. The whole was evaporated until the precipitate took on a compact and granular form, then filtered, and the filtrate was evaporated nearly to dryness. The residue was treated with nitric acid, first just to acidify, and then with a sufficient (measured) amount to make it certain that the boric acid was entirely free. The concentrated solution of the nitrates, nitric acid, and boric acid was drenched with methyl alcohol to precipitate the first and dissolve the last. The solution of boric acid was quickly separated from the precipitate by means of the vacuum filter, and the residue washed sufficiently with methyl alcohol. When much boric acid is present the precipitated nitrates should be dissolved in water, and the process of precipitation with methyl alcohol repeated; but when small quantities are dealt with, as was the case in the most of our work upon these waters, a single treatment leaves no boric acid in the residue. From the solution in methyl alcohol, the boric acid was separated and its amount estimated by a method devised by one of us and described elsewhere in full.*

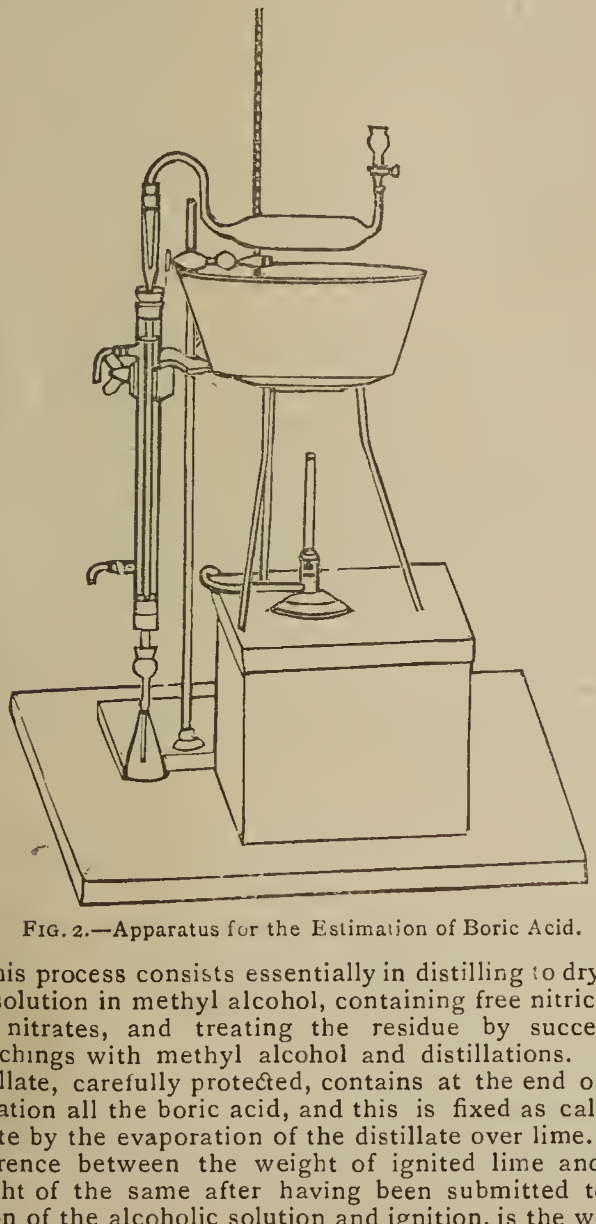

Fig. 2.—Apparatus for the Estimation of Boric Acid.

This process consists essentially in distilling to dryness the solution in methyl alcohol, containing free nitric acid and nitrates, and treating the residue by successive drenchings with methyl alcohol and distillations. The distillate, carefully protected, contains at the end of the operation all the boric acid, and this is fixed as calcium borate by the evaporation of the distillate over lime. The difference between the weight of ignited lime and the weight of the same after having been submitted to the action of the alcoholic solution and ignition, is the weight of boric anhydride in the solution.

The distillation was effected by means of an apparatus which consists of retort, condenser, and bath for heating (Fig. 2). For the last a bath of paraffin is on the whole most convenient. The condenser is set vertically to facilitate changing the level of the retort within the bath, and to secure at the same time continued and thorough washing of the tube by its own condensations. The retort, somewhat like the well-known drying tube of Liebig in general shape, is easily made of a pipette by bending the tube at one end to a right angle, at the other to a goose-neck, as shown. To the former end is fitted, by a rubber stopper or section of tubing, a glass funnel tube provided with a stop-cock; the end of the goose-neck passes tightly through a rubber stopper in the upper end of the condensing tube. This is essentially the apparatus; but it is convenient to attach, to receive the distillate, a small Erlenmeyer flask, which moves with the condenser and is joined to it, in the manner indicated in the figure, by means of a thistle-tube and a rubber stopper grooved to permit the free passage of air. In carrying out the distillation the liquid is introduced into the retort either by the funnel tube or previous to its insertion, the glass stop-cock is closed, the water started through the condenser, and the retort lowered into the hot paraffin, care being taken to begin the operation with the retort not more than half full, and so inclined that only the rear dips below the surface of the bath. If the precaution to heat the retort at the start in this manner be overlooked it may sometimes happen that the sudden and violent expulsion of air through the liquid will carry portions of it bodily into the goose-neck, and even into the condenser. With this point considered, the remainder of the operation presents no difficulty and requires little care. The size of the retort may be suited, of course, to the particular case in hand, but for most purposes a pipette of 200 c.m.^{3} capacity makes a retort of convenient dimensions, neither too large for the distillation of small charges nor too small to permit the treatment of 100 c.m.^{3} of liquid comfortably. The tube of the goose-neck should be wide enough to prevent the formation of bubbles in it; 0·7 c.m. is a good measure for the interior diameter. It is of advantage to heat the bath to a point considerably above the temperature at which the liquid to be distilled boils—something between 130° C. and 140° C. does very well for water, and is not too high for methyl alcohol—and under such circumstances, and when the retort is entirely submerged, it often happens that evaporation takes place with extreme rapidity from the surface of the liquid in perfect quiet and without actual boiling.

Experiment showed that six successive treatments by drenching with 10 c.m.^{3} of methyl alcohol and distillation to dryness were more than adequate to remove 0·2 grm. of boric anhydride entirely from a residue containing 2 grms. of sodium nitrate; but, in order to break up the crusted residue, which by its insolubility in the alcohol might effect to some extent the protection of the boric acid from the action of the alcohol, it was found best to introduce and evaporate 2 c.m.^{3} of water between the second and third, and again between the fourth and fifth distillations. In most of the cases with which we were concerned in the work upon these waters, four treatments by drenching and distilling, with one intermediate moistening with water, were entirely sufficient to volatilise the boric acid; but in every case the residue was examined for boric acid by the exceedingly delicate turmeric test, taking care to first oxidise nitrites by means of bromine, and to expel the last before applying the test.

When the solution of boric acid in methyl alcohol is put over lime and evaporated at once some volatilisation of the boric acid is apt to take place; but a short period of digestion—from five to fifteen minutes—is sufficient to fix the boric acid completely.

To secure the proper exposure before evaporation, with the least delay, the lime which is to retain the boric acid, first ignited in the crucible in which the evaporation is to be made subsequently, is transferred to the receiving flask attached to the condenser before the distillation is begun, and so has opportunity to exert its action upon the boric acid as the distillation progresses. At the end

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* *Bulletin of the United States Geological Survey*, No. 42. *Am Chem. Journ.*, vol. ix., p. 23.

of the distillation the distillate containing the alcohol, boric acid, nitric acid, and lime, is transferred again to the crucible, evaporated to dryness at a very gentle heat, and ignited to a constant weight over the blast-lamp. The greatest care is to be taken to secure similarity of conditions under which the crucible and lime are weighed before and after ignition, and definite periods of cooling before weighing—ten minutes is a suitable time—should be allowed to pass, in order to eliminate, as far as possible, the effect of atmospheric condensation upon the large surface of platinum.

The tendency of the process is to yield figures slightly larger than the truth, as was shown in the test analyses which are given in the full description of the process, to which reference has been made. In distilling 0·2 grm. of boric anhydride and fixing it in 1·5 grms. of calcium oxide, the mean error was shown to be about 0·0010 + grm. In the work upon the waters parallel determinations rarely differed by more than that amount.

Chlorine (*with Bromine and Iodine*).—The precipitation of chlorine, together with bromine and iodine, was usually effected without difficulty by treating the weighed portion of water—from 100 g. to 500 g., according to the circumstances—with nitric acid to a slightly acid reaction and silver nitrate in excess, directly and in the usual manner, excepting that the operation was effected in the cold, and that the whole was allowed to stand quietly in the dark for several hours to secure perfect subsidence of the precipitate. In only one or two cases did the silica, which the waters carry abundantly, give rise to trouble in the precipitation. In such cases comparative tests were made as just described upon portions treated previously with an excess of pure sodium hydrate, it having been noticed that certain very siliceous waters, which of themselves very quickly filled the pores of the filter with an invisible coating of silica, could be made to filter with rapidity by first treating them with sodium hydrate in excess, and then with nitric acid to slight acidity. Treatment with acid alone did not bring about the desired condition of the silica. In the case of the water of the Coral Spring the proportion of silica is so great and its character such that to secure satisfactory results we were obliged to convert the silica to hydrofluosilicic acid by the addition of hydrofluoric acid and nitric acid before precipitating the silver salt. The silver chloride (including the bromide and iodide) was collected upon asbestos in a perforated crucible, dried directly over the free flame of a Bunsen burner turned very low and at a temperature below its melting-point, and weighed. In the case of waters containing hydrogen sulphide in quantity precipitable by silver nitrate, the portion for analysis was rendered ammoniacal before the addition of the silver salt, and the precipitated silver sulphide was filtered off. The silver salts of the halogens were then precipitated from the filtrate by nitric acid, and the process was completed as described.

(To be continued).

THE ANALYSIS OF SUBSTANCES CONTAINING ALUMINA, LIME, AND MAGNESIA.

By L. BLUM.

The author some time ago pointed out the differences which may occur in the precipitation by ammonia of a mixture containing alumina, ferric oxide, and phosphoric acid. To avoid these irregularities he recommended to effect the precipitation with a slight excess of ammonia, and not to expel it by prolonged boiling, since it is not easy to hit the exact moment when all superfluous ammonia is expelled without an incipient splitting up of the ammonium chloride present into ammonia and hydrochloric acid. This opinion ran counter to the well-known fact that lime and magnesia can be perfectly separated from alumina and ferric oxide only by prolonged ebullition in presence of ammonium chloride. In accurate analyses R. Fresenius even recommends a repeated precipitation to effect complete separation. The author also has always found small quantities of lime in precipitates which had been re-dissolved. He therefore sought to determine the effect of the method of precipitation which he recommends upon the separation of the lime and the magnesia. He therefore instituted two series of experiments, in one of which (A) are given the results of a single precipitation with ammonia, and in the other (B) the results of a twofold precipitation. The proportion of alumina and ferric oxide in B was smaller than in A, as it was to be expected, but the lime also decreased simultaneously. In the precipitate obtained by the twice repeated action of ammonia, lime and magnesia were entirely absent. The lime carried down by ammonia in the first precipitation is in the mean 0·26 per cent. But this difference is small in comparison with that which may be produced by a prolonged boiling of the precipitated solution. If the excess of ammonia added is considerable, a repeated precipitation involved a total loss of 0·39 per cent. Special experiments proved that the decrease of lime could not be due to a solubility of calcium oxalate in water containing ammonium chloride. The chief part of the mean loss of 0·39 per cent comes upon the magnesia, though the results in Series B are rather higher than in Series A. When the precipitation of the alumina is repeated it is absolutely necessary, as Fresenius recommends, to evaporate the filtrate from the calcium oxalate to dryness and ignite the residue in order to expel the ammoniacal salts.

C. Meinecke, in a paper in the *Zeitschrift fur Angewandte Chemie*, has since found that in a single precipitation with ammonia and without boiling a complete separation of alumina and ferric oxide from lime and magnesia is not practicable. He finds that without such boiling his precipitate contained 0·72 per cent of lime and magnesia. The author, on the contrary, finds a difference in the alumina of 2·99 per cent. This he considers a proof of the correctness of his assumption that on prolonged boiling the ammonium chloride is decomposed, and re-dissolves a part of the precipitate.

Meinecke doubts this, but he concedes that on prolonged boiling the precipitated hydroxides may be converted into basic salts. Elsewhere he says that on washing a precipitate consisting of basic salts, even with warm water, they are partly decomposed, and colour the water yellow. The author's assertion that a prolonged boiling causes an error in deficiency is therefore not affected.—*Zeitschrift fur Analytische Chemie.*

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

(Continued from p. 113).

Method for the Analysis of Fermented Liquors.

A commission of experts, appointed in the year 1884 by the Chancellor of the Empire, to which was entrusted the establishment of uniform methods for the chemical investigation of wine, adopted the following resolutions, which were made public by the Prussian Minister for Commerce and Trade by a decree of the 12th August, 1884, which provides that they shall be rigidly adhered to in public institutions for the examination of food-stuffs,

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* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

and are recommended to the representatives of like private concerns :—

Resolutions of the Commission for Establishing Uniform Methods for the Analysis of Wines.*

Since, in consequence of improper manner of taking, keeping, and sending in of samples of wine for investigation by the authorities, a decomposition or change in the latter often occurs, the commission consider it advisable to give the following instructions :—

Instructions for Sampling, Preserving, and Sending in of Samples of Wine for Examination by the Authorities.

1. Of each sample, at least one bottle ($\frac{3}{4}$-litre), as well filled as possible, must be taken.

2. The bottles and corks used must be perfectly clean; the best are new bottles and corks. Pitchers and opaque bottles in which the presence of impurities cannot be seen are not to be used.

3. Each bottle shall be provided with a label, gummed (not tied) on, upon which shall be given the index number of the sample corresponding to a description of it.

4. The samples are to be sent to the chemical laboratory as soon as possible to avoid any chance of alteration, which, under some circumstances, can take place in a very short time. If they are, for some special reason, retained in any other place for any length of time, the bottles are to be placed in a cellar and kept lying on their sides.

5. If in samples of wine taken from any business concern adulteration is shown, a bottle of the water is to be taken which was presumably used in the adulteration.

6. It is advisable, in many cases necessary, that, together with the wine, a copy of these resolutions be sent to the chemist.

A.—*Analytical Methods.*

Specific Gravity.—In this determination use is to be made of a picnometer, or a Westphal balance controlled by a picnometer. Temperature, 15° C.

Alcohol.—The alcohol is estimated in 50 to 100 c.c. of the wine by the distillation method. The amount of alcohol is to be given in the following way :—In 100 c.c. wine at 15° C. are contained *n* grms. alcohol. For the calculation the tables of Baumhauer or Hebner are used. (The amounts of all the other constituents are also to be given in this way; in 100 c.c. wine at 15° C. are contained *n* grms.).

Extract.—For this estimation 50 c.c. of wine, measured out at 15° C., are evaporated on the water-bath in a platinum dish (85 m.m. in diameter, 20 m.m. in height, and 75 c.c. capacity, weight about 20 grms.), and the residue heated for two and one-half hours in a water-jacket. Of wines rich in sugar (that is, wines containing over 0·5 grm. of sugar in 100 c.c.) a smaller quantity, with corresponding dilution, is taken, so that 1 or at the most 1·5 grms. extract are weighed.

Glycerin.—One hundred c.c. of wine (for sweet wines see further on) are evaporated in a roomy, not too shallow, porcelain dish to about 10 c.c., a little sand added, and milk of lime to a strong alkaline reaction, and the whole brought nearly to dryness. The residue is extracted with 50 c.c. of 96 per cent alcohol on the water-bath, with frequent stirring. The solution is poured off through a filter, and the residue exhausted by treatment with small quantities of alcohol. For this 50 to 100 c.c. are generally sufficient, so that the entire filtrate measures 100 to 200 c.c. The alcoholic solution is evaporated on the water-bath to a syrupy consistence. (The principal part of the alcohol may be distilled off if desired). The residue is taken up by 10 c.c. of absolute alcohol, mixed in a stoppered flask with 15 c.c. of ether and allowed to stand until clear, when the clear liquid is poured off into a glass-stoppered weighing-glass, filtering the last portions of the solution. The solution is then evaporated in the weighing-glass until the residue no longer flows readily, after which it is dried an hour longer in a water-jacket. After cooling it is weighed.

In the case of sweet wines (over 0·5 grm. sugar in 100 c.c.) 50 c.c. are taken in a good-sized flask, some sand added, and a sufficient quantity of powdered slack lime, and heated with frequent shaking in the water-bath. After cooling 100 c.c. of 96 per cent alcohol are added, the precipitate which forms allowed to separate, the solution filtered, and the residue washed with alcohol of the same strength. The alcoholic solution is evaporated and the residue treated as above.

Free Acids (total quantity of the acid reacting constituents of the wine).—These are to be estimated with a sufficiently dilute normal solution of alkali (at least one-third normal alkali) in 10 to 20 c.c. wine. If one-tenth normal alkali is used at least 10 c.c. of wine should be taken for titration; if one-third normal, 20 c.c. of wine. The drop method (*Tupfel methode*), with delicate reagent-paper, is recommended for the establishment of the neutral point. Any considerable quantites of carbonic acid in the wine are to be previously removed by shaking. These "free acids" are to be reckoned and reported as tartaric acid ($C_4H_6O_6$).

Volatile Acids.—These acids are to be estimated by distillation in a current of steam, and not indirectly, and reported as acetic acid ($C_2H_4O_2$). The amount of the "fixed acids" is found by subtracting from the amount of "free acids" found, the amount of tartaric acid corresponding to the "volatile acids" found.

Bitartrate of Potash and Free Tartaric Acid.—(*a*) Quantitative detection of free tartaric acid :—20 to 30 c.c. of the wine are treated with precipitated and finely-powdered bitartrate of potash, shaken repeatedly, filtered off after an hour, and 2 to 3 drops of a 20 per cent solution of acetate of potash added to the clear filtrate, and the solution allowed to stand twelve hours. The shaking and standing of the solution must take place at as nearly as possible the same temperature. If any considerable precipitate forms during this time, free tartaric acid is present, and the estimation of it and of the bitartrate of potash may be necessary.

(*b*). Quantitative estimation of the bitartrate of potash and free tartaric acid :—In two stoppered flasks two samples of 20 c.c. of wine each are treated with 200 c.c. ether-alcohol (equal volumes), after adding to the one flask 2 to 3 drops of a 20 per cent solution of acetate of potash. The mixtures are well shaken, and allowed to stand sixteen to eighteen hours at a low temperature 0—10° C.), the precipitate filtered off, washed with ether-alcohol, and titrated. (The solution of acetate of potash must be neutral, or acid. The addition of too much acetate may cause the retention of some bitartrate in solution). It is best on the score of safety to add to the filtrate from the estimation of the total tartaric acid a further portion of 2 drops of acetate of potash, to see if a further precipitation takes place.

In special cases the following procedure of Nessler and Barth may be used as a control :—

Fifty c.c. of wine are evaporated to the consistency of a thin syrup (best with the addition of quartz sand), the residue brought into a flask by means of small washings of 96 per cent alcohol, and with continual shaking more alcohol is gradually added, until the entire quantity of alcohol is about 100 c.c. The flask and contents are corked and allowed to stand four hours in a cool place, then filtered, and the precipitate washed with 96 per cent alcohol; the filter-paper, together with the partly flocculent, partly crystalline precipitate, is returned to the flask, treated with 30 c.c. warm water, titrated after cooling, and the acidity reckoned as bitartrate. The result is sometimes too high if pectinous bodies separate out in small lumps, enclosing a small portion of free acids.

In the alcoholic filtrate the alcohol is evaporated, 0·5 c.c. of a 20 per cent potassic acetate solution added,

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* "Das Gesetz betreffend den Verkehr mit Nahrungsmittel," u.s.w., p. 184.

which has been acidified by a slight excess of acetic acid, and thus the formation of bitartrate from the free tartaric acid in the wine facilitated. The whole is now, like the first residue of evaporation, treated with (sand and) 96 per cent alcohol, and carefully brought into a flask, the volume of alcohol increased to 100 c.c., well shaken, corked, allowed to stand in a cold place four hours, filtered, the precipitate washed, dissolved in warm water, titrated, and for one equivalent of alkali two equivalents of tartaric acid are reckoned.

This method for the estimation of the free tartaric acid has the advantage over the former of being free from all errors of estimation by difference. The presence of considerable quantities of sulphates impairs the accuracy of the method.

Malic Acid, *Succinic Acid*, *Citric Acid.*—Methods for the separation and estimation of these acids cannot be recommended at the present time.

Salicylic Acid.—For the detection of this, 100 c.c. of wine are repeatedly shaken out with chloroform, the latter evaporated, and the aqueous solution of the residue tested with very dilute solution of ferric chloride. For the approximately quantitative determination it is sufficient to weigh the chloroform residue, after it has been again recrystallised from chloroform.

Colouring Matter.—Red wines are always to be tested for coal-tar colours. Conclusions in regard to the presence of other foreign colouring-matters drawn from the colour of precipitates and other colour reactions are only exceptionally to be regarded as safe. In the search for coal-tar colours the shaking out of 100 c.c. of the wine with ether before and after its neutralisation with ammonia is recommended. The ethereal solutions are to be tested separately.

Tannin.—In case a quantitative determination of tannin (or tannin and colouring-matter) appears necessary, the permanganate method of Neubauer is to be employed. As a rule the following estimation of the amount of tannin will suffice:—The free acids are neutralised to within 0·5 grm. in 100 c.c. with standard alkali, if necessary. Then 1 c.c. of 40 per cent sodic acetate solution is added, and drop by drop a 10 per cent solution of ferric chloride, avoiding an excess. One drop of ferric chloride is sufficient for the precipitation of 0·05 per cent of tannin. (New wines are deprived of the carbonic acid held in solution by repeated shaking).

Sugar.—The sugar should be determined, after the addition of carbonate of soda, by means of Fehling's solution, using dilute solutions, and, in wines rich in sugar, (*i.e.*, wines containing over 0·5 grm. in 100 c.c.), with observance of Soxhlet's modifications, and calculated as grape sugar. Highly coloured wines are to be decolourised with animal charcoal if their content of sugar is low, and with acetate of lead and sodium carbonate if it is high.

If the polarisation indicates the presence of cane sugar (compare under polarisation) the estimation is to be repeated in the manner indicated after the inversion (heating with hydrochloric acid) of the solution. From the difference the cane sugar can be calculated.

Polarisation.—1. With white wines:—60 c.c. of wine are treated with 3 c.c. acetate of lead solution in a graduated cylinder, and the precipitate filtered off. To 30 c.c. of the filtrate ie added 1·5 c.c. of a saturated solution of sodic carbonate, filtered again, and the filtrate polarised. This gives a dilution of 10 : 11, which must be allowed for.

2. With red wines:—60 c.c. wines are treated with 6 c.c. acetate of lead, and to 30 c.c. of the filtrate 3 c.c. of the saturated solution of sodic carbonate added, filtered again, and polarised. In this way a dilution of 5 : 6 is obtained.

The above conditions are so arranged (with white and red wines) that the last filtrate suffices to fill the 220 m.m. tube of the Wild polaristrobometer, of which the capacity is about 28 c.c.

In place of the acetate of lead very small quantities of animal charcoal can be used. In this case an addition of sodic carbonate is not necessary, nor is the volume of the wine altered. If a portion of the undiluted wine 220 m.m. long shows a higher right-handed rotation than 0·3° Wild, the following procedure is necessary:—

Two hundred and ten c.c. of the wine are evaporated on the water-bath to a thin syrup, after the addition of a few drops of a 20 per cent solution of acetate of potash. To the residue is added gradually, with continual stirring, 200 c.c. of 90 per cent alcohol. The alcoholic solution, when perfectly clear, is poured off or filtered into a flask, and the alcohol distilled or evaporated off down to about 5 c.c. The residue is treated with about 15 c.c. water and a little bone-black, filtered into a graduated cylinder, and washed with water until the filtrate measures 30 c.c. If this shows on polarisation a rotation of more than +0·5° Wild, the wine contains the unfermentable matter of commercial potato sugar (amylin). If in the estimation of the sugar by Fehling's solution more than 0·3 grm. sugar in 100 c.c. was found, the original right-rotation caused by the amylin may be diminished by the left-rotating sugar; the above precipitation with alcohol is in this case to be undertaken, even when the right-rotation is less than 0·3 Wild. The sugar is, however, first fermented by the addition of a pure yeast. With very considerable content in (Fehling's solution) reducing sugar and proportionally small left-rotation, the diminishing of the left-rotation may be brought about by cane sugar or dextrin or amylin. For the detection of the first the wine is inverted by heating with hydrochloric acid (to 50 c.c. wine, 5 c.c. dilute hydrochloric acid of specific gravity 1·10), and again polarised. If the left-rotation has increased, the presence of cane sugar is demonstrated. The presence of dextrin is shown as given in the section on "gum." In case cane sugar is present, well-washed yeast, as pure as possible, should be added, and the wine polarised after fermentation is complete. The conclusions are then the same as with the wines poor in sugar.

For polarisation only large, exact instruments are to be used.

The rotation is to be calculated in degrees Wild, according to Landolt (*Zeitschr. f. Analyt. Chemie*, vii., 9):—

1° Wild = 4·6043° Soleil.
1° Soleil = 0·217189° Wild.
1° Wild = 2·89005° Ventzke.
1° Ventzke = 0·346015° Wild.

Gum (*Arabic*).—For establishing the addition of any considerable quantities of gum 4 c.c. wine are treated with 10 c.c. of 96 per cent alcohol. If gum is present the mixture becomes milky, and only clears up again after several hours. The precipitate which occurs adheres partly to the sides of the tube, and forms hard lumps. In genuine wine flakes appear after a short time, which soon settle, and remain somewhat loose. For a more exact test it is recommended to evaporate the wine to the consistency of a syrup, extract with alcohol, of the strength given above. and dissolve the insoluble residue in water. This solution is treated with some hydrochloric acid (of specific gravity 1·10) heated under pressure two hours, and the reducing power ascertained with Fehling's solution, and calculated to dextrose. In genuine wines no considerable reduction is obtained in this way. (Dextrin is to be detected in the same way).

Mannite.—As the presence of mannite in wines has been observed in a few cases, it should be considered when pointed crystals make their appearance in the extract or the glycerin.

Nitrogen.—In the estimation of nitrogen the soda-lime method is to be used.

Mineral Matters.—For this estimation 50 c.c. of wine are used. If the incineration is incomplete, the charcoal is leached with some water, and burned by itself. The solution is evaporated in the same dish, and the entire ash gently ignited.

Chlorine Estimation.—The wine is saturated with sodic carbonate, evaporated, the residue gently ignited and exhausted with water. In this solution the chlorine is to be estimated volumetrically according to Volhard, or gravimetrically. Wines whose ashes do not burn white by gentle ignition usually contain considerable quantities of chlorine (salt).

Sulphuric Acid.—This is to be estimated directly in the wine by the addition of barium chloride. The quantitative estimation of the sulphuric acid is to be carried out only in cases where the qualitative test indicates the presence of abnormally large quantities. (In the case of viscous or very muddy wines a previous clarification with Spanish earth is to be recommended).

If in a special case it is necessary to investigate whether free sulphuric acid or potassium bisulphate are present, it must be proved that more sulphuric acid is present than is necessary to form neutral salts with all the bases.

Phosphoric Acid.—In the case of wines whose ashes do not react strongly alkaline the estimation is made by evaporating the wine with sodic carbonate and potassic nitrate, the residue gently ignited and taken up with dilute nitric acid; then the molybdenum method is to be used. If the ash reacts strongly alkaline the nitric acid solution of it can be used directly for the phosphoric acid determination.

The other mineral constituents of wine (also alum) are to be determined in the ash or residue of incineration.

Sulphurous Acid.—One hundred c.c. wine are distilled in a current of carbonic acid gas after the addition of phosphoric acid. For receiving the distillate 5 c.c. of normal iodine solution are used. After the first third has distilled off, the distillate, which must still contain an excess of free iodine, is acidified with hydrochloric acid, heated, and treated with barium chloride.

Adulteration of Grape Wine with Fruit Wine.—The detection of this adulteration can only exceptionally be carried out with certainty by means of the methods that have so far been offered. Especially are all methods untrustworthy which rely upon a single reaction to distinguish grape from fruit wine; neither is it always possible to decide with certainty from the absence of tartaric acid, or from the presence of only very small quantities, that a wine is not made from grapes.

In the manufacture of artificial wine together with water the following articles are known to be sometimes used:—Alcohol (direct, or in the shape of fortified wine), cane sugar, starch sugar, and substances rich in sugar (honey), glycerin, bitartrate of potash, tartaric acid, other vegetable acids, and substances rich in such acids, salicylic acid, mineral matters, gum arabic, tannic acid, and substances rich in the same, (*e.g.*, kino, *catechu*), foreign colouring matters, various ethers and aromas.

The estimation, or rather the means of detecting the most of these substances has been given above, with the exception of the aromas and ethers, for which no method can as yet be recommended.

The following substances may be mentioned here in particular, which serve for increasing the sugar, extract, and free acid:—Dried fruit, tamarinds, St. John's bread, dates, figs.

B.—*Rules for Judging of the Purity of Wine.*

I. (*a*). Tests and determinations which are, as a rule, to be performed in judging of the purity of wines:—Extract, alcohol, sugar, free acids as a whole, free tartaric acid qualitative, sulphuric acid, total ash, polarisation, gum, foreign colouring matters in red wines. (*b*). Tests and determinations which are also to be carried out under special circumstances:—Specific gravity, volatile acids, bitartrate of potash, and free tartaric acid quantitative, succinic acid, malic acid, citric acid, salicylic acid, sulphurous acid, tannin, mannite, special ash constituents, nitrogen.

The Commission considers it desirable, in giving the estimations generally performed, to adhere to the order of succession given above, (under (*a*).

II. The Commission cannot regard it as their province to give a guide for judging of the purity of wine, but thinks it advisable, in the light of its experience, to call attention to the following points:—

Wines which are made wholly from pure grape juice very seldom contain a less quantity of extract than 1·5 grms. in 100 c.c. wine. If wines poorer in extract occur they should be condemned, unless it can be proven that natural wines of the same district and vintage occur with a similar low content of extract.

After subtracting the "fixed acids" the remaining extract (*extractrest*) in pure wines, according to previous experience, amounts to at least 1·1 grms. in 100 c.c., and after subtracting the "free acids," at least 1 grm. Wines which show less *extractrest* are to be condemned, in case it cannot be shown that natural wines of the same district and vintage contain as small an *extractrest.*

A wine which contains appreciably more ash than 10 per cent of its extract content must contain, correspondingly, more extract than would otherwise be accepted as a minimum limit. In natural wines the relation of ash to extract approaches very closely 1 to 10 parts by weight. Still, a considerable deviation from this relation does not entirely justify the conclusion that the wine is adulterated.

The amount of free tartaric acid in pure wines, according to previous experience, does not exceed one-sixth of the entire "fixed acids."

The relation between alcohol and glycerin can vary in pure wines between 100 parts by weight of alcohol to 7 parts by weight of glycerin, and 100 parts by weight of alcohol to 14 parts by weight of glycerin. In case of wines showing a different glycerin relation, an addition of alcohol or glycerin may be inferred.

As sometimes during its handling in cellars small quantities of alcohol (at most 1 per cent by volume) may find their way into wine, this fact must be borne in mind in judging of its purity.

These proportions are not always applicable to sweet wines.

For the individual ash constituents no generally applicable limits can be given. The opinion that the better kinds of wine always contain more phosphoric acid than others is unfounded.

Wines that contain less than 0·14 grm. of mineral matter in 100 c.c. are to be condemned, if it cannot be shown that natural wines of the same kind and the same vintage, which have been subject to like treatment, have an equally small content of mineral matter.

Wines which contain more than 0·05 grm. of salt in 100 c.c. are to be condemned.

Wines that contain more than 0·092 grm. sulphuric acid (SO_3) corresponding to 0·20 grm. potassic sulphate (K_2SO_4) in 100 c.c., are to be designated as wines containing too much sulphuric acid, either from the use of gypsum or in some other way.

Through various causes wines may become viscous, black, brown, cloudy, or bitter; they may otherwise change essentially in colour, taste, and odour. The colour of red wines may also separate into a solid form; still, all these phenomena in and of themselves would not justify the condemnation of the wine as not genuine.

If during the summer-time an energetic fermentation commences in a wine, this does not justify the conclusion that an addition of sugar, or substance rich in sugar, *e.g.*, honey, &c., has taken place, for the first fermentation may have been hindered in various ways, or the wine may have had an addition of a wine rich in sugar.

The methods adopted by the "Union of Bavarian Chemists" differ considerably from the above in many particulars, so they will be given also, together with the methods adopted by the same body for the examination of beer* in somewhat condensed form.

(To be continued).

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* Hilger, "Vereinbarungen u. s. w.," p. 154.

NOTICES OF BOOKS.

Report of the Commissioner of Internal Revenue for the Fiscal Year ending June 30th, 1888. Washington: Government Printing Office.

This report contains more matter of chemical interest than it might have been supposed. We have first to notice the section on methylated spirits. From experiments made, curiously enough, by the *Microscopist* to the Department, it would appear that the methylic alcohol can be extracted from methylated spirit at a profit, leaving the ethyl alcohol in such a degree of purity as to be drinkable. We are the more inclined to accept this statement, as we know that the methylated spirit supplied in this country for technical uses is not unfrequently drunk by the workman employed. In fact methyl alcohol is not a very happy agent for the "denaturation" of excisable spirit. If used in the most impure form, as Kræmer, Gerick, and Dietze suggest, it most seriously interferes with its use in a variety of manufacturing operations. We think that the German regulations are wiser in requiring not one uniform agent to be added to alcohol for whatever purpose intended, but a variety of nauseous liquids which may be used in very small quantity, such as, in certain cases, Dippel's animal oil.

A letter from the Assistant Commissioner of Inland Revenue, Canada, mentions that the methylated spirit supplied in that country contains 25 per cent of wood-spirit, and that even this mixture is furnished only under bond to varnish manufacturers and "other persons engaged in the *mechanical* (*sic* !) arts." An inferior grade, sold without bond, consists of equal parts of the two alcohols.

Considerable space is given to oleomargarine and its manufacture. This subject has been needlessly complicated in America as well as in Enrope by reports that margarine butter, even though carefully prepared, was essentially injurious. Such statements are unfounded. It even happens, especially in warm climates, that margarine may remain sound and good, while natural butter becomes utterly rancid and unfit for use. All, therefore, that it is necessary for legislatures to do in this matter is to see that margarine shall be sold under its own name only, and especially that such deceitful names as butterine should be suppressed.

In this report we find descriptions of the best known methods of distinguishing between margarine and butter—none of them so absolutely decisive as it would seem desirable. An account is also given of the legislation adopted in various countries to prevent fraud in the butter trade. A useful regulation in the Russian law is that all artificial butters shall be dyed red with alkanet, a colour well adapted for this use, seeing that it is harmless, easily soluble in oily and fatty matters, and has a very high tinctorial power. The tubs or boxes in which margarine is dispatched or kept are to be stained red. Hotels, restaurants, and all public places in which food is prepared must exhibit a notice and state in their bills of fare that the dishes prepared on the premises are cooked with margarine, if such be used in their kitchens.

Proceedings of the American Pharmaceutical Association at the Thirty-sixth Annual Meeting, held at Detroit, Michigan, September, 1888; also the Constitution, Bye-laws, and Roll of Members. Philadelphia: American Pharmaceutical Association.

Among much other interesting matter we find here a discussion on a mysterious poison or reputed poison, the "Loco Weed," dreaded as a cattle poison in Colorado, New Mexico, and Kansas. It is said that horses, cows, and sheep eating this plant are first attacked with hallucinations which render them incapable of judging of the size and distance of objects. By degrees the locoed animal loses flesh, his walk becomes feeble and unsteady, the eyes are sunken and glassy, and the coat rough and lustreless. But the whole matter is involved in doubt. Three different plants, *Astragalus mollissimus*, *A. Bigelovii*, and *Oxytropis Lamberti*, each claim to be the genuine loco. On chemical investigation of *A. mollissimus* no poisonous principle was discovered, and no toxic effects were observed when extracts of the plant were administered to frogs, dogs, cats, or to human subjects. In reply to these negative results it is remarked that the experiments should have been made not on omnivorous or carnivorous animals, but upon herbivora, when different phenomena might have been observed. We may here remark that no such experiments could be made in Britain without the difficult formality of obtaining a "vivisection" license from the Home Secretary.

Further Mr. Sayre, to whom this inquiry had been entrusted, has not been able, after three years' search and after extensive journeys in the States infested by this plant, to find any unquestionable instances of poisoning of this kind. In the few cases met with the symptoms were either quite unlike those described as due to the poison, or they were capable of being referred to some other cause.

Meantime, the belief in the dangerous nature of the loco is so general that in Colorado a law has been enacted giving a record of 1½ per cent per lb. for all weed of this kind pulled up and weighed in a dried state. About 200,000 dollars have thus been already spent. As a natural consequence the *A. mollissimus* is grown for the sake of the reward, and is sent in along with a very promiscuous lot of plants, which the officials are not able to distinguish.

A paper on "Mineral Waters" contains some revelations of decided interest. One of the Continental springs is said to produce only two million bottles yearly, whilst the sales amount to eleven millions! Further, the proprietors of these springs force artificially a large volume of carbon dioxide into the water, and between the springs and the carbonating apparatus settling vats are placed in which the ferrous salts present become peroxidised and precipitated, and salt is added, as it is alleged, for the better preservation of the water.

Cream of tartar, as sold by grocers and used in baking-powders, seems to be heavily adulterated with starch, alum, and terra-alba. Sodium sulphate is also occasionally met with. One speaker in the discussion suggested that almost half the troubles of the digestive organs might be traced to the alum introduced into the stomach.

A Dictionary of Photography for the Amateur and Professional Photographer; containing Concise and Explanatory Articles; illustrated by many Specially Prepared Diagrams. By E. J. Wall. London: Hazell, Watson, and Viney, Limited.

The great number of amateur photographers who have now become quite an important interest, affords good scope for the work before us. The author, Mr. Wall, is widely and favourably known in photographic circles, and his competence as an adviser will not be called in question. In his preface he remarks that many treatises on photography are not calculated to be fully intelligible, save to persons versed in chemistry and optics. To meet this difficulty he now issues in a collected form certain articles which have already appeared in the *Amateur Photographer*. The information given in the pages before us is remarkable for its general accuracy, and only in a few comparatively unimportant instances could it be advantageously modified. In pronouncing nitric acid "extremely poisonous" the author might usefully have added "in the undiluted state," and when recommending great care in mixing sulphuric acid with water the caution might have been given to pour the acid into the water and not the water into the acid. The method of preparing oxalic acid here given, viz., by oxidising sugar or sawdust with nitric acid, is obsolete, the action of caustic alkalies upon sawdust being now preferred. But as the photographer, be he amateur or professional, does not make his own oxalic acid, the omission is very unimportant.

The most important error which we notice is in the table of atomic weights, where platinum is given = 198 instead of 194·8, as it appears from the most recent determinations.

The table of poisons and antidotes on p. 143 is not quite trustworthy. Sodium or magnesium sulphate is safe in case of lead poisoning, but zinc sulphate is not to be advised, since, if it should not at once act as an emetic, zinc acetate would be formed in the stomach, and would prove a worse enemy than lead acetate. For potassium bichromate, magnesia and chalk would be of little use, since the magnesium and calcium chromates are not insoluble.

As proof of the extent to which photography is now practised we may mention that it has now three weekly journals, besides one monthly and two annual organs. We note also that several hotel-keepers now advertise that they have a dark room at the service of photographers.

OBITUARY.

DR. ISIDOR SOYKA.

We feel great regret in announcing the premature death of Dr. Isidor Soyka, Professor of Hygiene at the University of Prague. The deceased, who was only in his thirty-ninth year, had attained a wide and well-merited reputation by his sanitary and bacteriological studies, and especially by his bacteriological museum, in which sixty species of these microbia were shown in full activity. Prof. Soyka shot himself on February 23rd in a fit of terror at the fate of his brother, who had become insane.—*Chemiker Zeitung*.

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. cviii., No. 8, February 25, 1889.

Remarks on the Conductivity and the Manner of Electrolysis of Concentrated Solutions of Sulphuric Acid.—E. Bouty.—The author, noting a marked change about (old notations) $SO_3 + 6HO$ or $7HO$, and again about $SO_3 + 16HO$, suggests that the former limit corresponds to the disappearance of the last trace of hydrogen peroxide, *i.e.*, the complete destruction of the hydrate $SO_3 2HO$, whilst the latter limit corresponds to the disappearance of the persulphuric acid and the destruction of an unknown hydrate.

Correction Concerning the Action of Sulphurous Acid upon the Alkaline Hyposulphites.—A. Villiers.—In the *Comptes Rendus*, vol. cvi., pp. 851 and 1354, the author describes a salt obtained by the action of sulphurous acid upon sodium hyposulphite as being a salt of a new oxy-acid of sulphur. He now finds that the product consists of the sodium trithionate and the tetrathionate.

On a Salt obtained by Saturating Phosphorous Acid with an Excess of Alkali.—L. Amat.—The crystals formed are simply disodic phosphite,—

$$P(OH)(ONa)_2 + 5H_2O.$$

It appears that phosphorous acid should be regarded as a bibasic acid.

On the Valence of Aluminium.—Alphonse Combes. The author recognises aluminium as trivalent.

Compound of Mannite with the Aldehyds of the Fatty Series.—J. Meunier.—Ethylic acetal, when freed from acids, forms a perfectly white mass having a slightly bluish reflection. The mass consists of fine needles melting at 174°, but which sublimes very distinctly if kept at temperatures above 10°. Under these circumstances a very small portion is decomposed.

New Neutral and Acid Ethers of the Camphols.—A. Haller.—The author examines the neutral succinates of dextro- and lævo-camphol, the racemic succinate, and the corresponding acid compounds.

Bulletin de la Société Chimique de Paris.
Vol. li., No. 4.

New Apparatus for the Concentration of Extracts in Vacuo.—L. A. Adrian.—The apparatus cannot be intelligibly described without the two whole-page figures with which it is accompanied.

On the Use of Cold in the Preparation of Pharmaceutical Extracts.—L. A. Adrian.—The author's object is to effect the subsidence and consequent elimination of foreign or undesirable matter by exposure to low temperatures.

The Constitution and the Acetonic Function of Nitro-camphor.—P. Cazeneuve.

On a Hydrochlorate of Nitro-camphor. Formation of a Polymer by Hydratation, Camphortrinitro-triphenol. — P. Cazeneuve. — These two papers do not admit of useful abstraction.

Justus Liebig's Annalen der Chemie.
Vol. ccl., Parts 1 and 2.

The Molecular Volumes of Liquids.—H. Kopp.—A treatise extending to 117 pages and incapable of insertion.

Researches on Aromatic Nitrites.—Here are included papers by Victor Meyer on benzylcyanide and hydratropic nitrile; by Hermann Janssen on contributions to a knowledge of the substantiability of the atoms of methylene-hydrogen in benzyl cyanide; by K. Neure on substituted benzyl cyanides, and by Howard V. Frost on the condensation of benzyl cyanide and its substitution-products with aldehyds and with amyl nitrite.

Communications from the Chemical Institute of the University of Strassburg.—A study by R. Fittig on the condensation of β-ketonic esters with bibasic acids, and including memoirs by F. von Eynern on acetacetic ester and succinic acid; by Paul Feist on the barium and calcium salts of uvic, carbuvic, and carbuvic-ethylic ester acid; by A. Dietzel on acetacetic ester and pyruvic acid; and by A. Schlœsser on benzoylacetic ester and succinic acid.

Communications from the Laboratory of Prof. Wislicenus at Leipzig.—These include papers by J. Wislicenus on the determination of the spacial position of atoms, and on other derivatives of pseudobutylene, of angelicic acid, and of tiglic acid; by O. Holz on the bromo-derivatives of pseudobutylene; by M. Pückert on the bromo addition products and the geometric configuration of angelicic and tiglic acids, and by M. Pückert on the conversion of hydro-bromo-crotonylene into monobrom-pseudobutylene.

Barium Sodium Hyposulphate.— K. Kraut. — Sodium hyposulphate, though crystallising in different systems, form isomorphous mixtures which take the form of the sodium salt.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Iron Oxide Paint.—A correspondent wishes to know where the raw material for this paint can be obtained.

Estimation of Glycerin.—Can any of your readers direct me to a work on the estimation of glycerin in waste lye; also, what the impurities hurtful to dynamite glycerin are, and how they may be estimated?—Glycerol.

MEETINGS FOR THE WEEK.

Monday, 18th.—Medical 8.30.
—— Society of Arts, 8. Cantor Lectures. "The Decoration and Illustration of Books," by Walter Crane.

Tuesday, 19th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Pathological, 8.30.
—— Sanitary Institute, 8. "Drainage and Construction," by Prof. H. Robinson, M.Inst.C.E.
—— Society of Arts, 8. "The Art of the Jeweller," by Carlo Giuliano.

Wednesday, 20th.—Society of Arts, 8. "Objects and Methods of the Society of Arts' Motor Trials," by Prof. A. B. W. Kennedy, F.R.S.
—— Meteorological, 7.
—— Geological, 8.

Thursday, 21st.—Royal, 4.30.
—— Royal Institution, 3. "Houses and their Decoration from the Classical to the Mediæval Period," by Prof. J. Henry Middleton, M.A.
—— Royal Society Club, 6 30.
—— Institute of Electrical Engineers. 8.
—— Chemical, 8. Ballot for the Election of Fellows. "The Molecular Weights of Metals," by W. Ramsay, F.R.S. "Some Compounds of Tribenzyl-phosphoric Oxide," by N. Collie.

Friday, 22nd.—Royal Institution, 9. "The Science of Animal Locomotion in its relation to Design in Art (illustrated by the Zoopraxiscope," by Eadweard Muybridge.
—— Sanitary Institute, 8. "Scavenging, Disposal o Refuse and Sewage," by H. Percy Boulnois, M.Inst.C.E.
—— Quekett Club, 8.

Saturday, 23rd.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.
—— Physical, 3. "On the Use of Lissajou's Figures in the Maintenance of a Uniform Rotation," and "On the Direct Determination of the Vibration Period of a Reed or Tuning-fork by means of a Morse Receiver," by Prof. J. V. Jones. "On the Clark Cell as a Source of Standard Currents," by Prof R. Threlfall and A. Pollock. "On the Maintenance of High Specific Resistances," by Prof. R. Threlfall.

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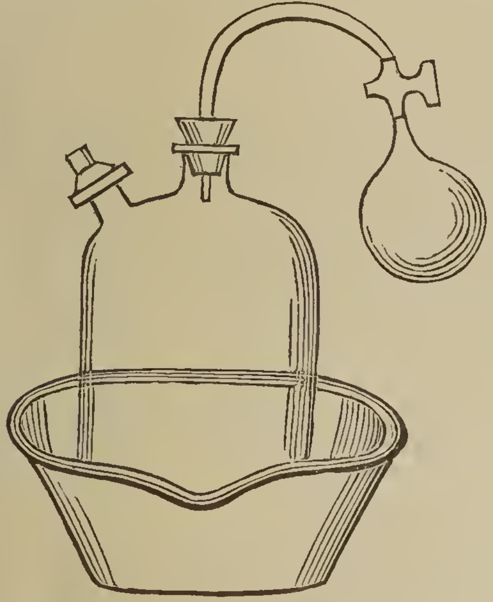
THE CHEMICAL NEWS.

Vol. LIX. No. 1530.

A SELECT METHOD OF PREPARING NITROGEN GAS.

By H. N. WARREN, Research Analyst.

The formation of nitrogen gas when required as an agent, either for the lecture-table or when in larger quantities for research, always presents more or less difficulty as regards its preparation. One process, still recorded in the various hand-books of science, being the action of nitric acid on raw meat; this method may, however, without doubt be regarded as nothing more than an alchemical memoir, since it would be evidently difficult to state, or enumerate, the complicated mixture of other gases which becoming evolved at the same time would naturally contaminate the product. The action of potassium nitrite when heated in a suitable apparatus in admixture with ammonium chloride produces, when prepared cautiously, a moderately pure gas, but owing to the inconstancy of the reaction the same is rendered considerably tedious, and unprofitable. As a third instance, the reaction that phosphorus affords when burnt in a limited supply of air, as, for instance, when confined by the aid of a bell-jar and in direct contact with water, at once presents an elegant and at the same time uncostly method of preparing a very pure gas, and direct from the atmosphere. This, although a favourite method of most demonstrators and others when experimenting with or illustrating the component parts of the atmosphere, yet at the same time few, if any, seem to have adopted a plan to recover, or more correctly to collect, the so prepared gas, which by a slight alteration in the form of apparatus to that generally employed may be procured in any desired quantity.



The accompanying figure, which is intended to illustrate the apparatus required, consists mainly of a doubly tubulated gas-receiver or bell-jar connected either with a bladder provided with a suitable stop-cock, or, if required in larger quantities, to an ordinary gas-holder, the outer vessel containing a sufficiency of water to allow of the gas-jar at the termination of the action to be immersed to the required height. In using the apparatus all that is necessary is to apply a hot wire to the pieces of phosphorus contained in a small brass dish, the same being allowed to float upon the surface of the water. This is most readily accomplished by withdrawing the stopper from the side tubule, inserting a hot wire in order to start the combustion of the phosphorus, and replacing the stopper. The apparatus and its contents, after the combustion of the phosphorus has terminated, is allowed to remain a few moments in contact with the water in order to allow of the fumes of phosphoric pentoxide occasioned by the combustion of the phosphorus to unite with the water. The stop-cock, in connection with the receiver intended for the reception of the gas, is now opened, the weight of the bell-jar exerting a pressure sufficient to allow of its contents to be discharged into the receiver. The tap in connection with the receiver is next closed, the stopper from the side tubule again withdrawn, thus allowing on raising the apparatus to the surface of the water to admit of a fresh supply of air, which may be proceeded with as before. By this method, operating with a jar capable of retaining one cubic foot of atmosphere, a gas-holder able to contain six cubic feet of nitrogen may be filled in less than an hour.

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

THE CHEMISTRY OF THE FLAX FIBRE.

By C. F. CROSS and E. J. BEVAN.

Flax "straw," as a matured dicotyledonous stem, is made up of wood, bast, and cortex. For the separation of the bast fibres—which constitute about 20 per cent of the weight of the stem—from wood and cortex, the well-known processes of retting and scutching are resorted to. The former, as ordinarily practised, consists in a spontaneous fermentation, set up by immersing the stems in stagnant water, which has the effect of breaking down the less resistant cellular tissue, which cements the fibres, as it were, to the wood on the one side and the cortex on the other. The scutching then thrashes out the more brittle wood, and, to a great extent, strips also the cortical tissues, leaving the textile fibre or flax, still containing residues of the wood ("sprit"), and a greater or less admixture of the cortical tissues, which have the effect of binding the fibre-bundles into ribands. Ordinary flax, therefore, is not the pure isolated bast, but, to borrow a term from the mineralogists, a concentrate; and, although the foreign or non-fibrous elements of the stem survive in very small proportion, they are of very considerable technical importance, conditioning, as they do, the very complicated bleaching treatment which flax goods, and notably linens, undergo in preparation for the white goods market.

It is a matter of common knowledge that the Mather-Kier and alkali process of treatment of the vegetable textiles have been recently introduced into Belfast, being first adopted by the firm of Fenton, Connor and Co. The results of the research, which we are about to describe in outline, have been obtained in the course of the work of developing and perfecting the process, as here applied.

The pure fibre substance is a compound of cellulose with a pectosic group. This was sufficiently established by Kolb, whose research upon its constitution is the only one with which we are acquainted (*Ann. Chim. Phys.* (4), xiv., 348). We are investigating the constitution of this non-cellulose group more closely, by means of the definite criteria which have been established by the later researches of Tollens and others (*Annalen*, ccxlix., 215—271). Amongst other results we may mention that by the action of nitric acid of 1·15 sp. gr., some quantity of mucic acid is formed; so far, however, we have not obtained of this product of decomposition more than from 1 to 2 per cent of the weight of the fibre. It should be pointed out, however, that the percentage on the non-cellulose constituent from which it is undoubtedly formed amounts to from 5 to 10. The other products of the action of this acid are:—(*a*) Oxalic and carbonic acids —no evidence has been obtained of the formation of saccharic acid. (*b*) Fatty and wax acids, resulting from the decomposition of the cuticular substances associated with the fibre, of which we shall treat subsequently. These are dissolved by alcohol from the disintegrated fibrous residue, which is for the most part an oxycellulose, and which, after exhaustion by this solvent, is obtained comparatively pure. With regard to the yield and properties of the oxycellulose, a comparative study of pure flax and cotton celluloses revealed no sensible differences. By the action of potassium permanganate in presence of caustic soda in excess, we obtained from pure bleached linen (flax cellulose) the following products:—An oxycellulose similar to the above (45 per cent); oxalic acid (18 per cent); and a soluble carbohydrate of the aldehyd-alcohol type (15 per cent), yielding furfurol on hydrolysis by acids. The condensation of the cellulose molecule to form this aldehyd by this particular method is noteworthy.

The Wood or Sprit.—This has all the characteristics of the typical ligno-celluloses (Chemical News, lix., 106) and we have not made it the subject of special study, having devoted ourselves rather to the *Cuticular Constituents*. Hot alcohol dissolves from the scutched fibre from 2 to 3 per cent of its weight of a mixture composed of—(*a*) A wax which separates out for the most part on cooling. This appears to be a mixture of a free wax alcohol and a compound of the same alcohol with a ketone-resin. The alcohol has the composition $C_{23}H_{47}.OH$. The products of saponification were variously fractionated, but no other alcohol appears to be present. It melts at 81° to 82°. The acetate, $C_{23}H_{47}.(C_2H_3O).O$, also analysed, melts at 65°. The products of resolution of the before-mentioned "resin" are oils of indifferent properties, which are still under investigation. (*b*) In the filtrate from the crystallisation of wax (*a*) there is contained a complex of constituents, which have so far been resolved as follows:—(1) A carbohydrate of the ligno-cellulose type, but soluble in water; converted by nitric acid into a highly acid derivative, which from its properties and analysis of the calcium salt, we identify as the compound obtained by the action of nitric acid upon the ligno-celluloses and similar bodies (Chemical News, xlvii., p. 77). (2) The green semi-fused residue from the extraction of the carbohydrate by boiling water is resolved by benzene into two bodies—(*α*) a brown residue or wax, resembling in general properties the wax described under (*a*), but yielding a wax alcohol on saponification melting at 74°, and (*β*) a bright green oil, which, when deprived of the solvent and on cooling becomes semi-solid. Both (*α*) and (*β*) yield a considerable proportion of indifferent oily products of saponification, which are still under examination.

We hope shortly to complete this research, when the results will be communicated in full.

ON THE
TRUE FORMULA FOR PERMANGANATES.*

By CHARLES M. BRADBURY, of Virginia.

(Continued from p. 124).

It now remains to be shown that $KMnO_4$ is not merely a possible formula for the salt it represents, but that it is the only correct one. This I hope to do by appeal (I.) to the results of certain experiments made with reference to this question, and (II.) to facts and principles generally recognised as parts of chemical science.

I.

(1).

If permanganates really contain two atoms of a monad base, there is no good reason why one of these may not be replaced by some other monad, thus producing a double salt. To test the possibility of producing such a salt, the following experiment was made:—

11·70 grms. of silver permanganate and 1·48 grms. potassium chloride were separately dissolved in the least quantity of hot water. The two solutions were then thoroughly mixed by shaking in a bottle with a well-ground glass stopper, and the mixture was set aside in a dark place for about twelve hours. The reaction to be expected (assuming ths correctness of the formula $\overset{I}{R}_2Mn_2O_8$) was—

$$Ag_2Mn_2O_8 + KCl = \left.\begin{matrix}K\\Ag\end{matrix}\right\} Mn_2O_8 + AgCl \quad .. \quad .. \quad (A).$$

The purple liquid was decanted from the precipitated silver chloride and placed under a bell-glass with a vessel containing strong sulphuric acid. The crystallisation occupied nearly a month. The mother-liquor was then poured off, and the small crystals were washed, dried over sulphuric acid, and analysed. The analysis gave, from 0·8120 grm. supposed double permanganate,—

Ag	0·3802
Mn	0·2025
K	0·0030

or—

		Calculated for $KAgMn_2O_8$.
Ag	46·83 per cent	28·05
Mn	24·93 ,, ,,	28·55
K	0·30 ,, ,,	10·16

So that the crystals examined were clearly not the double permanganate. Upon comparing the analysis with the calculated percentages of the elements in silver permanganate, it appears that the material was merely silver permanganate with a trace of potassium permanganate in it. The difference in solubility of the two salts readily accounts for the small proportion of the latter. Calculating the oxygen, there are found—

				Per cent.	Calculated for $Ag_2Mn_2O_8$.
Ag_2	0·3802				
O	0·0281		Ag	46·83	47·58
K_2	0·0030	or	Mn	24·93	24·23
O	0·0006		O	28·84	28·19
Mn_2	0·2025		K	0·31	—
O_7	0·2062				

Instead of reaction (A), the change that took place on mixing the two solutions was therefore merely—

$$2Ag_2Mn_2O_8 + 2KCl = K_2Mn_2O_8 + Ag_2Mn_2O_8 + 2AgCl,$$

or, as seems more probable,—

$$2AgMnO_4 + KCl = KMnO_4 + AgMnO_4 + AgCl.$$

(2).

An attempt was now made to prepare a double permanganate of potassium and sodium. The method first adopted was based on the suggestion that—

$$2K_2Mn_2O_8 + Na_2SO_4.10H_2O = 2\left.\begin{matrix}Na\\K\end{matrix}\right\} Mn_2O_8 + K_2SO_4 + Aq$$

ought to be a possible reaction, since potassium, being more basylous than sodium, might be expected to take sulphuric acid from that element. Hot solutions of the two salts were mixed in proper proportion, and set in a desiccator to crystallise. After ten days an abundant deposit of crystals, in general appearance reminding one of silver permanganate, was found. Upon analysis, however, they proved to be only potassium permanganate in crystals of rather unusual "habit."

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[*] Dissertation presented to the Faculty of the University of Virginia in application for the degree of Doctor of Philosophy. *Thesis*:—Permanganic acid is monobasic, and the permanganates are represented by the general formula $\overset{n}{R}(MnO_4)_n$.

			Calculated for $KMnO_4$.
K	0·2463	24·60 per cent	24·73
Mn	0·3526	35·22 ,, ,,	34·80
O (calcul.)	0·4091	40·87 ,, ,,	40·47

So that there seems to have been no chemical change of any kind.

A second trial was made on a different plan. Sodium sulphate, barium permanganate, and potassium permanganate were mixed in proportions to produce the reactions—

$$(1).\ Na_2SO_4.10H_2O + BaMn_2O_8 = Na_2Mn_2O_8 + BaSO_4 + Aq.$$

$$(2).\ Na_2Mn_2O_8 + K_2Mn_2O_8 = 2\left.\begin{matrix}K\\Na\end{matrix}\right\} Mn_2O_8.$$

The first of these, of course, took place as soon as the solutions were mixed; but the second did not occur. After allowing the mixture to stand for some hours, the clear solution was decanted into an evaporating dish, concentrated at a gentle heat, and placed in a desiccator. Within twelve hours potassium permanganate was deposited from the solution in small prismatic crystals of the appearance, in shape and colour, so characteristic of that salt.

(3).

If potassium permanganate really contains two atoms of potassium, it ought to be possible to replace one of these by hydrogen, thus forming an acid salt. Accordingly five grms. of potassium permanganate was dissolved, and treated with a quantity of hydrofluosilicic acid corresponding to one-half the potassium. The potassium silicofluoride was caught on an asbestos filter, and the filtrate concentrated over sulphuric acid. After a few days sufficient crystals were deposited for examination. They did not differ in appearance from many specimens of potassium permanganate, and upon attempting to determine water in 0·8193 grm., none was found. Hence the substance contained no hydrogen, and was, in fact, merely re-crystallised potassium permanganate.

(4).

The untrustworthy character of the only description accessible to me of the "acid permanganate of baryta" alleged by some to exist, has already been alluded to. As it would be unreasonable to reject assertions, which if true ought to be so easy to prove, without testing them by experiment, I endeavoured to prepare some of these crystals. An accurately weighed portion of barium permanganate was dissolved, and treated with just the amount of normal solution of sulphuric acid necessary, theoretically, to precipitate all the barium. After a couple of hours the clear solution was decanted and evaporated on a water-bath at a very gentle heat. When quite concentrated it was allowed to cool, but yielded no crystals of any kind, nor did further evaporation produce any; the final product was a black powder insoluble in water—MnO_2. A second portion of barium permanganate was now dissolved and treated in the same way, except that rather less sulphuric acid was purposely used than would precipitate all of the barium. But not even this, in which the conditions for forming an acid barium permanganate (if it can exist) were almost certainly present, yielded, on gradual evaporation, anything but a crust of manganic oxide and a little barium permanganate.

(5).

While it might be desirable to multiply experiments like those already described, which bear directly upon the question at issue, so as still further to reduce the chance of error in drawing a conclusion, circumstances have prevented this. But before passing on to further theoretical reasons (which are very strong) for receiving the monobasic formula, it may be well to describe a few other practical tests that have a less direct, but scarcely less important, bearing on the subject.

The arguments to be used in II. are largely dependent upon the isomorphism of the permanganates with the perchlorates. The *fact* can scarcely be questioned, as it seems to be recognised by all authorities. As opinions appear to differ as to its degree, an endeavour was made to determine this.

Several attempts were made to establish the exact isomorphism of potassium permanganate and potassium perchlorate according to the rule proposed by Kopp, that the test of strict isomorphism should be the growth of crystals of one of the substances, when suspended in a saturated solution of the other. This was found to be impracticable. Crystals of permanganate suspended in a saturated solution of perchlorate in every case dissolved entirely, and crystals of perchlorate, while easily coated or stained with permanganate, did not have the appearance of having grown, in a crystallographic sense.

There was no difficulty, however, in getting the salts to crystallise together, the crystals of the mixture being in some cases remarkably perfect in shape and beautiful in colour, varying according to the proportions of the constituents when examined with a lens.

Twelve different mixtures were prepared, six as nearly as possible in varying integral proportions—as one to two, one to three, five to one—the remainder being mixtures of accurately weighed portions of the salts, without any attempt at exact proportion. These were dissolved in hot water and left to evaporate in the air, loosely covered with filter-paper to exclude dust.

The result was in each case a mass of minute crystals, with every indication in colour, shape, and size, of being mixtures of permanganate and perchlorate. One or two of the solutions, which were allowed to evaporate to dryness, yielded what seemed to be two kinds of crystals, a lighter and a darker. The others gave crystals which, when drained, washed, and dried, had the appearance of being the same throughout, and were often, as before remarked, exceedingly well developed.

In no single instance, however, did analysis of these crystals indicate the proportions of permanganate and perchlorate that had been used in making them. In all of the analyses* that I considered most trustworthy (the amount of material taken was in most cases smaller than would have been desirable for accuracy), more perchlorate was found than was expected—often largely more—and less permanganate. As this excess was quite balanced by deficiency of the manganese, and was found even when especial care had been taken to exclude chlorine from any other source than the salt under examination, it must be accounted for otherwise than by supposing repeated error in the analyses. Two considerations at least would lead one to expect results similar to those found; first, that the perchlorate is the less soluble of the two salts, and would therefore crystallise in advance of the other; second, that the solution of permanganate is liable to decomposition when exposed to the air, while the perchlorate is stable.

As examples of this variation, I will give the results of analysis of specimens 7 and 8: Eighty-five m.grms. of No. 7 ought to have given, according to the proportions used in making the solution (0·7309 grm. permanganate to 0·3012 perchlorate), 25 m.grms. perchlorate and 60 m.grms. permanganate. The actual result was—

	Grm.	Grm.	
Instead of	0·025	0·070	perchlorate.
,, ,,	0·060	0·013	permanganate.
	0·085	0·083	

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* The method used with the first six samples was to ignite with excess of alkaline carbonate, dissolve the fused mass in water, acidify with nitric acid, and precipitate chlorine with silver nitrate. The silver chloride was caught on a filter, washed, the excess of silver nitrate removed from the filtrate by adding hydrochloric acid and again filtering, and the filtrate finally treated with ammonia and bromine to precipitate manganese. The other six were treated similarly, except that the manganese was precipitated first from the alkaline solution with hydrogen dioxide.

These crystals were well formed but small, not more than half a m.m. thick. Under the lens they appeared translucent, with a beautiful crimson colour.

No. 8 was in crystals so minute that to the naked eye they appeared as a purple red crystalline powder. The lens, however, revealed that the crystals were as well formed individually as No. 7, and that their colour by transmitted light was a rather faint red. The solution from which these separated had been made of 1·6814 grm. perchlorate and 0·3261 grm. permanganate. The 148 m.grms. used in analysis should have contained, therefore, 124 m.grms. of perchlorate and 24 of permanganate. The result was—

	Grm.	Grm.	
Instead of	0·024	0·011	permanganate.
,, ,,	0·124	0·138	perchlorate.
	0·148	0·149	

The results, on the whole, agree with the statement usually made, that these two salts are isomorphous to the extent of crystallising together in all proportions. Hence the right to make deductions from this isomorphism cannot be doubted.

II.

If it were possible to ascertain the vapour density of potassium permanganate, there would be no difficulty in choosing between the formula $KMnO_4$ and $K_2Mn_2O_8$, as, according to the law of Avogadro, the molecular weight of the compound would thereby be decided. But since this is impracticable, owing to the decomposition of the salt at a temperature as low as 240° C.,* the problem must be attacked by methods less direct.

It is assumed that the received formula for the perchlorates, $\overset{n}{R}(ClO_4)_n$, is correct. Granting this, it follows almost necessarily that the permanganates are represented by the analogous formula $\overset{n}{R}(MnO_4)_n$, from the following considerations.

(To be continued).

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month ending February 28th, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

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

London, March 7th, 1889.

Sir,—We submit herewith the results of our analyses of the 166 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from February 1st to February 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

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

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

Of the 166 samples examined, three were recorded as "very slightly turbid."

The water supplied to the metropolis during the past month, despite the unfavourable state of the weather and frequent prevalence of frost and heavy snow, continued to be of excellent quality; and its variation in mean composition, as compared with that of the previous month's supply, though not indeed of any significance, was in the direction of an increased degree of freedom from organic matter.

It may be well to re-state on this occasion that our estimate of the degree of freedom of the water from organic matter is based mainly on the concordance of two sets of determinations, namely, a daily determination, by means of permanganate of potash, of the weight of oxygen expended in the oxidation of the organic matter present in a daily collected sample of each Company's supply; and in a weekly determination, by the combustion process, of the weight of organic carbon present in a weekly sample of each Company's supply, collected on some one day during the week.

In this way the mean weights of oxygen expended in the oxidation of the organic matter present, per gallon, in the Thames-derived water in the months of January and February, were found to be 0·062 and 0·056 grain respectively; while the mean amounts of organic carbon present in 100,000 parts of the water were found to be 0·170 and 0·161 part respectively. The maximum amount found in any of the samples examined in February, or 0·173 part in 100,000 parts of the water, corresponds, as nearly as may be, to about one-third of a grain of organic matter per gallon.

In the case of the East London Company's water, the mean weight of oxygen absorbed from the permanganate was found to be 0·045 grain per gallon; and the mean amount of organic carbon was found to be 0·145 part in 100,000 parts.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

(Continued from p. 131).

Wines.

Methods of Investigation.

I. *Determination of Specific Gravity.*—This is to be done by means of a Westphal's balance or a picnometer, and always at 15° C.

II. *Determination of Extract.*—10 to 50 c.c. wine at 15° C. are evaporated in a platinum dish on the water-bath to the proper consistence, and then dried in a drying-oven at 100° C. to constant loss of weight. Constant loss of weight is assumed when three weighings, with equal intervals between the first and second and second and third, give equal differences between the successive weighings.

Weighings are to be made at intervals of fifteen minutes.

III. *Inorganic Matter.*—This is the incombustible ash obtained by burning the extract. Repeated moistening,

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* R. and S., II., ii., 22.

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

drying, and heating to redness are advisable to entirely get rid of all organic constituents.

IV. *Acidity.*—After shaking vigorously, to drive off carbonic acid, the wine is to be titrated with an alkali solution and the acidity expressed in terms of tartaric acid.

V. *Glycerin.*—(1). This is determined in dry wines as follows:—The alcohol is driven off from 100 c.c. wine, lime or magnesia added, and the mass evaporated to dryness. The residue is boiled with 90 per cent alcohol, filtered, and the filtrate evaporated to dryness. This residue is dissolved in 10 to 20 c.c. alcohol, 15 to 30 c.c. ether added, and the mixture allowed to stand until it is clear. It is then decanted from the sticky precipitate into a glass-stoppered weighing-bottle, evaporated to constant loss of weight, and weighed.

(2). The following method is employed for sweet wines:—One hundred c.c. wine are measured into a porcelain dish and evaporated on the water-bath to a syrupy consistence, mixed with 100 to 150 c.c. absolute alcohol, poured into a flask, ether added in the proportion of 1½ volumes to each volume of alcohol used, the flask well shaken, and allowed to stand until the liquid becomes clear. This is then poured off and the residue again treated with a mixture of alcohol and ether. The liquids are mixed, the alcohol and ether driven off, the residue dissolved in water, and treated as in (1).

(3). In all glycerin determinations it is necessary to take into consideration the loss of glycerin due to its volatility with water and alcohol vapour, and accordingly to add to the glycerin found 0·100 grm. for each 100 c.c. of liquid evaporated.

(4). It is necessary to test the glycerin from sweet wines for sugar, and if any is present it must be estimated by Soxhlet's or Knapp's method and its weight subtracted from that of the glycerin.

VI. *Alcohol.*—The determination must be made by distillation in glass vessels, and the results stated as follows:—One hundred c.c. wine at 15° C. contain x grms. or c.c. alcohol.

VII. *Polarisation.*—(1). The wine is decolourised with plumbic subacetate.

(2). A slight excess of sodic carbonate is added to the filtrate from (1). 2 c.c. of a solution of plumbic subacetate are added to 40 c.c. white wine, and 5 c.c. to 40 c.c. red wine, the solution is filtered and 1 c.c. of a saturated solution of sodic carbonate added to 21 or 22·5 c.c. of the filtrate.

(3). The kind of apparatus used and the length of the tube are to be given, and results estimated in equivalents of Wild's polaristrobometer with 200-m.m. tubes.

(4). All samples rotating more than 0·5 degree to the right (in 220-m.m. tubes, after treating as above), and showing no change, or but little change, in their rotatory power after inversion, are to be considered as containing unfermented glucose (starch sugar) residue.

(5). Rotatory power of less than 0·3 degree to the right shows that impure glucose has not been added.

(7). Wines rotating between 0·3 degree and 0·5 degree to the right must be treated by the alcohol method.

(7). Wines rotating strongly to the left must be fermented and their optical properties then examined.

VIII. *Sugar.*—This is to be determined by Soxhlet's or Knapp's method. The presence of unfermented cane sugar is to be shown by inversion, &c.

IX. *Potassic Bitartrate.*—The determination of potassic bitartrate as such is to be omitted.

X. *Tartaric, Malic, and Succinic Acids.*—(1). According to Schmidt and Hiepe's method.

(2). Determination of tartaric acid according to the modified Berthelot-Fleury method.

(3). If the addition of 1 grm. finely-powdered tartaric acid to 100 grms. wine produces no precipitate of potassic bitartrate, the modified Berthelot-Fleury method must be employed to determine free tartaric acid.

XI. *Colouring Method.*—(1). Only aniline dyes are to be looked for.

(2). Special attention is to be paid to the spectroscopic behaviour of the rosaniline dyes, as obtained by shaking wines with amyl alcohol before and after saturation with ammonia.

(3). A qualitative test for alumina is not sufficient evidence of the addition of alum.

XII. *Nitrogen.*—To be determined according to the ordinary method.

XIII. *Citric Acid.*—Presence to be shown by a qualitative test, as baric citrate.

XIV. *Sulphuric Acid.*—To be determined in the wine after adding hydrochloric acid.

XV. *Chlorine.*—To be determined in the nitric acid solution of the burnt residue by Volhard's method.

XVI. *Lime, Magnesia, and Phosphoric Acid.*—These are determined in the ash fused with sodic hydrate and potassic nitrate, the phosphoric acid by the molybdenum method.

XVII. *Potash.*—Either in the wine ash, as the platinum double salt, or in the wine itself, by Kayser's method.

XVIII. *Gums.*—Presence shown by precipitation by alcohol; 4 c.c. wine and 10 c.c. 96 per cent alcohol are mixed. If gum arabic has been added, a lumpy, thick, stringy precipitate is produced; whereas pure wine becomes at first opalescent and then flocculent.

Methods of Judging Purity—(Burtheilung).

Part I.

I. Commercial wines may be defined as follows:—(*a*). The product obtained by the fermentation of grape juice with or without grape skins and stems. (*b*). The product obtained by the fermentation of pure must, to which pure sugar, water, or infusion of grape skins has been added. It must contain not more than 9 per cent alcohol and 0·3 per cent sugar, and not less than 0·7 per cent acid, estimated as tartaric. (*c*). The product obtained in southern countries by the addition of alcohol to fermented or partly fermented grape juice. French wines are not included, however. (*d*). The product obtained by fermenting the expressed juice of more or less completely dried wine-grapes.

II. The above definitions do not apply to champagnes.

III. The following include the operations undergone by wines in cellars (*Kellermässige Behandlung*):—(*a*). Drawing and filling. (*b*). Filtration. (*c*). Clarification by the use of kaolin, isinglass, gelatin, or albumen, with or without tannin. (*d*). Sulphuring. Only minute traces of sulphurous acid may be contained in wine for consumption. (*e*). Adulteration of wine. (*f*). Addition of alcohol to wine intended for export.

IV. Wines, even if plastered, must not contain more sulphuric acid than that corresponding to 2 grms. potassic sulphate (K_2SO_4) per litre.

V. Medicinal wines are those mentioned in Parts I. and IV., with the following restrictions:—(*a*). They must not contain more sulphuric acid than corresponds to 1 grm. potassic sulphate per litre. (*b*). They must contain no sulphurous acid. (*c*). The percentage of alcohol and sugar to be given on the label. (*d*). These restrictions apply only to wines expressly recommended or sold for medicinal use.

Part II.

I. Improperly gallised wines are preparations of grape juice, pure sugar, and water, or grape-skin infusion, that contain more than 9 per cent alcohol or less than 0·7 per cent acid, or both, and preparations in which impure glucose has been used. The following facts enable us to detect them:—Small quantities of inorganic matter (phosphoric acid and magnesia), and right rotation if impure glucose is used. If the rotation exceeds 0·2° to the right, the wine is to be concentrated, freed from tartaric acid as far as possible, and again polarised.

II. Addition of alcohol is to be assumed if the ratio of alcohol to glycerin is greater than 10 to 1 by weight.

III. Addition of water and alcohol is recognised by the diminution in the quantity of inorganic matter, especially magnesia, phosphoric acid, and usually potash. Addition of water alone is recognised in the same way.

IV. Scheelisation, *i.e.*, addition of glycerin, is assumed if the ratio of glycerin to alcohol exceeds 1 to 6 by weight.

V. The presence of cane sugar is ascertained by a determination of sugar (by Soxhlet's or Knapp's method), before and after inversion.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 7th, 1889.

Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. P. Norman Evans, Percy A. E. Richards, and Thomas J. Underhill were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick William Boam, 2, De Montford Square, Leicester; William Frew, King James Place, Perth; James Hall, Grove House, Tottenham; James Bruce Miller, Rubislaw, Den North, Aberdeen; George Cannon McMurtry, 35, Binfield Road, Clapham, S.W.; John Charles Platts, 25, Harcourt Road, Crookesmoor, Sheffield; Duncan Taylor Richards, 12, Park Terrace, South Shields; John William Slater, 36, Wray Crescent, Tollington Park, N.; William John Waterhouse, 211, Lord Street, Southport; Mortimer Woolf, 3, Acoll Road, West Hampstead.

The following papers were read:—

23. "*The Decomposition of Carbon Disulphide by Shock; a Lecture Experiment.*" By T. E. Thorpe, F.R.S.

The author, in studying the action of the fluid alloy of potassium and sodium on carbon disulphide, obtained a yellowish brown solid substance which exploded with great violence when subjected to pressure or friction. If the explosion occurred in contact with carbon disulphide that substance was resolved into its elements.

As carbon disulphide is an endothermic compound the author was induced to try whether its vapour could not be resolved into its elements by the explosion of various detonating agents, *e.g.*, mercuric fulminate, in the manner indicated by Berthelot. It is found that such a decomposition is readily effected by exploding a charge of 0·05 grm. fulminate within a stout glass tube containing a few c.c. of carbon disulphide vapour. The carbon disulphide is at once resolved into carbon and sulphur, which line the inside of the tube. The experiment may be easily made with perfect safety, and forms a good illustration, for class purposes, of the resolution of an endothermic substance into its elements by sudden shock.

Discussion.

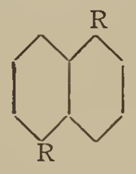
The President pointed out that the spectrum of mercury was rich in ultra violet rays, and suggested that perhaps the decomposition was induced by these rays.

Professor Thorpe, in reply, said that this explanation had not occurred to hin; he believed, however, that the effect was purely mechanical, inasmuch as Berthelot had, in fact, exploded nitrous oxide by sudden compression. In reply to Mr. Groves, he said that he had only experimented with the gaseous disulphide; he believed that no explosive compound was formed by treating the disulphide with sodium.

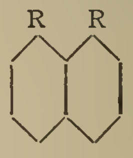
24. "*The Determination of the Constitution of the Heteronucleal αβ- and ββ-di derivatives of Naphthalene.*" By Henry E. Armstrong and W. P. Wynne.

In a recent communication (*Chem. Soc. Proceedings*, No. 58, 1888, p. 104) the authors have shown that proof has now been obtained that the two dichloronaphthalenes melting at 48° and 63·5° corresponding respectively to the Dahl and Badische modifications of betanaphthylaminesulphonic acid, are the 1 : 2′ and 1 : 3′ *heteronucleal* cichloronaphthalenes; at the same time they have insisted that it is impossible from existing data to determine whether the compound melting at 48° is the 1 : 2′, and that melting at 63·5° the 1 : 3′-derivative or *vice versâ*, and this they have done notwithstanding the evidence brought forward by Erdmann and Kirchhoff (*Annalen*, ccxlvii, 366; *Berichte*, 1888, 3447; *Chem. Soc. Proceedings*, No. 61, 1889, p. 8). These chemists have inferred that the dichloronaphthalene melting at 48° is the 1 : 3′-derivative, as they prepared it synthetically from metachlorobenzaldehyd; and they regard the isomeride which the authors have shown melts at 63·5° as the 1 : 2′-derivative, as they obtained it from parachlorobenzaldhyd. The authors have on several occasions criticised Erdmann and Kirchhoff's arguments and have pointed out their insufficiency, their main objection being that the position of the hydroxyl in the naphthol-derivatives prepared synthetically could not be determined; they have also suggested that in some cases the hydroxyl might take up the position indicated by Erdmann and Kirchhoff, and in others the alternative alpha-position. Moreover, it appears to them that the argument recently advanced by Erdmann (*Berichte*, 1888, 3447), in reply to their criticism, is deprived of its force by Erdmann's own admission that phenylisocrotonic acid is converted with exceptional ease into the corresponding lactone; however stable the lactone may be when formed, the fact that it is so readily producible is indicative of the manner in which the naphthol-hydroxyl might eventually assume a different position from that assigned to it by Erdmann. And even if no argument of this kind could be advanced, the fact that condensation is effected at a relatively high temperature and that it involves considerable molecular rearrangement, renders the occurrence of isomeric change both possible and probable.

Believing that, "as in the case of benzene there is little doubt that the constitution of naphthalene-derivatives will be determined eventually by the study of naphthalene-derivatives and not by synthetic methods of the character of those of Erdmann and Kirchhoff" (*Brit. Assoc. Rep.*, 1888; Chem. News., lviii., 295), they have devoted their attention to the study of the chloronaphthylaminesulphonic acids: by determining the relative positions of the three pairs of radicles Cl and NH_2, Cl and SO_3H, and NH_2 and SO_3H, in such acids, it is obviously possible to determine the relative positions of the three radicles in a heteronucleal chloramidosulphonic acid, and on this result the absolute orientation of the radicles may be based, *provided* that it can be shown how the radicles are situated in any one of the two pairs of hetero-di-derivatives obtainable from the tri-derivative. No absolute method, free from reproach, has yet been devised of determining the constitution of any known hetero-di-derivative of naphthalene, but in the case of the αα-compounds, arguments may be advanced which are of such weight as to leave but little room for doubt. The two possible hetero-αα-compounds are represented by the symbols—



I.



II.

There can be little doubt, and it is indeed generally held, that so-called α-dinitronaphthalene (m. p. = 216°) and the corresponding γ-dichloronaphthalene (m. p. = 107°) are compounds of type I., and that β-dinitronaphthalene (m. p. = 170°) and the corresponding ζ-dichloronaphthalene

(m. p. = 83°) are compounds of type II. Thus, β-diamidonaphthalene, according to Aguiar's observations on its behaviour towards nitrous acid and towards oxalates (*Ber.*, 1874, 313), behaves in an altogether peculiar manner, simulating that of an ortho-di-derivative, as pointed out originally by Ladenburg (*ibid.*, 1878, 1651). The pseudortho character of β-diamidonaphthalene and the corresponding di-derivatives is also established by Ekstrand's investigation of the nitronaphthoic acid corresponding to β-dinitronaphthalene (*ibid.*, 1883, 2881); by Bamberger's investigation of naphthalic acid (*ibid.*, 1887, 237); and by Erdmann's investigation of the α-amido-α-sulphonic acid obtained on reducing the so-called Schöllkopf α-nitronaphthalene-α-sulphonic acid (*Annalen*, ccxlvii., 343). On the other hand, an argument of great force in favour of the adoption of a formula of type I. for α-dinitronaphthalene and other corresponding uniform di-derivatives (derivatives containing two similar radicles) may be derived from the fact that all melt at higher temperatures than the isomeric αα-compounds; it is to be expected, on general grounds, that compounds of symmetrical structure would be thus distinguished.

By sulphonating 1 : 2 α-chloro-β-naphthylamine hydrochloride by means of four times its weight of an acid containing about 2 per cent of SO_3, the authors haves succeeded in obtaining three isomeric α-chloro-β-amidosulphonic acids. No. I. acid is produced in largest amount and almost exclusively if sulphonation be effected by heating at 70° for six hours. If the heating be prolonged for about six hours at a somewhat higher temperature, viz., about 100°, No. II. acid is the chief product. No. III. acid is chiefly produced if sulphonation be effected by heating during about six hours at about 160°. No. I. acid is very difficultly soluble in water; it is best purified by dissolving it as sodium salt in a large bulk of boiling hot water and precipitating by acid; the separated acid is at once filtered off, and these operations are several times repeated. It usually crystallises is glistening, flat, elongated prisms; its salts crystallise well, but are easily soluble, especially the sodium and ammonium salts. No. II. acid is slightly more soluble than the No. I. acid, and crystallises in a less characteristic manner; its salts are difficultly soluble; the sodium salt is especially characteristic, being almost insoluble in the presence of alkali; it crystallises with 4½ mols. H_2O in glistening, apparently monoclinic plates. No. III. acid is the most soluble, and yields very soluble salts, which do not crystallise well; it crystallises in tufts of needles. This acid is best separated from No. II. acid by means of the ammonium or sodium salts.

In order to determine the constitution of these acids the authors have, on the one hand, displaced the halogen by means of sodium amalgam, and, on the other, have displaced the β-amido-group by means of v. Baeyer's hydrazine method. They have already ascertained that the No. I. acid affords the Dahl modification of beta-naphthylamine sulphonic acid, and the No. III. acid the so-called δ-acid of Bayer and Duisberg; the investigation of the amido-acid from No. II. acid, and of the three chlorosulphonic acids derived from the three chloramidosulphonic acids is also almost completed.

In the number of the *Chemiker Zeitung* just to hand, mention is made of the title of a paper by P. Hellström, read at the Swedish Academy of Sciences on February 13th, from which it appears that the same subject is elsewhere being investigated, and it is on this ground alone that the authors are induced to communicate their results in the present incomplete form.

There is little doubt that under ordinary conditions of sulphodation chlorobetanaphthylamine will yield other products than those described, and in fact others have already been observed. The authors propose also to study the sulphonic acids obtained from other chloronaphthylamines, and have, in fact, already prepared acids from dichloralphanaphthylamine from 1 : 2 chloralphanaphthylamine and from bromalphanaphthylamine. It is anticipated that in this way it will be possible to determine the constitution of the dichloronaphthalenesulphonic acids, and hence to determine the manner in which substitution is effected in their formation. From their No. 1 chloramidosulphonic acid the authors have already prepared the corresponding dichloronaphthalenesulphonic acid, and find that it is identical with the chief product of the sulphonation of the 1 : 2 dichloronaphthalene melting at 34°, that, namely, which yields a sulphochloride crystallising in massive prisms melting at about 105° (*Brit. Ass. Report*, 1888; CHEMICAL NEWS, lviii., 296).

25. "*The Action of Chloroform and Alcoholic Potash on Phenylhydrazine.*" By S. RUHEMANN, Ph.D., M.A.

The author finds that together with the compound previously described by Mr. Elliot and himself (*Chem. Soc. Trans.*, 1888, 850), which he proposes to call *diisocyananilide*, there is formed a certain amount of formylphenylhydrazine, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}COH$. From paratolylhydrazine, in like manner, he has obtained formylparatolylhydrazine and diisocyanparatoluidide; the latter crystallises in faintly yellow plates, melting at 185°.

Diisocyananilide is converted by the action of methyl iodide into a methammonium iodide of the formula $C_{14}H_{11}N_4(CH_3).CH_3I$, the production of which is proof of the presence of an imido-group. On adding bromine to an acetic solution of the anilide, a mixture of a monobromo- (m.p. 220°) and a tribromo-derivative is precipitated; the solution containing a third substance (m. p. 131°) of the formula $C_{14}H_{10}Br_2N_4$.

The Anniversary Meeting will be held on Thursday, March 28th, at 8 p.m., when the President will deliver an Address on "Recent Researches on the Rare Earths as Interpreted by the Spectroscope."

PHYSICAL SOCIETY.

March 9, 1889.

Prof. REINOLD, F.R.S., President, in the chair.

PROF. R. THRELFALL and Prof. A. S. Herschel were elected Members of the Society.

Prof. O. LODGE read a paper "*On Magneto-optic Rotation by Transient Currents, with Reference to the Time required for the Production of the Effect.*"

If a piece of heavy glass or tube of carbon bisulphide be placed between two crossed Nicols and surrounded by a solenoid, light passes through when a Leyden jar is discharged through the wire. That the discharge is oscillatory may be proved by turning the analyser slightly to one side or the other, this having no effect on the result, or the beam may be examined by a revolving mirror, in which case a beaded band is seen when the discharge takes place. When the spark itself is analysed in the same way a serrated band results. The frequency of the oscillations being given by the formula—

$$n = \frac{1}{2\pi\sqrt{\frac{LS}{\mu K}}}$$

it is evident that n will be decreased by increasing the capacity, S, and self-induction, L, and this fact was demonstrated by connecting two condensers, first in series and then in parallel, and placing coils of wire in the circuit. The pitch of the sound emitted by the spark was by these means brought within the musical scale. Contrary to expectation, the insertion of a coil with an iron core produced little or no change in the pitch, the reason given being that the induced currents in the skin of the iron wire, due to such rapid oscillations of current, prevents the interior being magnetised. From the mathematical theory of the brightening of the dark field it appears that the relative brightness, B, when compared with the light field obtained from the uncrossed Nicols is given by—

$$B = \frac{1}{\tau}\int_0^\tau \sin^2\theta\,dt,$$

where τ is the time during which an impression can be accumulated on the retina and θ the angle through which the polarised beam is rotated. When θ is considered small—

$$B = 16\pi^2 k^2 n^2 . \frac{\frac{1}{2}SV_0^2}{R\tau},$$

where k = Verdet's constant, n = number of convolutions on the solenoid, R = resistance of circuit, and $\frac{1}{2}SV_0^2$ the initial energy of the static charge. The general solution is given as—

$$B = \frac{1}{2m\tau}\int_0^A \frac{1 - J_0(x)}{x}\,dx,$$

where $m = \frac{R}{2L}$, $A = 8\pi k n \mu V_0 \sqrt{\frac{S}{L}}$ and $J_0(x)$ Bessel function.

Taking the approximate solution, the question as to what is the best size of wire wherewith to wind the solenoid is considered, and as the insulation is very important it is concluded that the secondary of a Ruhmkorff coil is very suitable. The main interest of the experiment is said to lie in the evidence afforded of the practical instantaneity of the development of the rotary property in the substance under examination, for Villari (from experiments made on a glass drum revolving in a magnetic field) inferred that a distinct time between 1-800th and 1-400th of a second was necessary, whereas Prof. Bichat and Blondlot of Nancy, have concluded that the time required is less than 1-30,000th second. The author finds that carbon bisulphide is able to show the effect when the rate of alternation is 70,000 per second, and has no reason to believe that glass is in any way inferior. As a possible explanation of Villari's results he suggests that the strain due to centrifugal force would modify the components of the polarised beam and produce elliptic polarisation.

Mr. Ward mentioned that experiments similar to Villari's were now being carried out at the Cavendish Laboratory, a disc of glass being rotated about 200 times per second by means of a turbine. The results so far obtained do not confirm Villari's, but owing to difficulties in keeping the speed constant it is impossible to make exact measurements. It has, however, been found that the strain due to centrifugal force rotates the plane of polarisation, and elliptically polarises the beam, and that passing an alternate current round a stationary glass bar produces a distinct rotation of polarised light passing through it.

Referring to the oscillatory discharge of a jar, Prof. Rücker directed attention to Dr. E. Cook's experiments, described before the Society in June, 1888, when photographs showing the dust figures produced by sparks were exhibited, and pointed out that the frequency required to produce air waves of the length there indicated was of the same order as the rate of oscillatory discharge, viz., about one million per second. Prof. Rücker also wished to know whether glass behaved precisely like CS_2.

Dr. Lodge said his experiments were not exact enough to decide the latter question, and mentioned that Mr. Chattock had some time ago produced dust figures in tubes by jar discharges, and shown that the wave-length depended on the capacity and self-induction.

Prof. Ayrton suggested the use of a phonograph as a means of recording and reproducing the oscillations, in the same way as himself and Prof. Perry have analysed the current curves of alternating dynamos. The discharge could be passed through a small coil fixed to a diaphragm, and placed near a coil through which a steady current was passing, the attractions and repulsions serrating the surface of the rapidly revolving cylinder. By means of a mirror attached to a delicate magnifying spring the section of the surface may be determined. He also enquired whether the experiments shown do prove that the effect is instantaneous.

Dr. Thompson remarked that it was satisfactory to learn that Villari's results admit of an interpretation other than by time effect, and thought it advisable to vary the experiment by rotating a bar of glass, but Mr. Ward said he attempted that experiment four years ago and abandoned it on account of the enormous speed required.

Dr. Lodge showed "Some Experiments allied to those of Hertz," and pointed out that all the effects were due to resonance. The plates of an air condenser were connected by a wire loop and placed near a Holtz machine in action. On adjusting the distance between the plates to a particular value, sparks were observed to pass between them, but on increasing or decreasing that distance the sparks ceased. It was also shown that the sparking was interrupted if the connecting loop was replaced by a coil, though the coil was effective when connected to a condenser of smaller size, thus demonstrating that the time constant of the condenser circuit was all important. Another important condition to be observed in such experiments is that the receiving circuit must be closed except at the sparking place, so as to permit the surgings of electricity to take place freely.

Other experiments were shown in which two spheres provided with rods terminating in knobs were used as a Hertz's oscillator, and sparks could be obtained from straight pieces of wire of suitable length held at some distance from the spheres.

Dr. Lodge remarked that sparks could be obtained from almost any scrap of wire or metal in close proximity to an induction coil and oscillator, but to produce the effects at considerable distances careful timing of the receiving circuit was necessary.

The author also described the results of some experiments on the velocity with which electric waves travel along wires, and concluded (contrary to Hertz) that this was not greatly different from the velocity of light.

Owing to the late hour the other papers announced to be read were postponed.

NOTICES OF BOOKS.

Report on the Cost and Efficiency of the Heating and Ventilation of Schools, for the Use and by the Request of the School Board of Dundee. By Thomas Carnelley, D.Sc., F.C.S. Dundee: Winter, Duncan, and Co.

We have here a very elaborate and useful investigation on an important point in the working of schools. Some of the facts here brought to light are surprising. The consumption of coal per head varies excessively in different towns. Thus, in Dundee and Aberdeen it is 42 lbs. per head, whilst in Nottingham, with a milder climate, it reaches 195 lbs. Hence, as Dr. Carnelley puts it, "either the children are being comparatively frozen in Dundee and Aberdeen, or they are being roasted in Leeds and Nottingham." In Dundee one fire is allotted for 80 scholars, whilst in many towns the allowance is one for 60.

This difference does not depend, as we might think, on the nature of the heating-apparatus, whether open fires, stoves, large hot-water pipes at low pressure, small hot water pipes and coils at high pressure, or hot air. The difference in working cost among these systems is much smaller than it is commonly supposed. We generally assume that in an open grate from 70 to 90 per cent of the heat generated escapes uselessly up the chimney. But the figures here given are not easily reconciled with this view. Closed stoves are certainly more economical, as are also, in some cases, steam-pipes, but hot-water pipes are found in some towns more costly than open fires, though they are cheaper in others.

The working cost of heating is much influenced by the system of ventilation adopted, according as it is "natural" or "mechanical." In the former the foul air escapes by the chimney or by ventilators in the ceilings, whilst sewer-gas and ground-air are very liable to be drawn in with the entrance current. On the mechanical system, fresh air, admitted at inlets 12 to 15 feet from the ground and filtered through coarse jute cloth, is heated to the desired temperature and forced into the school-rooms by means of fans. From a sanitary point of view the mechanical system has a very decided advantage. In schools ventilated respectively on these two systems, if we take the temperature, the proportions of carbonic acid, of organic matter, and of micro-organisms in the air as 1 each, in a naturally ventilated school the temperature will be 0·66, the carbonic acid 1·7, the organic matter 7·0, and the micro-organisms 9·2. To get an equally pure atmosphere by opening windows and doors the rooms would be scourged with draughts, and during the greater part of the year they would be chilled to a dangerous degree.

The expense of the mechanical system is admittedly higher, but the perfection of the ventilation thus obtained would render school-rooms lower by one foot to two feet quite wholesome and pleasant. Thus, a very considerable economy would be effected in the building of schools. Dr. Carnelley decidedly recommends this system. His "Report" will be of great value to all persons concerned in the establishment and working of schools.

The Farmer's Guide to Manuring. By A. M. Pearson, Agricultural Chemist. Melbourne: R. S. Brain, Government Printer.

Some of the Agricultural Problems of Victoria. A Paper read before the Royal Commission on Vegetable Products. By A. M. Pearson (formerly of Bombay). Shepparton: Callandar and Co.

In the former of these pamphlets the author recognises the preponderating importance of Ville's four principles, nitrogen, phosphoric acid, potash, and lime. But he immediately adds that the farmer should simply buy the three former, as phosphoric acid is in general supplied in combination with lime. He recommends that the manures required on different soils and for different crops should be ascertained by trial plots.

In the treatise on the Agricultural Problems of Victoria he brings forward the same lesson, which is well worth putting in practice. Towards the conclusion he touches on a very important fault, not merely of the Australians, but of the British nation everywhere. They are too apt to content themselves with one or two staple products, agricultural or manufacturing, overlooking scores of minor industries which, if individually small, sum up to a mighty total. The Australian farmer makes a staple of wool, and the crops which he cultivates are generally the same as his fathers have been accustomed to grow in Britain with a yearly temperature lower by 10° F. and a very different rainfall. Mr. Pearson points out a number of products which India consumes largely, and which she imports at present to a large extent from alien countries situate at a much greater distance. Why, he asks, should not Australia supply India with wines, jams, dried fruit, olives and olive oil, pickles, &c.? He might have added that Australia should do a large export trade in silk, essential oils, cork, medicinal drugs, gums, and tanning matters. We may here remark that the cultivation of the *Pyrethrum roseum*, the plant from which "Persian Insect Powder" is made, has been successfully introduced in Victoria. We believe that the cultivation of such crops as those just enumerated must afford remunerative employment to five times as many persons as does sheep-farming. The author mentions the efficient preservation of butter and eggs for the Indian and British markets as a desideratum. Mr. Pearson's advice is most excellent. To develop the latent capabilities of all parts of the Empire and to bring them into increased connection with each other is a noble and a patriotic task.

CORRESPONDENCE.

A CHEMICAL PROBLEM.

To the Editor of the Chemical News.

Sir,—I have encountered in a sample of caustic potash, which was supplied to me as pure, a substance which has caused me an infinite amount of trouble and perplexity. The following are a few of the reactions given by this substance:—

(1). When the potash was fused with a quantity of potassium nitrate in a silver crucible, and the melt after the fusion was dissolved out by water, a peculiar looking liver-coloured matter, which collected into a spongy mass, remained undissolved, and the clear supernatant liquid, on being boiled, yielded a further small quantity of the same matter.

(2). This liver-coloured residue was easily soluble in HCl, in which it dissolved without evolution of gas.

(3). Water added to the HCl solution, even when the quantity of substance present was very minute, produced a white precipitate which was very well shown as an opalescent layer at the contact of the liquids, and which dissolved or remained permanent on shaking up the liquids according as the HCl or the H_2O was in excess. Heating also caused the precipitate to re-dissolve, even when the quantity of acid was very small. In the latter case it was re-produced as the liquid cooled.

(4). The compound dissolved in HCl could be precipitated by concentration as a white (faintly yellow—the HCl solution was amber coloured) subcrystalline salt, which dissolved in ammonium hydrate, but was immediately re-precipitated on expelling the ammonia by boiling as a white powder, which readily re-dissolved in ammonia or in HCl.

(5). The substance gave no decided bead colourations, but was (the crystals obtained by concentration from HCl solution) immediately reduced to a white, easily fusible bead in even a moderately reducing flame when placed in the flame in contact with a microsmic salt bead.

(6). Sulphuretted hydrogen in acid solutions gave a *dark brown* precipitate, almost exactly resembling the substance described in (1) in appearance.

(7). This sulphide was soluble in ammonium sulphide and also in strong hot HCl.

It is singular that the potash when H_2S was passed through it gave no precipitate (it darkened in colour), not even on adding HCl, till acid after the formation of a quantity of potassium sulphide. This makes it appear as though the action of the fused nitre had something to do with the conversion of the substance into the state in which it gives the above reactions.

I feel disposed to call this an elusive element whatever it is, and at any rate I suppose it must have eluded the manufacturer who supplies the potash as pure. I have tested it in innumerable ways, and I have had the assistance of a first class chemist, Mr. Barfoot, of Chesterfield, and at last I have been forced to conclude that the element present is a stranger.

It certainly is not antimony, bismuth, nor tin, nor is it tellurium, to which many of its reactions point, for it is not precipitated by sulphurous acid nor by a soluble sulphite under any circumstances, this test having been repeatedly tried with the utmost care.

I have collected a little of the substance and forwarded it to you in the form of sulphide, as I thought it might interest you.—I am, &c.,

R. Snowdon.

Staveley Iron Works, Chesterfield,
March 13, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 9, March 4, 1889.

Separation of Zinc and Cobalt.—H. Baubigny.—This memoir will be inserted in full.

Observations on Saccharification by Diastase.—L. Lindet.—The accumulation of maltose in worts arrests saccharification. When the maltose disappears in the state of alcohol and carbonic acid or of an insoluble phenylhydrazine compound the diastase resumes its saccharifying action upon the dextrine.

On the Phthalates; New Neutral and Acid Ethers of the Camphols.—A. Haller.—These ethers are formed under the same conditions as the succinates. The author has obtained the neutral and acid phthalates (dextro- and lævo-rotatory), and the neutral and acid racemic phthalates.

Biedermann's Central-Blatt fur Agricultur Chemie. Vol. xviii., Part 2.

The Origin of Nitric and Nitrous Acid in Nature by the Evaporation of Water, by Alkaline Substances and by the Soil in itself.—Dr. Anton Baumann.—The author mentions that every kind of calcium carbonate, thoroughly washed in water to remove any existing nitrogen compounds, and dried at a high temperature, was found to contain nitrous acid. The same phenomenon was also observed in other substances, especially in those of a basic nature. Hence it was assumed that basic substances possess the property of converting ammonia, or even atmospheric nitrogen, into nitrogen oxides. This supposition was decidedly refuted by the result of the experiments. The phenomena observed are explained by the fact that in consequence of the combustion of the coal-gas used for heating the drying-stove nitrogen acids are formed and are absorbed by basic substances. The view of Franke that the soil, in virtue of the calcium carbonate which it contains, is able to convert ammonia into nitric acid is erroneous, and is founded on imperfect experiments. — *Land. Versuchsstationen.*

Detection of Nitrates in the Soil.—Prof. Kreusler.—Frank reports that the quartz grains of soil, even after repeated washing in water, are coloured blue with sulphuric acid containing diphenylamine, whence he inferred a peculiar surface reaction of the granules, by means of which they fix nitrates. Dr. Kreusler finds that certain oxides of iron and manganese give the same reaction. The brucine reaction is produced by the higher oxides of manganese just as it is by nitrates.—*Landwith. Jahrbucher.*

Studies and Investigations on the Humoid Compounds of Arable and Moor-land Soils.—C. G. Eggertz.—The author maintains that humic and ulmic acids do not naturally occur in peat and similar products, but are artificial laboratory products. The existence of the indifferent insoluble bodies, humine and ulmine, is very doubtful, whilst the soluble compounds, crenic and creno-hydrochloric acids, doubtless exist as independent bodies. He divides the products of decay existing in the soil into two classes—*mulloids,* which may be extracted by treatment with ammonia or potassa-lye, and *humoids,* which are obtained by acting upon the carbohydrates with mineral acids. He refutes the view of Mulder, that the nitrogen of the mull-substances is exclusively present as ammonium mullate.—*Neddelanden fran konigl. Landbruks-Akademiens Experimentalfält.*

Condition of Sulphur and Phosphorus in Plants, in the Soil, and in Humus.—MM. Berthelot and André.—From the *Comptes Rendus.*

The Peats of Alsace-Lorraine and their Value in Agriculture. — Dr. Barth. — The Alsacian peats of Dambach have a much less power of absorbing ammonia and alkalies than those of Holland and of Salm. The Lorraine peats of Bitsch and Ham are useful only as a material for composts.

Action of Artificial Manures upon White Mustard.—P. Budrin and Dr. Strecker (*Journal fur Landwithschaft*).—The yield of white mustard can be much increased by the use of nitrogenous manures—preferably sulphate of ammonia—either alone or along with phosphates. The effects of kainite do not appear favourable.

Adulteration of Linseed Meal.—Dr. E. Eidam.—The adulterant is the residue of castor-oil seeds, a poisonous purgative. The recognition of this fraud is effected by means of low microscope powers, when the characteristic longitudinal marbling of the castor seeds is detected.

The Chemical Action of Some Micro-organisms.—R. Warington.—From the *Journal of the Chemical Society.*

The Occurrence of Typhus Bacilli in Soils.—E. Mace.—From the *Comptes Rendus.*

Chemical Composition of Farmyard Manure.—F. Sestini (*Chem. Centralblatt*).—The author's results deviate in many cases widely from the accepted averages.

Adulteration of Bone-meal with Mineral Phosphates.—N. von Lorenz (*Oester. Ung. Zeitschrift fur Rubenzucker Industrie*).—The author's method turns on the recognition of fluorine in the mineral phosphates.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. iii., No. 33.

Utilisation of Sewage.—An account of the Berlin irrigation works. It is remarked that at least one hectare of irrigation ground is required to absorb and utilise the sewage of 250 persons, and the authorities hope to reduce the proportion to 200 persons. The land cannot be continuously treated with sewage, which would injure the crops and create sediments. Fields of cereals receive sewage only three or four times yearly, and not at all after the plant has germinated. Vegetables may be irrigated three or four times weekly.

Journal de Pharmacie et de Chemie. Vol. xix., No. 5.

New Proximate Principle in the Ergot of Rye.—Ergosterine, the principle in question, has been confounded with the cholesterine of animals. It has the composition $C_{52}H_{40}O_2,H_2O_2$. It crystallises from alcohol in nacreous tablets, and from ether in fine needles. It is quite insoluble in water and dissolves in 500 parts of cold alcohol at 96 per cent, and in 32 parts at the temperature of ebullition; in 45 parts of cold chloroform and in a few parts of the same liquid when hot. It melts at 154°, and boils in a vacuum at 185°. It is dextro-rotatory, and its specific gravity is 1·040. Ergosterine is slowly oxidised in contact with air, becoming coloured and odoriferous. It is not attacked by strong boiling alkaline solutions. It is a monoatomic alcohol. If treated with nitric or hydrochloric acid and ferric chloride ergosterine gives the coloured reactions of cholesterine, but its reaction with sulphuric acid and chloroform is quite different. Strong sulphuric acid colours cholesterine brown and dissolves it incompletely, and agitation with chloroform extracts the greater part of the coloured product and turns orange-yellow, passing into red and violet on exposure to the air. Ergosterine, on the contrary, dissolves completely in the acid, and chloroform, if shaken up with the mixture, remains almost colourless.

The Sap of *Bassia latifolia*.—E. Heckel and Fr. Schlagdenhauffen.—The *Bassia latifolia* or Mohwa is a large sapotaceous tree, very common in India, and yields a small quantity of sap capable of furnishing gutta-percha, though only to the extent of 1·8 per cent.

Commercial Oleic Acid; its Falsification with Linoleic Acid; the Industrial Inconvenience of this Fraud and the Means for its Detection.—MM. Granval and Valser.—If the sophisticated oleic acid is used in spinning woollen yarns, no harm ensues if the yarns are woven at once; but if the yarns remain exposed for some weeks to air and light they assume a strong yellow colour, which cannot be removed. Besides, the the thread becomes rougher and glutinous, and occasions much waste and trouble in weaving. If we mix a few drops of the sophisticated oleic acid with an equal volume of soda-lye an intense yellow colour is produced, whilst pure oleic acid, if similarly treated, merely takes a grey colour. If we spread upon a plate of lead, previously scraped clean, a thin layer of oleic acid containing linoleic acid, and place for comparison a similar layer of pure oleic acid upon another plate of lead, the next morning the impure acid will be more or less completely resinified, whilst the pure acid is scarcely altered.

A New Reagent for Free Hydrochloric Acid in the Gastric Juice.—Dr. Boas.—The author prepares a solution containing, in 100 parts of dilute alcohol, 5 parts of resorcine and 3 parts of cane-sugar. Two or three drops of this reagent are added to five or six drops of gastric juice, and the mixture is heated in a porcelain capsule over a very small flame. After complete evaporation a rose-coloured or bright red coating is seen on the sides of the capsule if hydrochloric acid is present. If the heat is too strong the sugar is carbonised and the reaction may be masked. Albumenoid matters interfere by totally or partially neutralising the acid.—*Pharm. Zeitung.*

New Method of Determining Hydrochloric Acid in the Gastric Juice.— J. Sjögvist.—If gastric juice, mixed with barium carbonate, is evaporated to dryness the free acids are converted into barium salts. If the mixture is ignited the barium chloride undergoes no change, whilst the barium salts of the organic acids are re-converted into carbonate. The ash is exhausted with water, the chloride is dissolved out, and the barium in solution is determined volumetrically with potassium bichromate in presence of acetic acid. Tetramethylparaphenylenediamine paper may be used as an indicator.—*Zeitschrift für Physiologische Chemie.*

MISCELLANEOUS.

Treatise on Manures. — Dr. A. B. Griffiths's "Treatise on Manures" will be published in a few days by Messrs. Whittaker and Co., of Paternoster Square.

The Chemical Laboratory of Wiesbaden.—In the winter term 1888 to 1889 there were 58 students on the books. Of these, 38 were from Germany, 5 from England, 4 from North America, 3 from Sweden, 3 from Russia, 2 from Spain, 1 from Holland, 1 from France, and 1 from Italy. Besides the directors, Geh. Hofrath Prof. R. Fresenius, there are engaged as teachers Prof. Dr. H. Fresenius, Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. F. Hueppe, and Architect F. Brahm. The assistants in the Instruction Laboratory are 2 in number, in the Private Laboratory 15, and in the Versuchstation 3. Besides the scientific researches a great number of analyses were undertaken in the different departments of the Laboratory and the Versuchstation 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 advertising columns.

Iron Oxide Paint.—The ingredients can probably be obtained from Herring's, 40, Aldersgate Street, E.C.—G. A. Keyworth, Hastings.

Iron Oxide Paint.—Noticing in your last issue a query as to where the raw material for iron oxide paint can be obtained, we beg to inform you that we are makers of a pure quality of levigated iron oxide testing over 94 per cent iron, calculated as Fe_2O_3. This is ready for use by paint-makers, requiring only the addition of boiled oil.—Brooke, Simpson, and Spiller (Limited).

White Glaze for Bricks, &c.—I shall feel obliged if any reader of the Chemical News will advise me what book to get which will give me reliable information on this subject. I am acquainted with the manufacture and use of coloured glazes; but the white glazes I have tried have unequal expansion and contraction with the body of the brick, and in consequence crack in fine network fissures.—A Potter.

MEETINGS FOR THE WEEK

Monday, 25th.—Medical, 8.30.
—— Society of Arts, 8. Cantor Lectures. "Instruments for the Measurement of Radiant Heat," by C. V. Boys, F.R.S.

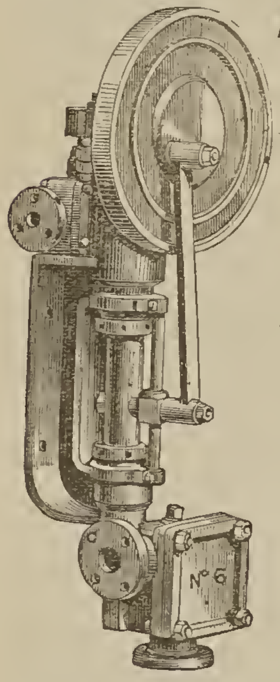
Tuesday, 26th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin —II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Royal Medical and Chirurgical, 8.30.
—— Sanitary Institute, 8. "Sanitary Appliances," by Prof. W. H. Corfield.
—— Society of Arts, 8. "Borneo," by Robert Pritchett

Wednesday, 27th.—Society of Arts, 8. "Objects and Methods of the Society of Arts' Motor Trials," by Prof. A. B. W. Kennedy, F.R.S. (Adjourned Discussion).

Thursday, 28th.—Royal, 4.30.
—— Royal Institution, 3. "Houses and their Decoration from the Classical to the Mediæval Period," by Prof. J. Henry Middleton, M.A.
—— Institute of Electrical Engineers, 8.
—— Chemical, 8. (Anniversary Meeting). Address by the President on "Recent Researches on the Rare Earths as Interpreted by the Spectroscope." Election of Office Bearers and Council

Friday, 29th.—Royal Institution, 9. "Yeast," by A. Gordon Salamon, F.C.S.
—— Society of Arts, 8. "The Progress of the Railways and Trade of India," by Sir Juland Danvers.
—— Sanitary Institute, 8. "Food (including Milk), Sale of Food and Drugs Act," by C. E. Cassal, F.C.S.

Saturday, 30th.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.


Nº 6

THE CHEMICAL NEWS.

Vol. LIX. No. 1531.

ON THE COMPOSITION OF WATER.*

By Lord RAYLEIGH, Sec.R.S.

During the past year I have continued the work described in a former communication on the relative densities of hydrogen and oxygen,† in the hope of being able to prepare lighter hydrogen than was then found possible. To this end various modifications have been made in the generating apparatus. Hydrogen has been prepared from potash in place of acid. In one set of experiments the gas was liberated by aluminium. In this case the generator consisted of a large closed tube sealed to the remainder of the apparatus; and the aluminium was attached to an iron armature so arranged that by means of an external electro-magnet it was possible to lower it into the potash or remove it therefrom. The liberated gas passed through tubes containing liquid potash,‡ corrosive sublimate, finely powdered solid potash, and, lastly, a long length of phosphoric anhydride. But the result was disappointing, for the hydrogen proved to be no lighter than that formerly obtained from sulphuric acid.

I have also tried to purify hydrogen yet further by absorption in palladium. In his recent important memoir,§ "On the Combustion of Weighed Quantities of Hydrogen and the Atomic Weight of Oxygen," Mr. Keiser describes experiments from which it appears that palladium will not occlude nitrogen—a very probable impurity in even the most carefully prepared gas. My palladium was placed in a tube sealed, as a lateral attachment, to the middle of that containing the phosphoric anhydride, so that the hydrogen was submitted in a thorough manner to this reagent both before and after absorption by the palladium. Any impurity that might be rejected by the palladium was washed out of the tube by a current of hydrogen before the gas was collected for weighing. But as the result of even this treatment I have no improvement to report, the density of the gas being almost exactly as before.

Hitherto the observations have related merely to the densities of hydrogen and oxygen, giving the ratio 15·884, as formerly explained. To infer the composition of water by weight, this number had to be combined with that found by Mr. Scott as representing the ratio of volumes. The result was—

$$\frac{2\times 15{\cdot}884}{1{\cdot}9965}=15{\cdot}914.$$

The experiments now to be described are an attempt at an entirely independent determination of the relative weights by actual combustion of weighed quantities of the two gases. It will be remembered that in Dumas's investigation the composition of water is inferred from the weights of the oxygen and of the water, the hydrogen being unweighed. In order to avoid the very unfavourable conditions of this method recent workers have made it a point to weigh the hydrogen, whether in the gaseous state, as in the experiments of Professor Cooke and my own, or occluded in palladium, as in Mr. Keiser's practice. So long as the hydrogen is weighed, it is not very material whether the second weighing relate to the water or to the oxygen. The former is the case in the work of Cooke and Keiser, the latter in the preliminary experiments now to be reported.

Nothing could be simpler in principle than the method adopted. Globes of the same size as those employed for the density determinations are filled to atmospheric pressure with the two gases, and are then carefully weighed. By means of Sprengel pumps the gases are exhausted into a mixing chamber, sealed below with mercury, and thence, by means of a third Sprengel, are conducted into a eudiometer, also sealed below with mercury, where they are fired by electric sparks in the usual way. After sufficient quantities of the gases have been withdrawn, the taps of the globes are turned, the leading tubes and mixing chamber are cleared of all remaining gas, and, after a final explosion in the eudiometer, the nature and amount of the residual gas are determined. The quantities taken from the globes can be found from the weights before and after operations. From the quantity of that gas which proved to be in excess the calculated weight of the residue is subtracted. This gives the weight of the two gases which actually took part in the combustion.

In practice, the operation is more difficult than might be supposed from the above description. The efficient capacity of the eudiometer being necessarily somewhat limited, the gases must be fed in throughout in very nearly the equivalent proportions; otherwise there would soon be such an accumulation of residue that no further progress could be made. For this reason nothing could be done until the intermediate mixing chamber was provided. In starting a combustion this vessel, originally full of mercury, was charged with equivalent quantities of the two gases. The oxygen was first admitted until the level of the mercury had dropped to a certain mark, and subsequently the hydrogen down to a second mark, whose position relatively to the first was determined by preliminary measurements of volume. The mixed gases might then be drawn off into the eudiometer until exhausted, after which the chamber might be re-charged as before. But a good deal of time may be saved by replenishing the chamber from the globes simultaneously with the exhaustion into the eudiometer. In order to do this without losing the proper proportion, simple mercury manometers were provided for indicating the pressures of the gases at any time remaining in the globes. But even with this assistance close attention was necessary to obviate an accumulation of residual gas in the eudiometer, such as would endanger the success of the experiment, or, at least, entail tedious delay. To obtain a reasonable control, two sparking places were provided, of which the upper was situate nearly at the top of the eudiometer. This was employed at the close, and whenever in the course of the combustion the residual gas chanced to be much reduced in quantity; but, as a rule, the explosions were made from the lower sparking point. The most convenient state of things was attained when the tube contained excess of oxygen down to a point somewhat below the lower sparking wires. Under these circumstances each bubble of explosive gas readily found its way to the sparks, and there was no tendency to a dangerous accumulation of mixed gas before an explosion took place. When the gas in excess was hydrogen the manipulation was more difficult, on account of the greater density of the explosive gas retarding its travel to the necessary height.

In spite of all precautions several attempted determinations have failed from various causes, such as fracture of the eudiometer and others which it is not necessary here to particularise, leading to the loss of much labour. Five results only can at present be reported, and are as follows:—

December 24, 1888	.. ..	15·93
January 3, 1889	.. ..	15·98
,, 21, ,,	.. ..	15·98
February 2, ,,	.. ..	15·93
,, 13, ,,	.. ..	15·92
Mean	.. ..	15·95

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* A Paper read before the Royal Society, March 7, 1889.

† *Roy. Soc. Proc.*, February, 1888 (vol. xliii., p. 356).

‡ Of course this tube was superfluous in the present case, but it was more convenient to retain it.

§ *Am. Chem. Jour.*, vol. x, No. 4.

This number represents the atomic ratio of oxygen and hydrogen as deduced immediately from the weighings with allowance for the unburnt residue. It is subject to the correction for buoyancy rendered necessary by the shrinkage of the external volume of the globes when internally exhausted, as explained in my former communication.* In these experiments the globe which contained the hydrogen was the same (14) as that employed for the density determinations. The necessary correction is thus four parts in a thousand, reducing the final number for the atomic weight of oxygen to—

$$15{\cdot}89,$$

somewhat lower than that which I formerly obtained (15·91) by the use of Mr. Scott's value of the volume ratio. It may be convenient to recall that the corresponding number obtained by Cooke and Richards (corrected for shrinkage) is 15·87, while that of Keiser is 15·95.

In the present incomplete state of the investigation, I do not wish to lay much stress upon the above number, more especially as the agreement of the several results is not so good as it should be. The principal source of error of a non-chemical character is in the estimation of the weight of the hydrogen. Although this part of the work cannot be conducted under quite such favourable conditions as in the case of a density determination, the error in the difference of the two weighings should not exceed 0·0002 grm. The whole weight of the hydrogen used is about 0·1 grm.;† so that the error should not exceed three in the last figure of the final number. It is thus scarcely possible to explain the variations among the five numbers as due merely to errors of the weighings.

The following are the details of the determination of February 2, chosen at random:—

Before combustion—

$$G_{14}+H+0{\cdot}2906=G_{11} \qquad \text{pointer } 20{\cdot}05$$

After combustion—

$$G_{14}+H+0{\cdot}4006=G_{11} \qquad \text{pointer } 20{\cdot}31$$

$$\text{Hydrogen taken}=0{\cdot}1100-0{\cdot}00005=0{\cdot}10995 \text{ grm.}$$

Before combustion—

$$G_{13}+O=G_{11}+2{\cdot}237 \qquad \text{pointer } 20{\cdot}00$$

After combustion—

$$G_{13}+O=G_{11}+1{\cdot}357 \qquad \text{pointer } 19{\cdot}3$$

$$\text{Oxygen taken}=0{\cdot}8800+0{\cdot}0001=0{\cdot}8801 \text{ grm.}$$

At the close of operations the residue in the eudiometer was oxygen, occupying 7·8 c.c. This was at a total pressure of of 29·6 − 16·2 = 13·4 inches of mercury. Subtracting 0·4 inch for the pressure of the water vapour, we get 13·0 as representing the oxygen pressure. The temperature was about 12° C. Thus, taking the weight of a c.c. of oxygen at 0° C., and under a pressure of 76·0 c.m. of mercury to be 0·00143 grm., we get, as the weight of the residual oxygen—

$$0{\cdot}00143\,\frac{7{\cdot}8}{1+12\times0{\cdot}00367}\,\frac{13{\cdot}0\times2{\cdot}54}{76{\cdot}0}=0{\cdot}0046 \text{ grm.}$$

The weight of oxygen burnt was, therefore,—

$$0{\cdot}8801-0{\cdot}0046=0{\cdot}8755 \text{ grm.}$$

Finally, for the ratio of atomic weights—

$$\frac{\text{Oxygen}}{\frac{1}{2}\text{ Hydrogen}}=15{\cdot}926$$

In several cases the residual gas was subjected to analysis. Thus, after the determination of February 2, the volume was reduced by additions of hydrogen to 1·2 c.c. On introduction of potash there was shrinkage to about 0·9, and, on addition of pyrogallic acid, to 0·1 or 0·2. These volumes of gas are here measured at a pressure of ⅓ atmosphere, and are, therefore, to be divided by 3 if we wish to estimate the quantities of gas under standard conditions. The final residue of (say) 0·05 c.c. should be nitrogen, and, even if originally mixed with the hydrogen—the most unfavourable case—would involve an error of only 1-2000th in the final result. The 0·1 c.c. of carbonic anhydride, if originally contained in the hydrogen, would be more important; but this is very improbable. If originally mixed with the oxygen, or due to leakage through indiarubber into the combustion apparatus, it would lead to no appreciable error.

The aggregate impurity of 0·15, here indicated, is tolerably satisfactory in comparison with the total quantity of gas dealt with — 2000 c.c. It is possible, however, that nitrogen might be oxidised, and thus not manifest itself under the above tests. In another experiment the water of combustion was examined for acidity, but without definite indications of nitric acid. The slight reddening observed appeared to be rather that due to carbonic acid, some of which, it must be remembered, would be dissolved in the water. These and other matters demand further attention.

The somewhat complicated glass blowing required for the combustion apparatus has all been done at home by my assistant, Mr. Gordon, on whom has also fallen most of the rather tedious work connected with the evacuation of globes and other apparatus, and with the preparation of the gases.

A METHOD OF EXAMINING RATE OF CHEMICAL CHANGE IN AQUEOUS SOLUTIONS.*

By G. GORE, LL.D., F.R.S.

This research supplies an outline of a method of examining chemical change, based upon the application of the "voltaic balance" to measuring the relative amounts of voltaic energy of electrolytes (see *Roy. Soc. Proc.*, vol. xliv., pp. 151, 294; *Ibid.*, vol. xlv., p. 268), and the rate of chemical change is indicated by alterations in amount of such energy.

The author gives an example of two liquids, viz., a solution of equivalent proportions of potassic iodide and chlorine, and one of chloride of potassium and iodine, which, although having the same ultimate chemical composition, are greatly different, viz., as 31·76 to 1·0, in amount of voltaic energy.

The results of the experiments show that the solution of potassic iodide and chlorine was very unstable, highly sensitive to rise of temperature, had a great tendency to lose its voltaic energy, to change its chemical composition, and approach that of the other mixture. That the solution of the latter was very much more stable and much less sensitive to heat, but had a feeble tendency to absorb energy, to change its chemical composition, and approach that of the solution of potassic iodide and chlorine. The effect, therefore, of heating both liquids was to produce two portions possessing similar chemical composition and properties, consisting of about 0·23 part of potassic iodide, 74·49 of potassic chloride, 126·8 of iodine, and 0·0497 of chlorine. They also show that the solution of potassic iodide and chlorine decomposes spontaneously at 12° C. into potassic chloride and free iodine; that more than six days are necessary to effect the complete chemical change at that temperature; and that the rate of chemical

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* The necessity of this correction was recognised at an early stage, and, if I remember rightly, was one of the reasons which led me to think that a re-determination of the density of hydrogen was desirable. In the meantime, however, the question was discussed by Agamennone ("Atti (Rendic nti) d. R. Acad. dei Lincei," 1885), and some notice of his work reached me. When writing my paper last year I could not recall the circumstances; but since the matter has attracted attention I have made inquiry, and take this opportunity of pointing out that the credit of first publication is due to Agamennone.

† It was usual to take for combustion from two-thirds to three-fourths of the contents of the globe.

* Abstract of a Paper read before the Royal Society, March 14, 1889.

change is much greater at the commencement of the action than towards its termination.

The collective results show that the "voltaic balance" method may be used to detect chemical changes of aqueous solutions and to measure their rate. Its great advantage over the colorimetric method is that it is equally applicable to colourless liquids; it is much more sensitive and exact usually than either the colorimetric or the thermo-chemical method, and it is quick and easy of performance. It is being used to detect and measure chemical changes produced by light in aqueous solutions. The degree of freedom of an aqueous solution of chlorine from hydrochloric acid and of iodine from hydriodic acid was ascertained much more readily by this method than by ordinary chemical analysis.

ON THE
SEPARATION OF ZINC AND COBALT.

By H. BAUBIGNY.

THE author has already shown how accurately zinc and nickel can be separated in an acid solution by means of sulphuretted hydrogen. He has also shown that in a distinctly acid solution the salts of cobalt are less easily transformed into sulphide than those of nickel, whence there was room to think that the method which had succeeded with nickel might be equally applicable to cobalt in presence of zinc. Experiment, however, showed that it is often defective. The process is accurate only if we have little cobalt in proportion to the zinc, 5 to 6 per cent at the most. Otherwise the precipitate of zinc contains cobalt and takes a watery green colour, due to the existence of a compound of the two sulphides of zinc and cobalt, which is, among sulphides, analogous to Rinman's green among the oxides. For if we mix weights of the sulphides of zinc and cobalt equal to those contained in the precipitate formed in the zinco-cobaltic liquid we have a blackish grey product. This green sulphide may in some cases contain as much as three or four per cent of its weight of cobalt sulphide.

If we operate as in the case of nickel, and even raise the percentage of acetic acid in the solution for a synthetic mixture of 0·249 grm. $ZnSO_4$ and 0·250 grm. $CoSO_4$, the green sulphide formed, and filtered after standing an hour at 16° gave 0·256 grm. of rose-coloured $ZnSO_4$, which, when treated anew by the same method, was resolved into 0·249 grm. $ZnSO_4$ and 0·007 $CoSO_4$.

If the proportion of zinc is notably increased, the weight of the cobalt sulphide precipitated with that of zinc increases, and in this case the sulphide turns black in less than an hour. This takes place with a mixture of 0·037 grm. $ZnSO_4$ and 0·4625 grm. $CoSO_4$ in an acetic solution of 25 per cent. After standing for sixteen hours the weight of the CoS formed was 0·130 grm. $CoSO_4$, or about 30 per cent of the cobalt taken for the experiment.

The action, therefore, varies with the nature of the elements, nickel or cobalt, placed in presence of zinc even under conditions where sulphuretted hydrogen alone acts neither on the salts of nickel nor those of cobolt—a fact not unprecedented in the history of the sulphides.

In any case the comparison of the two last experiments leads us to conclude that zinc sulphide, even in small quantities, is capable of provoking the decomposition of cobalt sulphate in the cold, in presence of sulphuretted hydrogen, and in a strongly acetic solution if there is not at the beginning of the experiment a decided quantity of free sulphuric acid. The author then sought to solve the problem of the separation of cobalt and zinc by taking as free acid sulphuric acid, suitably diluted, so as not to hinder the total precipitation of the zinc, confining himself, however, to the case where the weight of the free acid is about equal to that of the acid existing in combination in the salts present. Under such conditions, and letting the sulphide formed settle for three hours at 16° the following results were obtained:—

Mixture in 400 c.c.

	Taken.	Found.
$ZnSO_4$..	0·055 grm.	0·055 grm.
$CoSO_4$..	0·468 ,,	0·4685 ,,
SO_3 (free)	0·262	

If the weights found are satisfactory the cobalt sulphide had still a very faint green tint and the zinc sulphide a rose. These colours were due to slight traces of cobalt of about the tenth of a milligrm., so that the separation is evidently not absolute. Experiment shows that in the case of a mixture of the same total weight—about half a grm.—if the quantities of the two metals are less unequal the deviation between the weight of the salts taken and those found may extend to 2 m.grms. (in excess for zinc sulphate and in deficiency for cobalt) and increases in larger weights.

The green tint which zinc sulphide takes if formed in presence of considerable quantities of salts of cobalt has never been previously mentioned; still it may be observed on using citric and oxalic acids, which have been recommended by various authorities in reliance upon the different action of sulphuretted hydrogen upon the corresponding salts of zinc and cobalt in solutions acidulated with an excess of the same acid. This fact is not surprising, since sulphuric and nitric acids leave the chemist to encounter the same difficulties.

Cobalt and zinc, even as sulphates, cannot be accurately separated by sulphuretted hydrogen in presence of a small excess of free sulphuric acid, except the quantity of cobalt is relatively small. The separation is still sufficiently approximate if there is, on the other hand, very little zinc. But, except under these restrictions, the best method for obtaining a correct determination is to reconvert the zinc precipitate into sulphate, and submit it to a second determination. The author will subsequently give the conditions for separating zinc from nickel and cobalt by the dry way. It depends on the absolute fixity of nickel and cobalt chlorides at the boiling-heat of sulphur, whilst, at the same heat, zinc chloride has a considerable vapour-tension.—*Comptes Rendus* (vol. cviii., p. 450).

ON THE
TRUE FORMULA FOR PERMANGANATES.[*]

By CHARLES M. BRADBURY, of Virginia.

(Concluded from p. 138).

(1).

The Specific Heats of Potassium Permanganate and Potassium Perchlorate.

ACCORDING to the law of Dulong and Petit, the specific heats of elements in the solid state vary inversely as their atomic weights. In the present state of chemistry this law is received with reservations, yet a high degree of probability attaches to deductions from it.[†]

Although the fact established by Kopp,[‡] that the molecular heats of compounds are the sums of the atomic heats of their constituent elements, cannot be directly applied to fixing molecular weights by means of specific heats; yet it has been observed, in connection with the specific heats of solid compounds, that there is in general an inverse variation between their specific heats and

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[*] Dissertation presented to the Faculty of the University of Virginia in application for the degree of Doctor of Philosophy. *Thesis*:—Permanganic acid is monobasic, and the permanganates are represented by the general formula $\overset{n}{R}(MnO_4)n$.

[†] R. and S., II., i., 16.

[‡] R. and S., II., i., 20.

molecular weights, similar to that established by Dulong and Petit for the solid elements, *where the substances compared are of analogous composition.** Without assuming any closer analogy between permanganates and perchlorates than is actually revealed by analysis (thus leaving the question of the molecular weight of the former open), it would seem fair to expect from them conformity to this rule; for the only difference that analysis shows is the replacement of manganese in the one salt by chlorine in the other.†

It follows, then, that if the specific heats of potassium perchlorate and potassium permanganate as determined by experiment are nearly alike, their molecular weights will also be similar. According to Kopp,‡ the specific heat of potassium permanganate is 0·179; that of potassium perchlorate, 0·190. The molecular weight of $KClO_4$ is 138·25; that of potassium permanganate should, then, be somewhere near $(138·25 \times \frac{190}{179} =)$ 147+. But the formula $K_2Mn_2O_8$ requires a molecular weight of 314·42. By taking the formula $KMnO_4$ with half of this molecular weight there is an evident agreement (even though it be not very close) between the molecular weight as usually calculated, and as indicated by specific heat, *i.e.*, 157·21 and 147 + respectively.

(2).

The Specific Volume Relations.

The isomorphism of perchlorates with permanganates was announced by Mitscherlich,§ who made comparative measurements of the two classes of crystals. His results have been very generally received and confirmed by subsequent investigators.

According to the general law that *isomorphous compounds have equal specific volumes, while those whose crystal forms are approximately the same have also approximately equal specific volumes*,‖ the specific volumes of potassium perchlorate and potassium permanganates must be very nearly the same. But if $K_2Mn_2O_8$ be the correct formula for the permanganate, this is not the case; for the specific gravity of potassium permanganate is 2·644,¶ giving a specific volume (with this formula) of (314·42/2·644=) 118·9; whilst the specific gravity of the perchlorate is 2·47,¶ which gives a specific volume of (138·25/2·47=) 55·9. It is evident that this wide difference disappears when the formula $KMnO_4$ is substituted for $K_2Mn_2O_8$. The specific volume of potassium permanganate then becomes 59·4, which is not far from 55·9.

(3).

The General Chemical Relation of Isomorphous Bodies.

The relation referred to is thus concisely expressed by Richter:** "From the isomorphism of two compounds may be concluded an analogous chemical composition, a similar number of atoms in the molecule." This statement is qualified in its context as accuracy requires. With all necessary limitations, it yet adds something to the evidence which, as a whole, points so unmistakably to the monobasic character of permanganic acid and the heptad valence of the manganese in it. Potassium permanganate must, like potassium perchlorate, contain six and not twelve atoms in its molecule.

This paragraph, of course, is practically the same as the preceding, but presents the argument in more general form. As both are dependent on the isomorphism of the two salts compared, it should be noted that it is not essential to their validity that this isomorphism should be perfect, which is probably not the case. No investigator has been found, however, to deny at least a general isomorphism between the two classes of salts. Mitscherlich stated that the primitive form of both permanganate and perchlorate of potash is the right rhombic prism,* and this was afterwards alluded to by Gmelin, curiously enough, as an exception to the recognised rule that isomorphism argues chemical similarity, on the ground that "manganese bears no relation to chlorine."† That manganese does bear relations to chlorine is, as has been remarked, an unavoidable inference from the periodic system.

SUMMARY AND CONCLUSION.

It appears from the foregoing that there has not been, and is not now, any tangible proof in the shape of double salts to show that permanganic acid is dibasic; but that unless manganese be regarded as heptad in this acid, the monobasic formula is abnormal. But it is tolerably clear that manganese may be so regarded, notwithstanding its artiad character in most of its compounds; and it follows that the monobasic formula does not violate any law of chemistry, and being the simpler of the two should, according to the law of parcimony, be given precedence of the dibasic for this reason alone. In addition to this, however, it has been shown that the relations of permanganic acid to another acid known to be monobasic point conclusively to the monobasic formula as the only correct one; the relations, namely, between its potassium salt and that of perchloric acid with regard to (1) specific heat, (2) specific volume, and (3) crystal form.

The above arguments are not offered as a rigid demonstration of the thesis. The intrinsic difficulties of the subject are such as well nigh forbid an unanswerable course of reasoning, since the evidence is to a large extent merely negative in character. Nevertheless, the accumulated weight of the facts adduced in favour of the thesis—the facts of experiment, of authority, and of chemical law—are such as give to it a degree of probability that is only short of actual certainty.

ADDENDUM.

Dr. Auwers, of Göttingen, has recently given special attention to Raoult's method of determining molecular weights by observing the freezing-points of solutions. His published results have been obtained from organic substances, and with other solvents than water; and although M. Raoult himself seems to have determined "depression-coefficients" for various inorganic substances, I have not been able to find any detailed account of his work. It seemed worth while, therefore, to make an examination, even though a very brief one (as it necessarily was, owing to pressure of other work), of the relations between the freezing-points of solutions of substances whose molecular weights are well known, and of potassium permanganate.

Seven salts of potassium were examined—K_2SO_4, $KHCO_3$, K_2CrO_4, KNO_3, $KClO_3$, KIO_3, and $KClO_4$. In each case an accurately weighed portion (either one or two grms.) was dissolved in 100 molecules of water, or at the least multiple of 100 molecules that would dissolve it readily, and the solution was then frozen, the temperature of solidification being carefully noted. Where 200, 300, &c., molecules of water were used instead of 100, the observed depressions were multiplied by 2, 3, &c., respectively, since, other things being equal, the depression varies inversely as the amount of the solvent. The values thus found were as follows:—

	A.
1. K_2SO_4	2·38
2. $KHCO_3$	1·86
3. K_2CrO_4	2·60
4. KNO_3	1·65
5. $KClO_3$	1·73
6. KIO_2	2·00
7. $KClO_4$	1·80
Average value of T ..	2·00

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* "Watts' Dict.," iv., 36.

† Cf. Mitscherlich, *Ann. Chem. Phar.*, ii., 10; Serullas, *Ann. Chim. Phys.* (2), xlvi., 303; Mitscherlich, *Ann. Chim. Phys.*, xlix., [illegible]3.

‡ "Watts' Dict.," 1st Supp., 667.

§ *Ann. Chim. Phys.* (2), xlix , 129.

‖ "Fownes' Chem.," 232. Also "Watts' Dict."

¶ See "Notes on Work" (1), infra.

** "Inorganic Chemistry," 251.

* *Ann. Chem. Pharm.*, ii., 9.

† "Handb. of Chem.," i., 88.

If we reject the first three salts from consideration, on the ground that they are dibasic and not analogous to the others, the average value of T becomes 1·80.

Three separate solutions of potassium permanganate were made, of uniform strength, *i.e.*, 2 grms. of permanganate in 136·7 c.c. of water, or 600 molecules of water to 1 molecule of permanganate, supposing the permanganate to be $KMnO_4$. The solutions were frozen, and the *observed* depressions of the freezing-point below 0° C. were 0·33°, 0·32°, and 0·35°, an average of 0·33⅓°.

Supposing the true formula of the salt to be $K_2Mn_2O_8$, it is evident that the amount of water used was not really 600 molecules to one of the permanganate, but 1200, since on this hypothesis the same weight of the salt would have only half the number of molecules. Hence the observed depression, 0·33⅓°, must be regarded as $\frac{1}{12}$ of T, and T = 4·00.

Such a value of T is altogether in excess of any other value found, even for the salts known to be dibasic.

If, however, $KMnO_4$ be the correct formula, T becomes 2·00, which is exactly the average value for all the salts examined, and is not much greater than the average value (1·80) for the monobasic salts.

Hence, $KMnO_4$ is the true formula, and permanganic acid is monobasic.

NOTES ON WORK.

(1). *The Specific Gravities of Potassium Permanganate and Potassium Perchlorate.*

In selecting a liquid in which to take these specific gravities, the use of water being impossible, it was, of course, necessary not only that it should not dissolve the permanganate, but that it should be free from reducing action on that very easily decomposable salt. Refined petroleum was found to answer the purpose admirably. The liquid used was an illuminating oil of the best grade known as "Pratt's Astral Oil." Its sp. gr. at 20° C. was found to be 0·793. The crystals of permanganate were crushed to a rather coarse powder; 1·24 grms. were put into a miniature flask of about 25 m.m. diameter with long, gradually tapering neck, then covered with the oil, and gently agitated till free from air bubbles. The flask was next immersed in a bath of water at about 18° C.; it was roughly filled with oil at that temperature from another vessel already in the bath, and the whole was raised to exactly 20°. The liquid in the neck of the flask was carefully brought to the level of the mark with a very fine pipette. The flask was then removed, wiped dry, set in the balance-case for a quarter of an hour, and weighed. Similar precautions were observed in all of the filling and weighings.

The sp. gr. of the permanganate relative to the oil was found to be 3·334: which reduced to the standard of distilled water at 20° C., gives 2·644.

The sp. gr. of the perchlorate was taken in the same way. It was found to be 2·470.

(2). *The Preparation of Barium Permanganate.*

The manufacture of barium manganate, preparatory to converting it into permanganate, was found to be hardly so simple a matter as might be inferred from the language of many of the books. It is necessary to have the materials present in as nearly the right proportion as may be, a large excess of manganese dioxide preventing the formation of the manganate. The temperature must be properly regulated, otherwise no manganate is formed or, on the other hand, it is decomposed by excessive heat. Lastly, the reaction is very sensibly aided by blowing air into the crucible. This is in accordance with the observation of Desclabissac ("Watts' Dictionary," vii., 771), that contact of air is essential to the formation of good oxidation products, oxidising salts alone not being sufficient.

After several attempts with unsatisfactory results (including exposure of the material in a shallow tray in the muffle) nitrate of barium and manganese dioxide were taken in proportion of their molecular weights, the reaction—

$$Ba(NO_3)_2+MnO_2=BaMnO_4+2NO_2$$

—being assumed. That is, three parts of barium nitrate and one of manganese dioxide were finely pulverised, intimately mixed and placed in a No. 10 Beaufay crucible. The crucible was loosely covered with an iron sand-bath, through the middle of which was introduced an iron pipe reaching to the bottom of the crucible and connected with a small foot-bellows. The crucible was then placed in the wind-furnace and heated to bright redness, a current of air (sufficiently gentle to avoid blowing out the loose powder) being meanwhile kept up. The contents of the crucible now became liquid, and the air was briskly bubbled through. In a few minutes the mass stiffened. The current of air and the bright red heat were continued, however, for about three-quarters of an hour longer, at the end of which time a homogeneous mass of brilliant green manganate was found. Another charge, during the fusion of which the air-pipe became stopped, was duller in colour and not homogeneous. The same was true of a previous charge in which the air-blast was not used.

The manganate was pulverised and converted into permanganate with carbon dioxide, as usual.

(3). *Attempt to Prepare Sodium Manganate.*

It is stated in "Watts's Dictionary (iii., 818) on the authority of Gentele, that manganate of soda is produced when equal parts of finely pulverised manganese dioxide and sodium nitrate are heated to bright redness, in a muffle, for sixteen hours. Wöhler, however, is quoted as denying that any manganate can be formed in this way, for the reason that "the nitrate is entirely decomposed before the temperature is attained at which it can act on the manganese dioxide," and (we must infer) the remaining caustic soda, unlike caustic potash under similar circumstances, does not act on the manganese dioxide.

I followed the directions of Gentele with care, using a tray of Russia iron to hold the mixture of the two salts; but the result was entirely in accordance with Wöhler's statement. Within a half-hour after introducing the tray into the muffle, nearly all visible action had ceased; and after the sixteen hours of heating to bright redness had passed, the tray contained nothing but manganese dioxide and caustic soda.

It seemed possible that by heating the MnO_2 to redness and throwing into the fused nitrate, combination might be brought about. The attempt was made with the aid of the air-blast and wind-furnace used in the preparation of the barium salt, but even thus no manganate was formed. Lack of time forbade further experiments at the furnace, and the sodium permanganate wanted was easily made by mixing solutions of barium permanganate and sodium sulphate.

(4). *The Solubility of Potassium Permanganate.*

Not finding an extended statement of this solubility in any work to which I had access, I undertook to determine it.

A flat porcelain dish, about 6 c.m. deep and 25 in diameter, was covered outside with cotton-wool and heavy paper, and fitted with a wooden cover. The salt was placed in a small beaker, in sufficient quantity to ensure saturation of the solution, and the beaker was immersed in the bath in the dish through an opening made in the cover to fit it. The temperature of the bath was shown by a thermometer, introduced through the cover, and that of the solution by another suspended in it.

Starting at 0° C., the temperature was gradually raised by removing the ice and adding warm water, till thirty degrees was reached; from which point the increase was continued by the aid of a jet of steam led through the cover into the bath. At every five degrees rise in the temperature of the solution, 5 c.c. were removed to a weighed vial, which was then set in a steam-bath to evaporate. The solution was stirred, and then given time for the undissolved salt to subside, previous to the removal of each sample. The practical difficulties in getting trustworthy results increased with the temperature. The pipette was kept hot by suspension in a flask over boiling water, and rinsed with hot water each time it was used to avoid the otherwise inevitable accumulation of solid salt in it.

The following figures show the average of three determinations. From 0° to 30° the results of the three determinations were practically identical, 0° and 5° absolutely so. From 35° up there were occasional rather wide disagreements among the results, making the increase in the average less regular. T shows temperature, and W the weight of solid salt contained in 100 c.c. of a saturated solution at that temperature.

T.	W. (Grms).	T.	W.	T.	W.	T.	W.
0	3·0	25	7·0	50	13·7	75	22·8
5	3·3	30	8·2	55	15·6	80	24·8
10	4·0	35	9·7	60	16·7	85	26·6
15	4·9	40	10·6	65	19·2	90	28·6
20	5·8	45	13·1	70	22·2	95	32·8

The approximate solubility often given of 1 in 16 at 15°, agrees more nearly with that at 20° in the above.

(5). *Solubility of Potassium Perchlorate.*

This was found by the same method as the preceding; the results given are the mean of the two most reliable determinations.

T.	W. (Grms).	T.	W.	T.	W.	T.	W.
0	0·7	25	1·6	50	4·0	75	9·5
5	0·8	30	2·0	55	5·2	80	9·1
10	1·0	35	2·6	60	6·1	85	11·1
15	1·1	40	3·0	65	7·4	90	13·4
20	1·3	45	3·7	70	8·2	95	13·2

The apparent interchange between 75° and 80°, and 90° and 95° shows the results as actually obtained and confirmed by repeated determinations.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.[*]

(Concluded from p. 140).

Beer.

A.—*Methods of Investigation.*

By beer is to be understood a fermented and still fermenting drink, made from barley (or wheat), malt, hops, and water, and which was fermented by yeast.

I. *Determination of Specific Gravity.*—For this as well as all other determinations the beer is freed from carbonic acid, as far as possible, by half-filling bottles with it and shaking vigorously. It is then filtered. The specific gravity is then determined either by Westphal's balance or by a picnometer at 15° C.

II. *Determination of Extract.*—Seventy-five c.c. of beer are carefully weighed and evaporated in a suitable vessel to 25 c.c., care being taken to prevent boiling. After cooling water is added until the original weight is reached, and the specific gravity of the liquid taken as in I. The per cent of extract is obtained from this specific gravity by the use of a table constructed by Dr. Schultz, and is given as "per cent extract, Schultz."[†]

III. Alcohol is determined by distilling the beer. A piconometer of about 50 c.c. capacity and with a graduated neck is used as a receiver. The picnometer is carefully calibrated. 75 c.c. of beer are distilled until the distillate reaches about the centre of the scale on the picnometer. This is then cooled to 15° C., dried, and weighed, and the alcohol determined by means of Baumber's table.

$$A = \frac{D . d}{g}$$

The percentage of alcohol by weight is to be given. In very acid beers it is necessary to neutralise before distilling.

IV. *Original Gravity of Wort.*—This may be ascertained, approximately, by doubling the per cent by weight of alcohol found, as above, and adding the per cent of extract. As this procedure is not exact, it may be made more nearly so by using the formula—

$$\frac{100\,(E + 2{\cdot}0665\,A)}{100 + 1{\cdot}0665\,A}$$

V. *Degree of Fermentation.*—This is estimated by using the formula—

$$V_1 = 100\left(1 - \frac{E}{c}\right)$$

VI. *Sugar Determination.*—This is to be determined directly, in the beer previously freed from carbonic acid, by Soxhlet's method of weighing the reduced copper; 1·13 parts of copper correspond to 1 part anhydrous maltose.

VII. Determination of dextrin is seldom required, and if required is to be performed by Sachsse's method.

VIII. *Nitrogen.*—Twenty to thirty c.c. are evaporated in a Hofmeister "schälchen" or on warm mercury, and the extract burned with soda-lime. The nitrogen may also be determined by Kjeldahl's method.

IX. *Acids.*—(*a*). Total acids:—The carbonic acid is driven off from 100 c.c. of beer by heating in beakers for a short time to 40° C., and the beer then titrated with baryta water (one-fifth to one-tenth normal). The saturation point is reached when a drop of the liquid has no longer any action on litmus paper. The acidity is to be given in c.c. normal alkali required for 100 grms. beer and as grms. per cent of lactic acid. The indication "acidity" or "degree of acidity" is insufficient.

(*b*). Normal beer contains but a very small quantity of acetic acid. The determination of fixed acid in the repeatedly evaporated extract is to be cast aside. The acetic acid produced by souring of the beer is shown by the increase of total acids. A qualitative test of the presence of acetic acid in the distillate from beers containing acetic acid is sufficient. Neutralised beer is to be acidified with phosphoric acid and distilled. Weigert's method is recommended.

X. *Ash.*—Thirty to fifty c.c. of beer are evaporated in a large tared platinum dish, and the extract carefully burned. If the burning takes place slowly, the ash constituents do not fuse together.

XI. *Phosphoric Acid.*—This is to be determined in the ash obtained by evaporating and burning in a muffle 50 to 100 c.c. of beer to which not too much baric hydrate has been added. The phosphoric acid is determined in the nitric acid solution of the ash by the molybdenum method.

XII. *Sulphuric Acid.*—The direct determination is not permissible. The determination is to be made by using the ash prepared by burning with sodic hydrate and potassic nitrate or baric hydrate and proceeding in the ordinary way.

XIII. *Chlorine.*—This is to be determined in the ash prepared with sodic hydrate.

XIV. *Glycerin.*—Three grms. calcic hydrate are added to 50 c.c. of beer, evaporated to a syrupy consistence, about 10 grms. coarse sea-sand or marble added, and

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[*] Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

[†] Hilger, p. 123.

dried. The dry mass is rubbed up, put into a capsule of filter-paper, placed in an extraction apparatus, and extracted for six to eight hours with 50 c.c. alcohol. To the light coloured extract at least an equal volume of ether is added, and the solution, after standing awhile, poured into or filtered into a weighed capsule. After evaporating the alcohol and ether, the residue is heated in a drying-oven at 100° to 105° C. to a constant loss of weight. In beers rich in extract the ash contained in the glycerin can be weighed and subtracted. In case the glycerin contains sugar this can be determined by Soxhlet's method and subtracted.

XV. Hop substitutes are to be determined by Dragendorff's method. Picric acid is to be determined by Fleck's method. In examining for alkaloids, check experiments with pure beer must, in all cases, be made.

XVI. *Sulphites.*—One hundred c.c. of beer are distilled after the addition of phosphoric acid, and the distillate conducted into iodine solution. After one-third has distilled over, the iodine-coloured distillate is acidified with hydrochloric acid, and baric chloride added. If sulphites are not contained in the beer no precipitate is observed, but at the utmost a turbidity.

XVII. *Salicylic Acid.*—This may be shown qualitatively by shaking with ether, chloroform, or benzine. The solution is allowed to evaporate, the residue dissolved in water, and a very dilute solution of ferric chloride added. The addition of too much acid and too violent shaking is to be avoided. The smallest trace of salicylic acid may also be shown by dialysis, as it passes very readily through membrane.

Note.—All the results of an investigation are to be stated in percentages by weight.

B.—*Methods of Judging Purity of Beers.*

I. It is unjust to demand in a fermented beer an exact ratio of alcohol to extract, as the brewer cannot regulate the degree of fermentation within narrow limits. As a rule, Bavarian draught and lager beers contain from 1·5 to 2 parts of extract for each part of alcohol, but a smaller proportion of extract would not necessarily prove the addition of alcohol or glucose (the former to the beer, the latter to the wort).

II. The degree of fermentation of a beer must be such that at least 48 per cent of the original extract has undergone fermentation.

III. If glucose or other bodies poor in nitrogen have been used in appreciable quantity as substitutes for malt, the nitrogen contents of the beer extract will fall below 0·65 per cent.

IV. The acidity of a beer should not be greater than 3 c.c. normal alkali to 100 c.c. beer. Acidity of less than 1·2 c.c. normal alkali to 100 c.c. beer indicates previous neutralisation. If the acids are composed principally of lactic acid a larger quantity may be present.

V. The ash of normal beer is not above 0·3 grm. to 100 grms. beer.

VI. The amounts of phosphoric and sulphuric acids and chlorine in beer extract vary within such wide limits, that their determination signifies nothing as to the purity of the beer.

VII. The amount of glycerin in pure beer is not greater than 0·25 grm. to 100 grms. beer.

VIII. The following methods of clarifying beer are legal:—(*a*). Filtration. (*b*). Well-boiled hazel or beech shavings. (*c*). Isinglass.

IX. The following methods of preserving beer are legal:—(*a*). Carbonic acid. (*b*). Pasteurising. (*c*). Salicylic acid; this only for beers intended for export to countries where the use of salicylic acid is not forbidden by law.

Note.—The preceding methods are also to be used in the examination of imported beer.

C.—*Administrative Note.*

It is absolutely necessary that the beer be preserved in well-corked green glass bottles. Stone jugs and such vessels are not to be used.

The beer samples are to be protected from light and kept at a low temperature.

Care in making tests is, above all, necessary.

ANALYSES OF WATERS OF THE YELLOWSTONE NATIONAL PARK,

With an Account of the Methods of Analysis Employed.*

By FRANK AUSTIN GOOCH
and JAMES EDWARD WHITFIELD.

(Continued from p. 128).

Silica, Iron and Aluminum, Calcium, and Magnesium.—A single weighed portion of water served for the determination of silica, iron and aluminum, calcium and magnesium. The water was acidified with hydrochloric acid, evaporated to dryness in platinum over the water-bath, again acidified, and again evaporated. The residue was digested with hot water containing a little hydrochloric acid, and the solution was filtered from the residue of silica, which was ignited in platinum and tested as to its purity in the usual manner with hydrofluoric acid.

In the filtrate ammonia, in the slightest excess, precipitated ferric and aluminic hydrates from the boiling solution, and these were collected, ignited, and weighed as oxides in the usual manner. The lime was thrown out of the hot ammoniacal filtrate by ammonium oxalate, and the calcium oxalate filtered off after standing twelve hours in the cold. When the amount precipitated exceeded a few milligrms. it was dissolved in hydrochloric acid, reprecipitated by ammonia and ammonium oxalate, and collected upon a filter, the filtrate from the second precipitation being added to that from the first. The calcium oxalate was dried, ignited, and weighed as calcium oxide.

The filtrate (or the united filtrates) from the calcium oxalate was evaporated in platinum, and the residue was gently ignited to destroy the ammonium oxalate—which tends to delay the precipitation of the magnesia if permitted to remain in the solution—and dissolved in hydrochloric acid. From this solution the magnesia was precipitated in the usual manner by microcosmic salt and ammonia, and after standing twelve hours or more, the phosphate as collected upon asbestos in a perforated crucible, washed with the mixture of one part of ammonia to three of water, commonly used in the process, moistened at the end of the washing with a strong solution of ammonium nitrate in ammonia, ignited for a moment to redness, and weighed as the pyrophosphate.

Sodium, Potassium, and Lithium.—In some of the earlier work only sodium and potassium, of the alkalies, were determined in the natural water, and for the determination of the lithium portions of the concentrated water were treated by the method which will be referred to later. In the greater number of cases the same portion of the natural water served for the determination of the lithium as well as sodium and potassium. The portion for analysis was acidified in platinum with hydrochloric acid and evaporated to dryness. The residue was extracted with hot water slightly acidulated with hydrochloric acid, the solution was separated from the precipitated silica by filtration, and to the filtrate was added, with care to secure a sufficiency and yet to avoid a great excess, barium hydrate made from the nitrate, itself purified by precipitation by nitric acid. Filtration separated the precipitated hydrates of aluminum, iron, and magnesium, with barium

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* *Bulletin of the United States Geological Survey*, No. 47.

sulphate; and from the filtrate ammonium carbonate and ammonia precipitated, upon boiling, nearly the whole of the barium and calcium as carbonates. The filtrate from the precipitated carbonates was evaporated to dryness, and the residue was gently ignited to remove ammonium chloride, treated with hydrochloric acid, freed from the excess of acid by evaporation on the water-bath to dryness, dissolved in a very small amount of water, and treated again with a few drops of the solution of ammonium carbonate and ammonia. This treatment usually results in the precipitation of traces of barium carbonate which have previously escaped removal by the similar treatment of the larger volume of liquid. The filtrate from this last slight precipitate was again evaporated and treated as before; and, in case any further precipitation took place, the process was repeated until the purification was complete. Usually, however, the first precipitation in the larger volume of liquid and the second treatment in the solution reduced to small bulk are together sufficient to remove the barium carbonate completely. The filtrate from the last precipitate was evaporated in a weighed platinum dish, and the residue, consisting of the chlorides of sodium, potassium, and lithium, was dried, gently ignited, and weighed.

From the mixed chlorides the lithium salt was separated by a process which, devised by one of us during the progress of the worked and described elsewhere in full,* needs but brief outlining in this place. To the concentrated solution of chlorides amyl alcohol is added and heat is applied, gently at first to avoid danger of bumping, until, the water disappearing from solution and the point of ebullition rising and becoming constant for some minutes at a temperature approximately that at which the alcohol boils by itself, the chlorides of sodium and potassium are deposited, and the lithium chloride is dehydrated and taken into solution. At this stage of the proceeding the liquid is cooled, a drop or two of strong hydrochloric acid being added to re-convert traces of lithium hydrate possibly in the deposit, and the boiling is continued until the alcohol is again free from water. If the amount of lithium chloride present in the mixture of salts is small it is now found in solution; the chlorides of sodium and potassium, excepting the traces for which correction will be made subsequently, are in the residue; and the separation may be effected by filtration and the washing of the residue with amyl alcohol previously dehydrated by boiling. If, on the other hand, the weight of lithium chloride present exceeds ten or twenty milligrms. it is advisable, though not absolutely essential to the attainment of fairly correct results, to decant the liquid from the deposit, wash the latter with a little anhydrous amyl alcohol, dissolve in a few drops of water, and repeat the separation by boiling in amyl alcohol.

The filtrates, first measured apart, are united with the washings and evaporated to dryness, and the residue, treated with sulphuric acid in excess, ignited gently at first and finally to the fusing point, is weighed as the neutral lithium sulphate, containing traces of the neutral sulphates of sodium and potassium. From the weight thus found the subtraction of 0·00109 g. for every 10 c.m.^{3} of filtrate exclusive of washings makes the proper correction for the amounts of the sodium and potassium salts present, and the residual weight represents the pure lithium sulphate. In cases where the precipitate consists solely of sodium chloride, the correction upon the weight of the sulphate is 0·00050 g.; when potassium chloride constitutes the residue the correction amounts to 0·00059 g. for every 10 c.m.^{3} of filtrate. The alcohol used in washing has, within reasonable limits, no appreciable solvent effect upon the precipitate.

The precipitate, consisting entirely of sodium chloride and potassium chloride, is ready for the balance after drying for a few minutes directly over a flame turned low, if the filtration is effected by means of asbestos in the perforated crucible; if paper is used as the filtering medium, after the solution of the precipitate, the evaporation of the solution and the gentle ignition of the residue. The weight of the insoluble chlorides actually obtained is corrected for the solubility of the salts in amyl alcohol by adding 0·00092 g. for every 10 c.m.^{3} of amyl alcohol in the filtrates, exclusive of washings; 0·00041 g. of this representing the sodium chloride dissolved, and 0·00051 g. the potassium chloride. With due attention to the reduction of volume of the residual alcohol before filtering the correction may be held easily within narrow limits.

In applying this method to the analysis of the waters of the Yellowstone Park the practice of reducing the volume of amyl alcohol to about 15 c.m.^{3} before filtering was followed uniformly. The corrections, therefore, were always the same, and amounted to an addition of 0·0007 g. to the apparent weight of sodium chloride, 0·0008 g. to that of potassium chloride, and a subtraction of 0·0017 g. from the weight of lithium sulphate indicated by the balance. In many cases the lithium present in the waters, though capable of detection by the spectroscope, amounted to so little in the portions devoted to its determination that the application of the correction left nothing to be called lithium sulphate. In such cases the lithium is counted as a "trace."

From the mixture of sodium chloride and potassium chloride the potassium salt was separated as potassioplatinic chloride. The chlorides were dissolved in a small amount of water, platinic chloride was added in solution, in quantity considerably in excess of the amount necessary to effect the conversion of all the potassium and sodium present to the double platinum salts, and the mixture evaporated on the water-bath to the point at which the residue becomes pasty if removed from the bath and allowed to cool. The crust thus formed was drenched with alcohol of 80 per cent., digested in the cold until thoroughly disintegrated, filtered off on an asbestos felt, washed with alcohol of 95 per cent, dried at a gentle heat, and weighed.

The lithium and potassium having been thus found directly, the sodium is given, in the form of the chloride, by the difference between the sum of the lithium and potassium chlorides and the total weight of the three chlorides; or, by the difference between the weight of potassium chloride found and the weight of the chlorides of potassium and sodium found (the proper correction having been applied) after the separation of the lithium. It may be urged against the former plan that to bring the three chlorides to a definite condition for weighing is a difficult undertaking in view of the great tendency of lithium chloride to exchange chlorine for oxygen in the presence of water. Our experiments indicated, however, that under repeated treatments by moistening and ignition the mixed chlorides did not change in weight materially, and we are disposed to attribute the result in part to the protective influence of the sodium and potassium salts upon the relatively small amount of lithium chloride, and in part to the care taken to secure thorough drying at a low temperature previous to the gentle ignition. In our work upon the waters we weighed the three chlorides together and found the sodium chloride by deducting from this weight the weights of potassium chloride and lithium chloride deduced by analysis.

A weak point in the process which we have employed in the determination of the alkalies would seem to be found in the separation of the magnesia by means of barium hydrate. In connection with this subject it is of interest to note that in the greater number of waters magnesia was present only in inconsiderable quantity, and further, that in the case of those in which it did appear in appreciable amounts the examination of the solution of the lithium sulphate, after the separation by amyl alcohol, failed to indicate the presence of magnesia in amount sufficient to be precipitable by microcosmic salt in an ammoniacal solution and under the usual conditions of the test, though this would be the place in

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* *Bulletin of the U.S. Geological Survey*, No. 42, p. 73; *Am. Chem Jour.*, vol. 9, p. 33.

which magnesia should appear if it had escaped removal from the chlorides. We are constrained to believe, therefore, that the process of separation which we adopted was exact within reasonable limits.

Ammonia and Albumenoid Ammonia.—The determination of ammonia was effected in the usual manner by distilling a measured portion of water with sodium hydrate, and nesslerising the distillate. A second portion of water was distilled with sodium hydrate and potassium permanganate, and the distillate was nesslerised. The former process gives the combined ammonia present in the water; the latter the total ammonia, which includes, besides the ammonia existing as such in combination, that ammonia which is developed from other nitrogenous compounds by the action of the permanganate. The difference between the figures of the two processes is the albumenoid ammonia, so called. The composition of these waters renders them peculiarly liable to boil explosively, and some difficulty was experienced at first in the distillation; but the apparatus which is described in the paragraph on the determination of the boric acid proved to be of service in this case also, and made the determination practicable. The Nessler solution was very delicately adjusted, and the tests were made in small tubes and carried to the limit of 0·000001 g.

TREATMENT OF CONCENTRATED WATERS.

In the examination of the concentrated waters the whole sample was evaporated to dryness, and the residue thus left was extracted with hot water. It is usual in treating concentrated waters to add sodium carbonate during the evaporation, and to wash the residue until the washings cease to show an alkaline reaction. Four of the waters of which we had concentrated samples were, however, so alkaline of themselves that the addition of sodium carbonate was superfluous, and all were so siliceous that to wash the residue of evaporation until it was free from alkali was a matter of the greatest tediousness and difficulty. We found it best and sufficient to wash only to the vanishing point of the spectroscopic reaction for lithium in the washings. In this manner the separation of the greater part of the silica with the insoluble constituents of the water was effected without an entirely unreasonable expenditure of time and effort. The filtrate and washings were thoroughly mixed and made up to a definite weight. The residue was kept by itself for separate treatment.

The filtrate should contain the bromine, iodine, boron, arsenic, antimony; the copper, lead and tin, which can be present in the waters only in traces; the lithium, cæsium, rubidium, thallium, and part of the silicon and aluminum. The precipitate should contain the titanium, phosphorus, fluorine, iron, manganese, barium, strontium, calcium, magnesium, with the remainder of the aluminum and silicon.

Strength of the Concentrated Waters.

The degree to which the concentration of the waters had been carried in the field was fixed by the determination of the total amount of halogens in a weighed portion of the extraction of the residue of evaporation. This portion was diluted, acidified with nitric acid, treated with silver nitrate until the precipitate ceased to form, and the last was collected on asbestos in a perforated crucible, dried (over the free flame of a Bunsen burner turned low) at a temperature considerably below its melting point, and weighed. Determinations of this sort were made in duplicate. Knowing the weight of the silver salt thus found and the weight of the same precipitable from a known weight of the natural water, the exact value of the concentrated water, in terms of the natural water which it represented, became known.

Treatment of the Residue.

Fluorine.—The residue, dried by gentle heating, with the ash of the filter employed in separating and washing it, was placed in a retort of the pattern described in the section treating of the determination of boric acid in the natural water, drenched with strong sulphuric acid, and heated to 150° C., while a slow current of dry air was forced through the emulsion and thence directly into a U-tube partly filled with dilute ammonia. The fluorine contained in the water should appear in the residue as calcium fluoride, should be volatilised as silicon fluoride by the action of the sulphuric acid, and, if present in more than very small amounts, should be indicated by the precipitation of silica in the U-tube containing ammonia. Proceeding in this manner we found in the waters which we examined no fluorine; and on treating the ammoniacal liquid of the U-tube according to the method of Berzelius, with zinc oxide dissolved in ammonia, evaporating until the solution ceased to evolve ammonia, filtering, adding to the filtrate calcium chloride followed by sodium carbonate, boiling, igniting the precipitate and extracting it with acetic acid, we were not able to detect a residue of calcium fluoride: nor in the zinc oxide precipitated by the expulsion of the ammonia dissolving it could we discover silica.

Barium and Strontium.—The contents of the retort were transferred to platinum, treated with hydrofluoric acid (purified by re-distillation) in sufficient amount to volatilise all silica, and evaporated to dryness with a little sulphuric acid. To insure thoroughness of action this process of treatment was repeated. The residue was fused with sodium carbonate and the melt was extracted with hot water containing a few drops of alcohol. The precipitate was separated from the solution by filtration and digested with hot dilute acetic acid, which should dissolve the barium, strontium, calcium, and magnesium carbonates. The solution in acetic acid, separated by filtration from the portion unacted upon, was nearly neutralised with ammonia, and to it was added in solution an amount of ammonium sulphate equal to fifty times the weight of the alkaline earths present, the whole being permitted to stand quietly twelve hours. By this treatment barium and strontium should be precipitated as sulphates, while calcium and magnesium should remain dissolved. The sulphates of barium and strontium may be separated afterward by digestion during twelve hours (at the ordinary temperature and with frequent stirring) in ammonium carbonate, the decantation of the supernatant liquid, the repetition of the treatment with ammonium carbonate, and, finally, the action of hydrochloric acid upon the residue—the strontium carbonate dissolving and the barium sulphate remaining insoluble in this acid. This mode of separating the barium and strontium was not actually applied in our work, inasmuch as we obtained from the quantities of water with which we had to deal no precipitate by ammonium sulphate, and it is mentioned only for the purpose of completing the scheme of analysis.

The solution which had been treated with ammonium sulphate to precipitate barium and strontium was preserved for subsequent examination for manganese.

Phosphoric Acid.—The extract of the fusion in sodium carbonate was acidified with nitric acid, evaporated to small bulk, and from it the phosphoric acid was precipitated in the usual manner as a phosphomolybdate of ammonia. The precipitate, after standing twelve hours, was separated by filtration through a felt of asbestos in a perforated crucible, washed with the precipitant, and dissolved in ammonia. From this solution the phosphoric acid was precipitated by the magnesium and ammonium chloride mixture, and the ammonio-magnesium phosphate was filtered off on asbestos, washed with dilute ammonia (one part of ammonia to three of water), moistened with ammonium nitrate in ammonia, dried, ignited at a red heat, and weighed as magnesium pyrophosphate.

Manganese.—The residue left, after the extraction of the fusion in the sodium carbonate with water containing a little alcohol and the treatment with acetic acid, was fused again in a little sodium carbonate, the melt was dissolved in the crucible by heating with strong sulphuric acid, and this solution was poured into cold water. In this manner was obtained a solution containing the titanium and iron, and a part of the aluminum and manganese. From it all these elements, excepting the last, were precipitated by adding ammonia to an alkaline reaction followed by acetic acid to faint acidity, and boiling. The precipitate was kept for examination later. The solution was mixed with that which had been treated with ammonium sulphate in the test for barium and strontium, and to the mixture, heated on the water-bath, were added ammonia in excess and bromine water. The precipitate thus obtained was ignited and weighed as Mn_3O_4, it being so trifling that solution and re-precipitation as the phosphate was unnecessary.

Iron.—The precipitate of ferric, titanic, and aluminic hydrates was fused in a little sodium carbonate, the fusion was dissolved in strong sulphuric acid, this solution poured into cold water, and the dissolved iron, titanium, and aluminum were separated as follows, by a process devised by one of us and described fully elsewhere.* Tartaric acid, amounting to three times the weight of the oxides of iron, aluminum, and titanium present, was added to the solution, which was then made faintly ammoniacal and submitted to the action of a current of hydrogen sulphide. The precipitated ferrous sulphide was filtered off (care having been taken that the solution should still be alkaline before filtering), washed with hot water sufficiently but expeditiously, dissolved in hydrochloric acid, and the iron, first oxidised by bromine, was precipitated by ammonia and weighed as the oxide.

Titanic Acid.—The filtrate from the ferrous sulphide was acidified strongly with sulphuric acid, heated to the boiling point, and treated with potassium permanganate until its characteristic colour appeared. The final products of the action of the permanganate upon the tartaric acid are carbonic acid and water, but formic acid appears as an intermediary step in the oxidation. During the first action of the permanganate its conversion to manganous sulphate is rapid, but with the development of formic acid there takes place by its action upon the permanganate freshly added a precipitation of a brown hydrate of manganese, which, re-dissolving readily so long as tartaric acid remains, yields only slowly to the further action of the formic acid. When, therefore, manganic hydrate appears abundantly in the boiling solution and does not dissolve perceptibly, one may be reasonably certain that the conversion of the tartaric acid to at least the intermediary stage has been accomplished; but for the sake of greater security, the addition of the permanganate may be continued until the appearance of its colour. When the amount of tartaric acid in the solution is known, as should be the case always, a simple mode of proceeding is, perhaps, to employ for the oxidation the amount of permanganate theoretically required. A weight of potassium permanganate amounting to two and a half times the weight of the tartaric acid to be destroyed is sufficient to carry the oxidation to the ultimate limit, providing there be no deposition of a manganic hydrate.

The residual permanganate and the insoluble hydrate were reduced and dissolved by the addition of a little ammonium bisulphite to the acid solution, and, the excess of sulphurous acid having been boiled off, acetic acid was added to the clear solution in quantity sufficient to make the amount of the absolute acetic acid present from 7 to 11 per cent by volume; enough sodium acetate was introduced to fix all the sulphuric acid as sodium sulphate, and the solution was boiled. If titanium is present it is precipitated under these conditions, while the aluminum remains dissolved. If the quantity of the precipitate thus obtained is considerable, it should be filtered from the liquid in which it floats, and purified from the traces of manganese which it may carry by fusion in a small quantity of sodium carbonate, the solution of the melt in sulphuric acid, and re-precipitation by ammonia.

In the waters which we examined we found no precipitate of titanic hydrate at the point in the process where it should appear were titanium present.

(To be continued).

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* *Bulletin of the U.S. Geological Survey*, No. 27, p. 16; *Am. Chem. Jour.*, vol. vii., 1885—1886, p. 283.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 20th, 1888.

Mr. William Crookes, F.R.S., President, in the Chair.

Mr. Frank Bower was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. P. Carmody, F.I.C., The Laboratory, Somerset House; Edward Mitchell Chaplin, Westgate, Wakefield; John Curragh, Donaghadee, Belfast; David Ferrier, The Cottage, 50, High Street, Montrose; Conrad Gerland, Church, Lancashire; Alfred Miall Hanson, The Marjorie, Whalley, near Blackburn; Henry Joshua Phillips, Great Western Railway Laboratory, Swindon; Thomas John Underhill, 43, Chapel Road, West Norwood, S.E.

The following papers were read:—

96. "*On some Leadhills Minerals.*" By Norman Collie, Ph.D.

Up to the present time the analyses of the rare lead minerals which are to be found at the Leadhills in the southern highlands of Scotland have been both meagre and contradictory. The author communicates a number of analyses of some specimens of leadhillite, lanarkite, vanadinite, and other minerals, obtained from Dr. Wilson, of Wanlock-head, Leadhills, and also of a considerable number collected by himself. The investigation was undertaken for two reasons; the chief one being to ascertain whether in the large number of double carbonates, sulphates, phosphates, &c., found at Leadhills, the constituent salts were always present in molecular proportions, or whether they were only isomorphous mixtures. The other reason was to determine which among the conflicting analyses met with in the mineralogical treatises were the most probably correct. Two new minerals were met with:—(1) A pyromorphite, containing both copper oxide and vanadic acid; (2) an aragonite in which part of the calcium carbonate had been displaced by lead carbonate.

The other minerals analysed were leadhillite, lanarkite, caledonite, linarite, vanadinite, pyromorphite, plumbocalcite, calamine, dolomite, and strontianite.

97. "*Metallic Derivatives of Halogen Nitrophenols.*" By Arthur R. Ling.

Chlorobromoparanitrophenol, prepared by brominating chloroparanitrophenol, m. p. 110°, in acetic acid solution, separates from boiling water in colourless crystals melting at 137° with decomposition. The following metallic derivatives of this phenol are described:—

Potassium salt, $C_6H_2ClBrNO_3K{\cdot}H_2O$, golden-yellow needles.
Calcium salt, $(C_6H_2ClBrNO_3)_2Ca{\cdot}9H_2O$, yellow needles.
,, $(C_6H_2ClBrNO_3)_2Ca{\cdot}4H_2O$, yellow plates.
Barium salt, $(C_6H_2ClBrNO_3)_2Ba{\cdot}10H_2O$, yellow needles.
,, $(C_6H_2ClBrNO_3)_2Ba{\cdot}3\frac{1}{2}H_2O$, red needles.

The calcium-derivatives of the following were also examined:—

Dibromorthonitrophenol, red plates, containing 7 mols. H_2O.
Dichlororthonitrophenol, orange-yellow fibrous needles, containing 1 mol. H_2O.

Dichlororthonitrophenol, red crystals, containing 4 mols. H_2O.
Parachlororthobromorthonitrophenol, red plates, containing $4H_2O$.
Parabromorthoiodorthonitrophenol, red plates, containing $4H_2O$.

They are almost insoluble in cold and only sparingly soluble in boiling water.

A general feature of the calcium-derivatives of the nitrophenols, especially those of the orthonitro-series, seems to be the difficulty with which the water of crystallisation is removable on heating, *e.g.*, it was found impossible to completely dehydrate calcium dibromorthonitrophenol below a temperature at which it decomposed. The author also points out that as they lose their water of crystallisation, the calcium orthonitrophenol-derivatives change from red to an orange colour, which is at variance with the conclusions of Carnelley and Alexander.

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. cviii., No. 10, March 11, 1889.

Oxygenated Water and Chromic Acid; New Experiments.—M. Berthelot.—In a former paper the author has established that the reactions of hydrogen peroxide and chromic acid may be produced also if potassium dichromate is substituted for chromic acid. The unlimited decomposition of oxygenated water by this salt is due to the formation of an intermediate compound, which is incessantly formed and reproduced. This intermediate compound, which turns the liquid brown, has some such composition as- -

$$nCr_2O_3CrO_3,+3HO_2.$$

Use of Sodium Sulphite in Photography.—Paul Poire.—From a great number of experiments it results that with commercial sulphites it is always advantageous to take as a developing-bath a solution of sodium sulphite at 25 per cent, to which is added 1·5 grms. per cent of pyrogallic acid. There is no need to add carbonate unless the development is too slow.

A Small Portable Apparatus for the Easy and Safe Production of the Magnesium Flash.—Ad. Guébhard and P. Ranque.—The authors give a series of figures illustrating their apparatus.

On the α- and γ-Mono-chlor-acetoacetic Ethers. An Attempt at the Synthesis of Citric Acid.—A. Haller and A. Held.—This paper does not admit of useful abstraction.

Researches on Australene.—Ph. Barbier and J. Hilt.—Australene is an extract from the oil of turpentine of *Pinus australis* of South Carolina. It is a colourless liquid, very mobile, and of a slight odour. Its sp. gr. at 0° is 0·8789. Its rotatory power is $[\alpha]_D = +22{\cdot}85°$. If heated for two hours to 300° it is changed into the corresponding isoterebenthene.

The Influence of Thiophene and its Homologues upon the Colouration of the Derivatives of Benzene and its Homologues.—A. Bidet.—Nitrobenzene, even if prepared from crystalline benzene, always presents, after several distillations, a yellowish tiut, which deepens under the influence of light. If we use benzene freed from thiophene the nitrobenzene obtained, even on the first distillation, has merely a slight yellowish green tint, which is not affected by light. The addition of a single crystal of mono-nitro-thiophene restores to pure nitrobenzene the properties of ordinary nitrobenzene. Toluene, if freed from thiotoluene by processes similar to those used in the purification of benzene, is similar in colour to pure nitrobenzene. Phenol, prepared by means of a sulphone freed from thiophenic compounds, may be obtained in fine colourless needles, which do not turn yellow or red, even after months of exposure to light. The pure nitro-compounds may be converted into amines, and then the aniline or toluidine does not acquire that deep red-brown colour which the ordinary products always acquire after a time If we stop the purification of benzene at the moment when we can no longer trace a blue colouration with isatin we have still a nitrobenzene, which turns yellow, and the aniline derived from it takes the characteristic brown tint. Aniline, ortho-, and para-toluidine, if freed from thiophenic compounds, and being in suitable proportions to form "aniline for reds" yield merely traces of magenta on treatment with syrupy arsenic acid. The same amines, if prepared from pure materials, but to which nitrothiophene has been added before reduction, yield a red colouring-matter, exactly as does ordinary aniline for reds.

The Fertilising Properties of the Waters of the Nile.—A. Müntz.—It has been already demonstrated that the waters of the Nile owe little of their fertilising power to the presence of nitrates. The water of the Nile in time of flood in September contains per cubic metre :—

	Dissolved.	Suspended.
Nitrogen..	1·07 grms.	3·00 grms.
Phosphoric acid ..	0·40 ,,	4·10 ,,
Potash	3·66 ,,	150·00 ,,
Lime	48·00 ,,	70·50 ,,

Hence the mud is the main fertilising agent.

The Slow Combustion of Certain Organic Matters.—Th. Schlœsing, Jun.—The author, referring to a former paper on the slow combustion of tobacco and the part played in it by micro-organisms at different temperatures, extends researches of the same kind to dung. Lots of dung were first sterilised by heating for an hour to 115°, after which some of them were sown with a little of the drainings or the dust of fresh manure, whilst the others remained secluded from external germs. At 75·5° the portion treated with germs evolves fifteen times as much carbonic acid as simple chemical combustion.

Moniteur Scientifique, Quesneville. March, 1889.

Bleaching Cotton Tissues: the Saponification of Fatty Bodies upon the Fibre, followed by Observations Exerted by the Process of Bleaching upon the Oxides of Various Metals Previously Fixed upon the Fibre.—Albert Scheurer.—This memoir is taken from *Bulletin de la Société Industrielle de Mulhouse* and is too extensive for insertion. M. Scheurer considers that the great novelty of the Mather and Platt process consists rather in its mechanical arrangements than in the chemical operations which it renders admissible.

Researches on Narcotin.—This paper, taken from *Liebig's Annalen*, does not admit of abstraction.

On Tartar Emetic.—Professor Dunstan and Miss L. E. Boole.—From the *Pharmaceutical Journal.*

The Examination of Commercial Phenol, and of Phenic Disinfecting Powders.—Rowland Williams.—From the *Journal of the Society of Chemical Industry.*

On New Explosive Substances.—This paper contains a description of Favier's explosive, a mixture of mononitronaphthaline with ammonium nitrate, enclosed in an envelope composed of the same substances mixed with 4 per cent of paraffin. Then follows an account of the "Flameless Powder," invented by Schœneveg, of Dudweiler, and worked on a large scale by the "Flameless Explosives Company," of London. It is possible identical with the substance known under the barbarous name "Grisoutite." It is alleged to be incapable of igniting explosive mixtures of gases, or air holding coal-dust in suspension. It is described as consisting of explosive gelatin mixed or coated with oxalic acid or oxalates, in order both to increase its shattering power and to prevent spontaneous combustion and the production of flame. Romite, the invention of Sjoeberg, consists of two portions which are afterwards mixed together. One of these consists of ammonium nitrate, naphthaline, and rectified paraffin oil; the other mixture is composed of potassium chlorate, naphthaline, and paraffin oil. The Carbodynamite of W. D. Borland is essentially nitroglycerin absorbed in the charcoal of cork, or a mixture of the latter substances with kieselguhr and soda-ash.—*Chemische Industrie.*

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Estimating Carbon in Steel.—In Eggertz's colouration process for estimating carbon in steel the colour of steel solutions is darkened by heating in boiling water. How is this? Should the estimation and comparing of the colours be conducted warm or cold?—Young Analyst.

MEETINGS FOR THE WEEK

Monday, April 1st.—Medical, 8.30.
— Society of Arts, 8. Cantor Lectures. "Instruments for the Measurement of Radiant Heat," by C. V. Boys, F.R.S.
— Society of Chemical Industry, 8. "The Action of Water on Lead," by Dr. P. F. Frankland. "Economy of Pure Caustic Soda," by Messrs. Cross and Bevan.
— Royal Institution, 5. General Monthly Meeting.
Tuesday, 2nd.—Institute of Civil Engineers, 8.
— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
— Sanitary Institute, 8. "Infectious Diseases and Methods of Disinfection," by Sbirley F. Murphy.
— Society of Arts, 8. "The Argentine Republic," by F. K. Smythies.
— Pathological, 8.30.
Wednesday, 3rd.—Society of Arts, 8. "Fruit Growing for Profit in the Open Air in England," by W. Paul.
— Geological, 8.
Thursday, 4th.—Royal, 4.30.
— Royal Institution, 3. "Houses and their Decoration from the Classical to the Mediæval Period," by Prof. J. Henry Middleton, M.A.
— Chemical, 8.
Friday, 5th.—Royal Institution, 9. "True and False Humour in Literature," by the Rev. Canon Ainger.
— Geologists' Association, 8.
— Sanitary Institute, 8. "General Powers and Duties of Inspectors of Nuisances—Method of Inspection," by J. F. J. Sykes, B.Sc.
Saturday, 6th.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.

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PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that Leopold Casella and Company, of Frankfort-on-the-Main, Germany (Assignees), have applied for leave to amend the Specification of Letters Patent No. 9214 of 1885 granted to Meinhard Hoffmann and Arthur Weinberg, both of Mainkur, near Frankfort-on-the-Main, in the Empire of Germany, for "The production of new azo-colours."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 20th March, 1889.

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 month from the date of the said Journal.

(Signed)
H. READER LACK,
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THE CHEMICAL NEWS.

Vol. LIX. No. 1532.

RELATIVE AMOUNTS OF VOLTAIC ENERGY OF DISSOLVED CHEMICAL COMPOUNDS.*

By G. GORE, LL.D., F.R.S.

In this investigation the author has measured, by the "voltaic balance" method, the amounts of relative voltaic energy or of chemical affinity for zinc of nearly 250 aqueous solutions of chemical compounds; including those of elements with elements; elements with monobasic, bibasic, and tribasic acids; acids of all these classes with each other; elements with monobasic, bibasic, tribasic, and tetrabasic salts; monobasic, bibasic, and tribasic acids with all these classes of salts; and all these classes of salts with each other in large variety; and he offers the results as additional evidence in support of the conclusion that "*every electrolytic substance or mixture, when dissolved in water, unites chemically in definite proportions by weight with every other such dissolved body*," provided no separation of substance occurs;" and that "there may probably be discovered thousands of such compounds, which only exist whilst in aqueous solution, and are decomposed on evaporating or crystallising their solutions" (*Roy. Soc. Proc.*, vol. xliv., p. 267). The results are given in the form of a volta tension series of electrolytes.

NOTE ON A SAMPLE OF PALMITIC ACID.

By J. C. A. WILSON.

Some time ago the author had reason to examine a sample of white palmitic acid. On examining it for the iodine equivalent it gave 25 per cent, corresponding to 28 per cent oleic acid approximately. The mean combining weight was 265, and the melting-point 48 Centigrade. On carefully treating it by the process depending on the solubility of the lead salt in ether, it gave 2 per cent oleic acid.

These results are very paradoxical, and I may point out the statement of Benedict, who found distilled stearic acid absorbing 14 per cent iodine to yield no oleic acid on treating the lead salts with ether.

In connection with this may be mentioned the fact that J. C. A. Wilson and M. Satzeff (*Jour. Prak. Chem.*, xxxvii., 269) find oxystearic acid to be converted into isoleic acid on distillation, melting at 43° C.

The Laboratory, Tottington,
March 27, 1889.

ESTIMATION OF INSOLUBLE PHOSPHATES.

By VINCENT EDWARDS, F.C.S.

The following short and simple method of estimating the insoluble phosphate in superphosphates, &c., may be of interest to your readers, especially to manure works chemists, who are frequently required to test a sample of manure at a short notice:—I treat five grms. in the usual way, and test the water solution for soluble phosphate; the residue filter, and all is then dissolved with dilute HCl and $4NO_3$ in a beaker placed in a water-bath; about half an hour will suffice to dissolve out all the phosphates; the solution is then filtered, 20 c.c. of a solution of phosphates of lime in dilute nitric acid added (about 5 grms. $Ca_3P_2O_8$ to the litre is a good strength), and the whole made up to 250 c.c.; 50 c.c. of this solution = 1 grm. is taken, ammonia added till alkaline, made acid with acetic acid, and then titrated with uranium solution—being heated to boiling on the first addition of the uranium. The strength of the added phosphate of calcium being known, the quantity of uranium required to precipitate one-fifth of it is deducted from the result. I have found this plan very useful when the sample contains large quantities of gypsum, and when the results are required in a few hours after the mixing is made up. An allowance must be made for iron and alumina, but this can be determined accurately once for all, and the amount will not vary much. I generally add 0·5 per cent for phosphate in combination with these matters.

The Laboratory,
Wicklow Chemical Works,
March 26, 1889.

GYMNEMIC ACID.

By DAVID HOOPER, F.C.S., F.I.C.

Some years ago it was discovered by Mr. Edgeworth that the leaves of *Gymnema sylvestre* had the peculiar property of destroying the power of the tongue to appreciate the taste of sweet substances. In the early part of 1887 Sir M. E. Grant Duff, then Governor of Madras, interested himself in the subject, and forwarded me from his grounds in Grundy Park a supply of the leaves for investigation. A paper containing the results of a chemical examination, with their proximate analysis, has already been published,* and now some notes are sent relating to the chemistry of the principle possessing this singular property, which was discovered at that time.

Gymnemic acid exists in the leaves in the form of a potassium salt, and is best prepared by treating the aqueous solution of the alcoholic extract with a mineral acid, washing the precipitate, and drying in a current of hot air or over a desiccator.

The acid is a brittle black resinous substance of a greenish colour when reduced to powder. It is insoluble in water, soluble in alcohol (with an acid reaction), ether, benzol, and chloroform, and slightly in amylic alcohol and carbon bisulphide. With potash, soda, and ammonia it affords fine red solutions with an orange-coloured froth, and precipitated on the addition of acids. It dissolves in concentrated sulphuric and nitric acids with intense red colour, and in both mixtures it is destroyed and precipitated by water. Prolonged contact with nitric acid forms a soluble nitro-compound or product soluble in water. It fuses at about 60° C. into a black liquid of thick consistence; above 100° it gives off creosotic fumes, and, at a higher temperature, burns with a bright smoky flame, leaving no ash. It is thrown down as a bulky grey mass with plumbic acetate, and the lead salt may be decomposed by hydrogen sulphide in the presence of spirit. It is also precipitated by ferric chloride, silver nitrate, barium and calcium salts, but not by tannin, picric acid, and gelatin solution. It forms insoluble salts with alkaloids, and this accounts for its masking the taste of quinine and other bitter substances.

The acid, dried at 100° C., was submitted to combustion with cupric oxide.

(*a*). 0·2152 grm. gave 0·4807 grm. CO_2 and 0·1706 grm. H_2O.
(*b*). 0·2738 ,, 0·6080 ,, ,, ,,

From these experiments may be deduced the empirical formula $C_{32}H_{55}O_{12}$; the re-calculation of the elements from such a formula shows a close correspondence with the mean percentage found.

---

* Abstract of a Paper read before the Royal Society, March 14, 1889.

* *Nature* and *Pharm. Journ. and Trans.*, April, 1887.

	(*a*).	(*b*).	Mean.	Calculated for $(C_{32}H_{55}O_{12})$.
Carbon	60·92	60·55	60·73	60·85
Hydrogen ..	8·80	8·61	8·71	8·71
Oxygen	30·28	30·84	30·56	30·44
	100·00	100·00	100·00	100·00

The silver salt of gymnemic acid is a black brittle powder; it afforded 14·02 per cent of metal on combustion. Theory for $C_{32}H_{54}O_{12}Ag$ requires 14·63 per cent of metallic silver.

Gymnemate of lead is insoluble in acetic acid, and forms a black uncrystallisable powder. A weighed portion of the dried salt gave 15·19 per cent of plumbic oxide. Theory for $(C_{32}H_{54}O_{12})_2Pb''$ requires 15·20 per cent of PbO.

There is evidence that gymnemic acid is a monatomic acid from the compositions of its silver and lead salts, and its molecular weight, 631, agrees with its power of saturating alkali. It was found by experiment that 0·631 grm. of the acid, treated with centinormal solution of caustic soda, did not strike a red colour with phenolphthalein until sufficient solution, equivalent to about 0·040 grm. of NaHO, had been added.

I have not obtained the acid or its salts in anything approaching a crystalline condition; they dry as do tannic acid and the tannates. Ammonium gymnemate exhibits the characters of the drug better than other salts.

The acid is a glucoside. After boiling for about an hour with dilute hydrochloric acid a dark resinous mass, devoid of the peculiar property of gymnema leaves, remains, and the liquor contains a body which readily reduces Fehling's solution.

Gymnemic acid occurs in other species of *Gymnema* besides *sylvestre*. *G. hirsuta* contains a considerable quantity, and *G. montanum* leaves contain it in a smaller proportion.

Ootacamund, India.

VOLUMETRIC ESTIMATION OF NICKEL.

By THOMAS MOORE.

THE process which I now describe is one based on the results of a large number of experiments carried out with the object of finding a volumetric method, to be at once sufficiently rapid and accurate for all practical purposes. The principle finally selected is that of the formation of the double cyanide of nickel and potassium in alkaline solutions by the addition of potassic cyanide. It is, however, impossible to judge of the end of the reaction by the disappearance of the blue colour, owing to the production of a yellowish tint which effectually conceals any further change, so that recourse must be had to indicators. In the first experiment excess of potassic cyanide was added, and this excess titrates back in neutral solution by iodine and starch, but in no case could a distinct blue be obtained. Titration of excess of cyanide by argentic nitrate is inadmissible, since the nickel compound is decomposed thereby. If, however, a small quantity of cupric ferrocyanide is added to the ammoniacal solution of nickel, then the potassic cyanide, no alteration in colour will take place with the copper compound until the nickel is completely converted into the double cyanide, and a very small quantity of potassic cyanide over and above what is required immediately destroys the copper salt, and the solution undergoes a distinct change in colour, thus indicating the end of the reaction.

A considerable number of experiments made with the process (checked by comparison with the figures obtained by electrolytically depositing the nickel) have amply proved that it is reliable and quite accurate enough for all ordinary purposes.

Solutions.—Potassic cyanide (pure): 22·5 grms. per litre. 20 c.c. of this are equal to about 0·1 grm. nickel. Cupric ferrocyanide: dissolve 2·25 grms. of cupric sulphate in one litre of water, and add a solution of potassic ferrocyanide until it ceases to produce any further precipitation. Thoroughly agitate before use.

Process.—If the solution contains much free ammonia, as in the filtrate from iron and nickel separation, neutralise part of it by addition of hydric chloride; if acid, add ammonia until strongly alkaline, then run in the potassic cyanide from a burette, stirring continually until the blue colour completely disappears and the solution takes a yellowish tint; when this happens add a measured quantity of cupric ferrocyanide sufficient to impart a distinct colour to the solution; the amount required for this purpose is variable, and depends upon the free ammonia present; now add the cyanide more cautiously, until finally one drop causes a distinct change of colour in the solution. A little practice is necessary to recognise the change, but after a few trials no difficulty will be experienced. The amount of cyanide necessary to decolourise the copper salt is so small that it may often be neglected; but if desired, the error may be eliminated by ascertaining how much cyanide is necessary to decolourise 100 c.c. of the copper solution, and reckoning out the difference in the usual way. Of course it is first necessary to standardise the cyanide solution with one of nickel of known strength.

The process gives equally good results in the presence of sulphates, nitrates, chlorides, or acetates, also in the presence of large quantities of ammoniacal salts, but large quantity of free ammonia should be avoided, owing to the solubility of the cupric ferrocyanide therein.

Appended are a few of the results obtained compared with those found electrolytically in different ores.

Electrolytically.	Volumetrically.
6·55 per cent Ni.	6·49 per cent Ni.
8·60 ,,	8·70 ,,
6·35 ,,	6·37 ,,
9·55 ,,	9·60 ,,
7·85 ,,	7·77 ,,

Thio, New Caledonia,
February 8, 1889.

NOTES ON RECENT AND FUTURE RESEARCH.

By SAMUEL E. PHILLIPS.

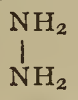
WE have long considered ammonia as the indifferent or non-carbonising hydride of the radical "amidogen," H,H_2N, and that $A=(NH_2)$ would probably be a 1 vol. representative of H, as so familiar in the teeming amido-compounds.

A recent number of *Nature* announces the discovery by Dr. Theodor Curtius, "who has succeded in preparing the long sought for hydride of N, 'amidogen.' This remarkable body has hitherto baffled all attempts at isolation," &c.

The Doctor is apparently a victim to a very common abuse of "Avogadro-law," which has greatly marred and confused his achievement. As H is one vol., and its hypothetic molecule, H_2, 2 vols; so it may be, and is, with other radicles of H equivalence. When the methyl body, "silico-methyl," was discovered, and found to be 1 vol., its 2 vol. molecule would be either $(Si_2E_3)_2$ or (Si_4E_6), but surely there is nothing in "Avogadro-law" to make it the latter rather than the former. But this is just the abuse I complain of, and mad theory contends that it is of ethane rather than methyl constitution, as "di-silico-hexethyl." However, Ladenburg, as a man of genius and a great chemist, speaks only of "silico-triethyl" in his lucid picture of the methyl-derivatives.

Cacodyl is another case, and one of amidogen type $(AsMe_2)$. As it ought to be, so it is, 1 vo., whereupon *theory* steps in, and declares it not to be $(AsMe_2)_2$ but (As_2Me_4); but they are compelled to admit that with chlorine it splits into "two atoms of cacodyl chloride," $(AsMe_2)C_2$.

In like manner Dr. Curtius makes the *molecule* of amidogen to be not $(NH_2)_2$, but—



$$\begin{array}{c} NH_2 \\ | \\ NH_2 \end{array}$$

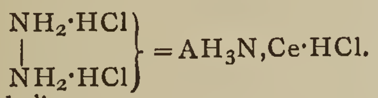
and then speaks of it as "amidogen or hydrazine, as it is variously called."

Who then are the culprits? I have never seen the two things thus confused. This reminds me that a great deal too much value is assigned to this 2 vol. law. Here we have hydrazine, $A,H_2N = 2$ vols., and 2 atoms of amidogen, $(NH_2)_2$, 2 vols., both containing the same number of elements, where *the law* is powerless in that discrimination, which chemism is so well fitted to supply. One is an ammonia with a whole train of plain consequents. The other is a radical evincing wholly different characters. One combines with H chloride to form, not a *hydrochloride*, but a chloride of ammonium. The other does nothing of the kind, and the hydrate of the text is utterly anomalous, and inapplicable to amidogen.

His "hydrate of amidogen" =

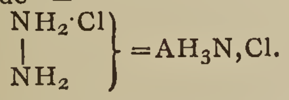
$$N_2H_4{\cdot}H_2O = AH_3N,O{\cdot}HO.$$

His "dihydrachloride" =



$$\left.\begin{array}{c} NH_2{\cdot}HCl \\ | \\ NH_2{\cdot}HCl \end{array}\right\} = AH_3N,Ce{\cdot}HCl.$$

And the "monohydrochloride" =



$$\left.\begin{array}{c} NH_2{\cdot}Cl \\ | \\ NH_2 \end{array}\right\} = AH_3N,Cl.$$

As hydrazine salts these are perfectly normal, but it is a great mistake to regard the two first as mono- and dihydro-compounds; one is an oxyhydrate precisely as the other is a chlorhydrate; but any attempt by halving to make them "amidogen" compounds is quite impracticable. What then does Mr. Fischer say to this intruder on his domain?

Wokingham Road, Reading.

ON THE

WAVE-LENGTH OF THE PRINCIPAL LINE IN THE SPECTRUM OF THE AURORA.*

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

Notwithstanding the large number of determinations by different observers, since Angström in 1867, of the wave-length of the principal (and frequently the only) line in the spectrum of the Aurora, this value has not yet been accepted as definitely fixed with the degree of accuracy which is required for a final inquiry into its chemical origin. The uncertainty within rather wide limits, which seems still to obtain, has arisen mainly from the circumstance that in nearly all cases the observations have been made with a small direct-vision spectroscope, and under conditions which do not admit of an accurate determination of the value sought for. About half the number of some twenty-four observers agree pretty well, but among the results given by the others the differences are very large in relation to the accuracy which is required, though they are not greater, perhaps, than was to be expected from the circumstances under which the observations were made.

I think it is very desirable, therefore, that I should put on record some observations of the spectrum of the Aurora which I made in the year 1874, but which up to the present time have remained unpublished. These observations were made with a powerful spectroscope, and under conditions which enabled me to determine the wave-length of the principal line within narrow limits of error. The spectroscope was made by Sir Howard Grubb on the automatic principle of his father, Mr. Thomas Grubb. It is furnished with two "Grubb" compound prisms; each has 5 square inches of base, and gives about twice the dispersion of a single prism of 60°.

The object-glasses of the collimator and telescope are 1·25 inch in diameter. The definition is very good. Though the automatic arrangement works well, I always take the precaution to measure only small differences of position of the line to be determined from lines near it, the wave-lengths of which are known.

The observations were made on February 4, 1874. There was a brilliant Aurora, showing a whitish light; a direct-vision spectroscope resolved this light into a brilliant line in the yellow and a faint continuous spectrum.

The "Grubb" spectroscope was directed from the window of the observatory upon the brightest part of the Aurora. In the first instance an estimation by eye was made of the position of the bright line by comparing it in the instrument with the spectrum of a spirit lamp. The bright line was seen to fall on the more refrangible side of the line, for which Watts gives the wave-length 5582,* Angström and Thalén 5583†, by from one-fifth to one-fourth of the distance of this line from the beginning of the band. If we take one-fourth, we have $\lambda 5569{\cdot}6$; one-fifth gives $\lambda 5572{\cdot}3$. The mean of these values gives for the—

Aurora line $\lambda 5570{\cdot}9$ . . . . (1).

The cross-wires of the spectroscope were then brought upon the line, and the reading 3476 showed the line to fall about midway between two strong lines in the spectrum of tin, $\lambda 5564$ and $\lambda 5587$ respectively, according to my measures.‡ The position of the cross was then compared directly with those lines in the spectrum of an induction spark taken between electrodes of tin. The further details of this comparison are not given in my note-book, but the result only, which placed the—

Aurora line at $\lambda 5571$ . . . . (2).

Consulting my map of the chemical elements, I found that there was a line of tellurium very near this place, namely, at $\lambda 5575$; I therefore brought the spark from tellurium before the slit, when the cross appeared on the more refrangible side of the tellurium line. The measure of the distance of the cross from this line came out equal to $\lambda 0003$. The place given in my paper for this line of tellurium is 5575. Thalén gives for the same line 5574·1.§ If we take the mean of these values and deduct 0003, we get for—

The line of the Aurora $\lambda 5571{\cdot}5$ . . . . (3).

There are strong lines of iron very near this position in the spectrum, and I made use of these also for a further determination of the place of the Aurora line. The cross, after having been placed upon the line of the Aurora, was confronted with these lines in the spectrum of iron.

The condensed account in my note-book does not give further particulars of this comparison, but states only that the place of the—

Aurora line came out $\lambda 5571{\cdot}5$ . . . . (4).

Summing up these determinations we have—

(1). Eye-estimation	$\lambda 5570{\cdot}9$
(2). From tin	5571·0
(3). From tellurium	5571·5
(4). From iron..	5571·5

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* A Paper read before the Royal Society, March 7th, 1889.

* *Phil. Mag.*, vol. xli., 1871, p. 14.

† "Spectres des Métalloides," *Nov. Act. Upsal. Sci.*, ser. 3, vol. ix., p. 29.

‡ "Spectra of the Chemical Elements," *Phil. Trans.*, 1864, p. 139.

§ *Brit. Assoc. Rep.*, 1885, p. 292.

From these values I think that we are justified in taking for the Aurora line, as a position very near the truth,—

λ5571 ± 0·5 . . . . (5).

Among the numerous determinations of other observers, those of Professor H. C. Vogel in 1872[*] seem to me to have great weight. A direct-vision spectroscope with a set of five prisms was used. The reduction of the readings of the micrometer into wave-lengths was based upon the repeated measures of 100 lines of the solar spectrum.

The screw had been thoroughly examined. After each observation of the Aurora lines, readings were taken of the lines of sodium or of hydrogen. The observations extended over four nights. On three nights four separate readings were obtained; on the fourth night two only. Vogel gives as the mean result of the fourteen observations—

Aurora line λ5571·3 ± 0·92 . . . . (6).

Perhaps I should state that I find from a remark in my note-book that at the time of my observations in 1874 I was not aware of Vogel's results, and I could not, therefore, have been biassed in any way by them.

The recent observations on the spectrum of the Aurora by Gyllenskiöld at Cap Thordsen in 1882, deserve special mention.[†] With a Hoffmann spectroscope, furnished with a scale, he obtained at Cap Thordsen in 1882 a mean result of λ5568 ± 1·6. Later, in 1884, at Upsala, with a Wrede spectroscope furnished with a micrometer screw, a mean value for the Aurora line, λ5569 ± 6·2.[‡] Gyllenskiöld discusses in detail nearly all the recorded observations of the spectrum of the Aurora from 1867 to 1882, and then brings them together in a table with such probable errors as the original statements of the observers enabled him to assign to them. I think it is desirable to give that part of his list which contains the observations of the brightest line:—

1867.	Angström	Upsala	λ5567 ±	1·0
1868.	Struve	Poulkowa	5552	14·9
	Lemström	Tromsœ	5659	14·0
1869.	Peirce	Etats Unis	5565	10·8
1870.	Proctor	.. .. ..	5995	25·0
1871.	Smyth	Edinburgh	5579	9·5
	Lindsay	Aberdeen	5680	50·0
	Barker	New Haven	5594	13·0
1872.	Vogel	Kiel	5571	0·9
	Denza	Moncalieri	5568	11·9
	Donati	Florence	5569	10·0
	Oettingen	Dorpat	5548	30·0
	Respighi	Rome	5574	10·0
	Wijkander	Spitzberg	5572	1·0
1873.	Backhouse	Sunderland	5660	10·0
	Barker	New Haven	5569	13·9
	Lemström	Enare	5569	0·5
1874.	Backhouse	Sunderland	5570	10·0
	Maclear	"Challenger"	5522	37·1
1879.	Nordskiöld	Pitekaie	5563	10·0
1880.	Copeland	Dunecht	5572	2·0
1882.	Gyllenskiöld	Cap Thordsen	5568	1·6
1884.	„	Upsala	5569	6·2

Gyllenskiöld then calculates by the method of least squares the mean value of all the determinations, and finds the following result[§]:—

Mean value of the 23 observations, λ5570·0 ± 0·88 . (7).

The recent measures by C. C. Krafft[‖] depart largely from Gyllenskiöld's mean value. Krafft found on—

1882, November	2	λ5595
„ „	11	5586

and measures with the same instrument, made by Schroeter on November 17th, gave λ5587.

Now, though Angstrom's original value λ5567 may not be quite accurate, his observation fixed a limit towards the red, beyond which the Aurora line cannot lie. Angstrom says, "sa lumière était presque monochromatique et consistait d'une seule raie brillante située à gauche" (on the more refrangible side) "du groupe connu des raies du calcium."[*] The position of the most refrangible line of this calcium group is accurately known; according to[†]

Kirchhoff	λ5580·9
Thalén	5580·9
Huggins	5581·0

It is certain, therefore, from Angstrom's first observation in 1867 alone, that the Aurora line lies well on the more refrangible side of wave-length 5580. This limit towards the red was confirmed afterwards by Angstrom himself; he says later that the yellow line falls almost midway between the second and third line of the shaded carbon group.[‡] The positions of these lines of comparison are, according to Angström and Thalén, λ5538 and λ5583.[§]

It follows that Krafft's values, λ5586, λ5587, and λ5595, must be from some cause inaccurate. A possible explanation may be found in the small number of solar lines employed by Krafft for the reduction of the measures into wave-lengths. The curve was drawn through the six Fraunhofer lines B, C, *a*, D, E, and *b*. There was no control for the curve between D and E, and a very small deviation of the curve from its true position here would be sufficient to account for the position of less refrangibility of from λ0016 to λ0024, which his measures give for the Aurora line.

It should be stated that Krafft expresses regret that more attention could not be given to the spectroscopic observations. He says:—"Leider gestatteten die obligatorischen Beobachtungen nicht, den spectroscopischen Untersuchungen die gehörige Aufmerksamkeit angedeihen zu lassen . . . . Ich glaubte ausserdem diese Messungen um so mehr auslassen zu können, als der Platz der gewöhnlichen Nordlichtlinie oft und sehr genau bestimmt ist."

To sum up, we have the following values for the principal line of the Aurora:—

(6).	1872, Vogel	λ5571·3 ±	0·92
(5).	1874, Huggins	5571·0	0·5
(7).	Gyllenskiöld's mean of 23 observers from 1867 to 1884	5570·0	0·88

These values agree closely, and fix within very narrow limits the position in the spectrum, where we have to seek the chemical origin of the line.

Gyllenskiöld, from his observations of the changes which occur in the spectrum of the Aurora, comes to the conclusion that: "le spectre de l'Aurore boréale résulte de la superposition de plusieurs spectres différents," and that "la raie principale forme un de ces spectres élémentaires; elle apparait très souvent seule." A similar view was taken many years ago by Angström[‖] and by Vogel.[¶]

[After consideration I think that I ought to point out that Mr. Lockyer's recent statement[**] that:—"The characteristic line of the aurora is the remnant of the brightest manganese fluting at 558," is clearly inadmissible, considering the evidence we have of the position of this line.

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[*] *Leipzig Math. Phys. Berichte.*, vol. xxii., p. 285.

[†] *Observations faites au Cap Thordsen, Spitzberg, par l'Expédition Suédoise*, vol. ii., p. 1; Aurora Borealis, par Carlheim Gyllenskiöld, Stockholm, 1886.

[‡] *Ibid.*, p. 166.

[§] *Ibid.*, p. 169.

[‖] "Boebachtung-Ergebnisse der Norwegischen Polarstation," &c. A. S. Steen. Christiania, 1888.

[*] *Spectre Solaire*, Upsal, 1868, p. 42.

[†] *Brit. Assoc. Rep.*, 1884, p. 372.

[‡] *Nature*, vol. x., p. 211.

[§] *Acta Upsal.*, ser. 3, vol. ix., p. 29.

[‖] *Nature*, vol. x., p. 210.

[¶] *Leipzig Math. Phys. Berichte*, vol. 23, p. 298.

[**] *Roy. Soc. Proc.*, vol. xlv. (1889), p. 234.

In support of this statement Mr. Lockyer says:—Angström gave the wave-length of the line as 5567, and since then many observers have given the same wave-length for it, but probably without making independent determinations. Piazzi Smyth, however, gives it as 558, which agrees exactly with the bright edge of the manganese fluting. R. H. Proctor also gives the line as a little less refrangible than Angström's determination. He says:—'My own measures give me a wave-length very slightly greater than those of Winlock and Angström'" (*Nature*, vol. iii., p. 468).

By reference to Gyllenskiöld's table it will be seen that the probable errors of the determination by Piazzi Smyth and Procter, 5579 ± 9·5 and 5595 ± 25·0 respectively,[*] are too large to entitle these measures to special weight.

Mr. Lockyer says further:—"Gyllenskiöld's measures with the Wrede spectroscope also give 5580 as the wave-length of the characteristic line. I feel justified, therefore, in disregarding the difference between the wave-length of the edge of the manganese fluting and the generally accepted wave-length of the Aurora line."

Gyllenskiöld's single measure of 5580, on which Mr. Lockyer relies, differs widely from the values which Gyllenskiöld himself assigns to this line, namely, from observations at Cape Thordsen in 1882, λ5568 ± 1·6, and from observations at Upsala in 1884 with the Wrede spectroscope, λ5569 ± 6·2.

Speaking of Krafft's observations, Mr. Lockyer says[†]:—"The wave-lengths obtained for the Aurora line were 5595, 5586, and 5587. Unlike most observations, these place the Aurora line on the less refrangible side of the manganese fluting. Hence we have an additional reason for neglecting the difference between the wave-length of the brightest edge of the manganese fluting and the commonly accepted wave-length of the Aurora line, as given by Angström. . . . . These observations are the latest which have been published, and were obviously made with a full knowledge of all previous work, so that their importance must be strongly insisted upon."

I have already pointed out that Krafft's measures were not made under circumstances which assured to them a high degree of accuracy; and Krafft's own words, which I have quoted, disclaim expressly any special attempt on his part to re-determine the position of the principal line with a higher degree of accuracy than the observers who preceded him.—March 4].

ANALYSES OF WATERS OF THE YELLOWSTONE NATIONAL PARK,

With an Account of the Methods of Analysis Employed.[‡]

By FRANK AUSTIN GOOCH
and JAMES EDWARD WHITFIELD.

(Concluded from p. 156).

Treatment of the Aqueous Solution.

The aqueous solution, its degree of concentration having been determined in the manner already described, was divided into five portions. Two of these were taken for the determination of bromine, iodine, lithium, cæsium, rubidium, and thallium, in duplicate; two for the determination in duplicate of arsenic, antimony, tin, copper, lead, and boron; and the remaining portion was reserved to be used in an emergency.

Iodine and Bromine.—The portion for the determination of the elements of the former group was weighed and evaporated to a pasty condition. The residue was thoroughly extracted with strong alcohol, treated with water, reduced again nearly to dryness, and again extracted with alcohol. The extract was evaporated after the addition of a drop or two of a strong solution of sodium hydrate, and this residue was extracted with alcohol like the former residue. The residues of the extractions with alcohol were kept for subsequent treatment. The alcoholic solution containing presumably all the iodine and bromine, with a small proportion of the chlorine originally in the water, was evaporated to dryness, and the solution of the residue in water was acidulated with sulphuric acid mixed with a solution of ferric sulphate introduced into a retort of the pattern previously described and figured in connection with the determination of boric acid in the natural waters, and distilled. The distillate was collected in a U-tube attached to the condensing tube and sealed with carbon disulphide and water. If iodides are present in the retort to the minutest degree the iodine is set free as such, its characteristic colour appears in the seal of carbon disulphide, and its amount may be determined by titration in the usual manner with sodium hyposulphite.

In the waters which we examined iodine was not present in sufficient quantity to appear in the test of the amounts at our disposal.

To the liquid remaining in the retort after the distillation had been prolonged sufficiently to ensure the complete volatilisation of the iodine a few crystals of potassium permanganate were added, and the distillation was continued. This distillate was collected as before in a U-tube joined to the condenser, but the seal was made with chloroform and water. At the beginning of the operation the seal of the U-tube showed in most cases the characteristic colour of bromine, but this was discharged before the end of the operation by the excess of chlorine and replaced by the colour of the latter. The contents of the U-tube were transferred to a beaker and treated with pure sodium hydrate and zinc, and from the solution of sodium bromide and chloride thus obtained the silver salts were precipitated by silver nitrate, in the usual manner, after acidifying with nitric acid. The silver bromide and chloride thus precipitated were collected together upon asbestos in a perforated crucible, dried, weighed, and dissolved in potassium cyanide. From the cyanide solution the silver was deposited by electrolysis, according to the process described elsewhere by one of us for the indirect estimation of bromine in the presence of chlorine.[*] In this manner we obtained the weight of the mixture of silver chloride and silver bromide, and the weight of the silver contained in the mixture. The amounts of bromine and chlorine in the mixed salts were determined from these data by the solution of a simple algebraical equation.

Lithium.—The contents of the retort after the distillation of the bromine were united with the residues of the extractions by alcohol, the excess of sulphuric acid was volatilised, the residue dissolved in hydrochloric acid, the sulphates converted to chlorides by means of barium chloride, the baric sulphate thus formed separated by filtration, alumina, silica, and barium carbonate precipitated by ammonium carbonate and separated by filtration, and the solution evaporated to dryness. The residue was gently ignited to remove ammonium chloride, dissolved in water acidulated with hydrochloric acid, and this solution, concentrated until just ready to deposit, was drenched with strong alcohol. The sodium chloride precipitated was washed with alcohol until the spectroscope indicated entire freedom from lithium chloride. The alcoholic solution of lithium chloride was evaporated to dryness, and the residue was dissolved in a little water acidulated with hydrochloric acid. This solution was treated with a little pure barium hydrate (made from the nitrate precipitated from nitric acid) to remove traces of magnesia, and filtered, and from the filtrate the barium was removed by treatment with ammonium carbonate,

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[*] Gyllenskiöld's statement of Proctor's value is based on *Nature*, vol. iii., p. 347 and p. 68.

[†] *Roy. Soc. Proc.*, vol. xlv. (1889), p. 241.

[‡] *Bulletin of the United States Geological Survey*, No. 47.

[*] *Bulletin of the U.S. Geological Survey*, No. 42, p. 89; *Am. Chem. Jour.*, vol. viii., p. 421

repeated if necessary. From the solution of lithium chloride thus obtained the lithium was separated according to Mayer's method* by evaporation with hydro-disodic phosphate and sodium hydrate, the treatment of the residue with sufficient hot water to dissolve the salts, which should be soluble with the aid of gentle heat, the addition of an equal volume of ammonia, and digestion in the cold during twelve hours. The precipitate was filtered upon asbestos in a perforated crucible, washed with a mixture of equal parts of ammonia and water, ignited, and weighed. The filtrate from this precipitate was evaporated, and the residue of evaporation again treated as before to recover traces of lithium; and a similar process of treatment was applied to the filtrate from the second precipitate. The three precipitates thus obtained contained presumably all the lithium as the tribasic phosphate.

This is the method of determining lithium which was employed previous to the development of the process which has been described in connection with the account of the determination of lithium in the natural waters (see *ante*). Were the work to be repeated we should unquestionably employ the amyl alcohol process exclusively, although it may be said for the determinations by Mayer's method that their actual error was very much diminished by the use of comparatively larger portions of material for the analysis, and we are confident that the results are, on that account, fairly trustworthy.

Cæsium, Rubidium, and Thallium.—The filtrate from lithium phosphate was freed from ammonia by boiling; the phosphoric acid was precipitated by ferric chloride and ammonia, with the usual precautions to secure a suitable proportion of the iron salt and to keep the excess of ammonia at the lowest possible limit, and removed by filtration; the filtrate from ferric phosphate and ferric hydrate was evaporated to dryness and gently ignited to remove ammonium salts; the residue thus left was dissolved in water and treated with platinic chloride in excess of the amount necessary to convert all the alkaline chlorides present to platinum salts.

The precipitate by platinic chloride was extracted by boiling repeatedly with small portions of water, and the residues of this treatment were tested from time to time spectroscopically. The characteristic lines of cæsium and rubidium appeared more distinctly toward the end of the process of extraction when they were visible at all. Thallium, which should appear, if present, in the intermediate extracts, failed to show itself in any of the waters.

Arsenic, Antimony, Tin, Copper, and Lead.—The weighed portion of the concentrated solution was acidified with hydrochloric acid, heated to 70° C., and submitted to the action of a current of hydrogen sulphide during several hours. The precipitated sulphide was filtered off upon anthracene in a perforated crucible, following the method described by one of us.† The crucible with the adherent filter of anthracene and the precipitate were placed in a small beaker, drenched with benzol, and gently warmed until the anthracene dissolved. Water containing sodium hydrate was added and, after sufficient digestion on the water-bath, the liquid and precipitate were transferred to a paper filter, previously moistened with water. In this manner the aqueous solution, carrying the arsenic, antimony, and tin, if present, was permitted to traverse the filter, while the sulphides of copper and lead, with possibly free sulphur, remained with the benzol upon the filter. After thorough washing with water the receptacle for the filtrate was changed, the filter was moistened with alcohol, and thus the benzol, with the anthracene in solution, was induced to pass through the paper, which, with the residue upon it, was washed with benzol followed by alcohol and then by water. The filter was carefully incinerated, and the ash was digested with a few drops of nitric acid. The solution thus obtained was evaporated to dryness, the residue was moistened with hydrochloric acid, and, after the volatilisation of the most of the acid, dissolved in hot water. From this solution hydrogen sulphide should precipitate copper and lead as sulphides. In the single case of that water which had been concentrated in porcelain no black sulphide was obtained at this point in the operation; in other cases, a trifling black precipitate fell, which subsequent examination proved to be copper sulphide exclusively, doubtless originating in the concentrating vessel.

The second precipitation with hydrogen sulphide was introduced to test the presence of copper and lead, in the process just outlined, because the residue left upon the filter when the benzol is washed from it is apt to be dark in colour, even in the absence of black sulphides.

The alkaline filtrate from the benzol and the insoluble residue were acidified with hydrochloric acid, after the addition of a drop or two of ammonium sulphide; the precipitate was filtered off on asbestos in a perforated crucible; the filter and precipitate were dried and treated in a small beaker with fuming nitric acid; the solution in nitric acid was evaporated to dryness, the residue was dissolved in hydrochloric acid, and from this solution, made strongly alkaline with ammonia containing some ammonium sulphide (the last to keep tin, if present, in solution), but kept small in volume, the arsenic was precipitated by the magnesium chloride mixture. The liquid was briskly stirred and then allowed to stand quietly for twelve hours at least. The precipitate was transferred by means of the mother liquor, without the use of other liquid, to a perforated crucible carrying an asbestos felt, washed with a mixture of one part of ammonia to three of water, dried carefully, ignited in an atmosphere of oxygen, and weighed as magnesium pyroarsenate.

The filtrate from the ammonio-magnesium arsenate, which should contain the antimony and tin of the water, was evaporated to remove the great excess of the ammonia, and acidified with hydrochloric acid. The sulphur thus precipitated should carry with it the antimony and tin as sulphides, In no case were we able to detect antimony in this precipitate. In one or two cases there were evidences of the presence of tin, but this doubtless came from the lining of the vessel in which concentration was effected; in the water which was concentrated in porcelain no tin was found.

Boric Acid.—The filtrate from the original precipitate by hydrogen sulphide in the acid solution was warmed gently, submitted to the action of a current of air to blow out the excess of hydrogen sulphide, brought nearly to neutrality by the addition of sodium carbonate, made faintly alkaline with ammonia, filtered from the precipitate thus thrown down, and evaporated nearly to dryness after the addition of enough sodium hydrate to expel the ammonia and yet preserve strong alkalinity. The residue was acidified with hydrochloric acid and extracted thoroughly with alcohol, and the alcoholic solution was made alkaline with sodium hydrate and evaporated to dryness. This residue was dissolved in water, just acidified with hydrochloric acid, and from the solution the last traces of silica, alumina, lime, and phosphoric acid were removed by the action of ammonia and ammonium carbonate, and filtration. In the filtrate the boric acid was determined according to Marignac's process, by treatment with magnesium chloride, ammonium chloride, and ammonia, evaporation to dryness, ignition at a red heat, extraction with boiling water, and the repetition upon the extract of the process of evaporation, ignition, and extraction. The residues left after extraction were together ignited and weighed, and the magnesia in the weighed material was determined by precipitation as the ammonio-magnesium phosphate and weighing as the pyrophosphate. The difference between the weight of the residue and its contents in magnesia is boric acid.

This was the process which we employed in the earlier determinations. The process which was developed later,

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* Fresenius's "Quant. Anal.," 6th Aufl., Band II., p. 215.

† *Bulletin of the U.S. Geological Survey*, No. 42, p. 86; *Am. Chem. Journ.*, vol. vii., 1885—86, p. 87.

and applied to the determination of boric acid in the natural waters, is preferable.

Statement of the Results of Analysis.

In stating the facts deduced from the analysis of the waters, it has seemed best to adopt the plan of recording the oxygen acids as anhydrides, the basic elements as such, and the oxygen which must exist in combination with the bases by itself; thus avoiding an arbitrary division of the basic elements among the oxygen acids and halogens. The basic oxgen, so-called, of the alkaline waters was found by computing the amount of oxygen which would exist in the oxides of the basic elements and deducting from this amount the weight of oxygen equivalent to the halogen discovered by analysis. In the case of waters which carried such an excess of acid that the halogens may be supposed to be uncombined with bases, the basic oxygen is the amount of oxygen which would exist in the oxides of the basic elements. In waters of such acidity that a portion only of the halogen may be supposed to be in combination with basic elements the equivalent in oxygen of the amount of halogen which is regarded as in combination was deducted from the total amount of oxygen of the oxides in computing the basic oxygen. The halogen which remains uncombined with the basic elements was, as a matter of course, assumed to be in association with hydrogen.

The hypothetical combination of the elements found in the waters must necessarily be largely imaginary, for nothing is more plainly evident than the impossibility of stating authoritatively, in the present condition of knowledge, the actual division of a number of acids among a number of bases in solution. This we do know, that the combination is determined not only by the relative proportions of all the constituents, but by the absolute quantities of all associated in a definite amount of liquid. It is with no purpose, therefore, of attempting to represent actual conditions of combination, but only for the sake of securing a common ground of comparison among themselves and with other waters, that we have assumed arbitrarily the existence in these waters of the definite and simple combinations of the following scheme:—

In alkaline waters, bromine has been combined as KBr; B_2O_3 as $Na_2B_4O_7$; As_2O_3 as $NaAsO_2$; P_2O_5 as Na_2HPO_4; chlorine has been assigned to the bases in the order NH_4, Li, K, Na; SO_3 has been linked with such bases as remain in the order NH_4, Li, K, Na, Mg, Ca; residual bases have been classed as neutral carbonates in the order Mg, Ca, Na; residual sodium has been represented as $NaSiO_3$; aluminum and iron have been put down as Al_2O_3 and Fe_2O_3; and residual CO_2 and SiO_2 have been shown as such.

In making up the hypothetical composition of acid waters the same general arrangement has been kept as far as possible in order to secure ready comparison with the alkaline waters. Though the relative avidity of hydrochloric acid is greater at ordinary temperatures than that of sulphuric acid, we have nevertheless represented hydrochloric acid as the free acid whenever it became necessary to represent one of them as free.

The sulphuric acid indicated by the analysis has been combined with the bases in the order Ca, Mg, Al_2, Fe_2, Na, K, Li, NH_4; the residual bases have been combined with chlorine in the same order; the anhydrides B_2O_3, As_2O_3, P_2O_5, SiO_2, CO_2, and residual SO_3, have been stated as such; residual chlorine has been represented as HCl, and H_2S as such.

It is apparent that in some instances combinations have been imagined which might exist under some of the circumstances encountered, but which are improbable under other conditions met with in waters of a generally similar character; thus, for the sake of uniformity, we have represented the boric acid of the alkaline waters invariably as $Na_2B_4O_7$, and the phosphoric acid as Na_2HPO_4, regardless of the variable action of an excess of alkaline carbonate upon these salts in hot solutions and under prolonged digestion. So, also SiO_2 has been stated as free, when, if so, it must have been in solution in the presence of the carbonates of sodium, magnesium, and calcium; the neutral carbonates have been represented as such in the presence of free carbonic acid, both in hot and in cold waters; and potassium has been arbitrarily associated with bromine; and ammonium, lithium, and potassium have been preferred to other bases in combining the chlorine.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

March 23, 1889.

Prof. Reinold, F.R.S., President, in the chair.

The following gentlemen were elected members:—Sir James M. Douglas, Sir Douglas Galton, Messrs. C. W. Biggs, C. Capito, A. C. Cockburn, R. E. Crompton, J. M. Gorham, C. G. Gümpel, W. H. Massey, E. Moynihan, F. J. Mudford, R. W. Paul, and C. E. Spagnoletti.

Prof. J. V. Jones read "*Notes on the Use of Lissajou's Figures to Determine a Rate of Rotation, and of a Morse Receiver to Measure the Periodic Time of a Reed or Tuning-fork.*"

In determining resistance absolutely by the B.A. or by Lorenz's method it is important to know the speed of rotation at the instant when the deflection of the galvanometer needle is observed. To determine this, an arm carrying a mirror is caused to oscillate by a pin placed eccentrically in the end of the spindle, and a Lissajou's figure is obtained by using another mirror mounted on a vibrating reed driven electrically. Equality of period is obtained when the resulting elliptical figure is permanent, and the frequency of the reed is determined subsequently. In making the experiments it is found convenient to control the speed of the disc by braking it either with the finger or a piece of wood. The reed consists of a rectangular steel rod 100 c.m. long and section 1·51×0·60 c.m., and the length of the vibrating segment can be altered by sliding it through a clamp. To permit of this change without altering the electrical contacts, the latter are formed by two independent springs, one of which is always in contact with the rod. For determining the frequency of the reed a second pair of contacts are operated by the vibrator, and the currents recorded by a Morse receiver, whilst simultaneously the paper receives marks from a pen controlled by a standard clock. The limit of accuracy of this part of the experiment is found to be 1-10th per cent, due to changes in the reed's frequency. This is a serious defect, and the author of the paper asked for advice as to the precautions necessary to obtain reeds of constant pitch.

Prof. Ayrton, whilst recognising the extreme importance of determining speed accurately, suggested that the inconstancy of the reed may be due to the impulse being given at the end instead of at the middle of its swing, and recalled an experiment shown before the Society by Prof. Perry and himself, in which the pitch of an electrically driven fork was varied greatly by altering the adjustment of the contact-screw. Referring to Dr. Thompson's modification where two tuning-forks drive each other, it was pointed out that the method requires the synchronism of the two forks to be very exact.

Mr. Blaikley enquired whether any doors were opened or closed during the experiments, as the pitch of a reed is affected by the size of its resonance chamber. He also stated that the pitch of reeds driven pneumatically could be maintained constant to 1 part in 10,000, and mentioned that two forks nearly in unison influence each other's period when near together.

Referring to the two forks mentioned by Prof. Ayrton, Prof. S. P. **Thompson** said it was advantageous to mount such forks on sounding-boxes, for, when placed at a suitable distance apart, they then exert considerable mutual control.

The sketch put on the board by Prof. Jones led Dr. **Thompson** to suppose that a perfect method of driving forks had been devised, for two springs were shown touching opposite sides of the box, and such an arrangement might be used to complete the circuit only when the reed is in the middle position. He also believed that forks give greater constancy than single reeds, and mentioned some recent improvements in which one prong of an electrically driven fork is made of phosphor bronze.

Mr. T. H. **Blakesley**, reasoning from ideas suggested by Mr. Stroh's experiments on vibrating membranes, concluded that the periods of forks placed $\frac{1}{4}$ wave-length apart would not uninfluence each other.

In reply to a question from Mr. F. J. Smith, Prof. **Jones** thought there could be no "creeping" of the reed through the clamp. He also stated that he had been led to use a reed from the results obtained in Delaney's system of telegraphy, and the fact that Lord Rayleigh considered electrically driven forks satisfactory.

Dr. **Hofford** read extracts from the following papers:—

"*On the Clark Cell as a Source of Standard Currents.*" By Prof. R. **Threlfall** and Mr. A. **Pollock**.

The authors find, contrary to ordinary ideas, that Clark cells can be used to send currents of considerable magnitude without the E.M.F. being appreciably changed, and have constructed cells which give 0·001 ampere steadily for half an hour. This result has been obtained by increasing the size of the cell, so that each electrode is about five square inches in area and the internal resistance is about six ohms. For the ordinary small test-tube cell, the resistance of which may be about 1500 ohms, the current ought not to exceed 0·00001. On closing the circuit the P.D. (potential difference) drops almost instantaneously to its steady value, and, when the circuit is opened rises equally rapidly to very nearly the original E.M.F. The cells completely recover in time. If the current sent be too large the P.D. falls for a time, and afterwards rises and tends towards a fixed value. In this respect Clark's cells are greatly superior to large Daniell's sending current through the same resistance. The paper contains several tables and curves, as well as valuable results respecting the close agreement between the E.M.F. of a great number of different cells.

"*On the Application of a Clark's Cell to the Construction of a Standard Galvanometer.*" By Prof. R. **Threlfall**.

A large cell as above mentioned, together with a known platinoid resistance, are used to standardise a reflecting galvanometer, constructed with a single movable coil, sliding in guides so as to vary the constant in known proportions. Two controlling magnets are carried on opposite sides of a sleeve sliding on a central tube enclosing the long fibre, and a small hollow copper cylinder in oil acts as a damper. The tangent law was found by calculation to be practically correct up to 15°, and the scale is curved so as to read tangents on a scale of equal divisions. To give this result the approximate polar equation to the curve is shown to be $r=f(1+0{\cdot}207\,\theta^2+0{\cdot}0269\,\theta^4)$. In standardising the instrument a known current is sent through it from the Clark cell, and the controlling magnets adjusted till the spot comes to a fiducial mark on the scale. By varying the position of the coil currents ranging from 0·001 to 0·4 ampere can be measured.

"*On the Measurement of High Specific Resistances.*" By Prof. **Threlfall**.

The chief points dealt with are the means for producing thin plates of material of known dimensions, the form and methods of magnetising the needles, and the arrangement of suspension found necessary when great sensibility is required. For producing the plates two plane platinised brass slabs are used and kept at a known distance apart by micrometer screws, whilst the material is melted between them. The screws are then withdrawn and the resistance determined by comparison with a megohm, using different E.M.F.'s in the two cases, so as to obtain about equal deflections. As regards the galvanometer, after many unsatisfactory attempts to use one made according to the Messrs. Gray's pattern, the coils of that instrument were mounted in the ordinary way, and used with an astatic combination of magnetised steel discs. Extreme care was taken to obtain discs exactly similar, and a pair of electro-magnets were made to magnetise them *in situ*, so as to obtain great astaticism. For suspending the magnets quartz fibres were found greatly superior to silk, the zero of the instrument being very indefinite, even with a silk fibre thirty inches long. Considerable difficulty was experienced in attaching the mirror to the needle on account of the distortion produced by ordinary elements; slow drying white paint was ultimately used and found satisfactory.

"*On the Measurement of the Resistance of Imperfectly-purified Sulphur.*" By Prof. **Threlfall** and Mr. A. **Pollock**.

The apparatus used is described in the previous paper, the galvanometer of 16000 ohms being arranged to give 1 division for 2×10^{-12} amp. A mean of the results obtained gives about 11×10^{13} ohms per c.c. as the specific resistance. In performing the experiments many precautions were required to prevent air currents and magnetic disturbances, and paraffin keys were found to give much better insulation than ebonite ones. In conclusion the authors enumerate the chief points to which attention should be paid in designing and using very sensitive galvanometers. They consider it desirable to use quartz fibres at least six feet long, to provide very fine adjustment for the controlling magnets, whose supports should be independent of the suspension arrangement, and believe the whole should be placed in a thick soft iron cylinder.

Mr. **Boys**, speaking of attaching mirrors to wires, said he found a very small speck of shellac varnish to be very satisfactory. As regards quartz fibres, Prof. Threlfall's method of producing them differed materially from his, and the fibres were much thicker. He considered it quite unnecessary to use fibres anything like six feet long, and thought fifteen inches quite sufficient where the weight to be supported was not large.

Prof. **Ayrton** regarded the results obtained from Clark's cells to be of extreme scientific and commercial importance, for they showed that a very convenient standard of E.M.F. could also be used as a standard for current.

Prof. **Thompson**, after commenting on the convenience of good E.M.F. standards, expressed a hope that Prof. Threlfall would be able to suggest a convenient method for producing a standard ampère.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, April 1, 1889.

Sir James Crichton Browne, M.D., LL.D., F.R.S.,
Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—Septimus Felix Beevor, B.A.; Professor J. A. Fleming, M.A., D.Sc.; John Langston, J.P., F.R.C.S.; and Major S. Flood Page.

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

Appointment. — Mr. Charles H. Piesse, A.K.C. (Lond.), M.R.C.S., F.I.C., &c., of Cassiobury House, Fulham, and New Bond Street, has been appointed Consul-General in London for the Principality of Monaco.

NOTICES OF BOOKS.

Exercises in the Preparation of Organic Compounds. By Professor Emil Fischer, of Wurzburg. Translated with Permission of the Author from the Second German Edition by Archibald Kling, F.I.C., Chief Assistant, Chemical Laboratory, Glasgow and West of Scotland Technical College. With a Preface by W. Dittmar, LL.D., F.R.SS.L. and E., Professor of Chemistry in the Glasgow and West of Scotland Technical College. Glasgow: W. Hodge and Co. London and Edinburgh: Williams and Norgate.

Teachers of chemistry and students who aim at acquiring a sound knowledge of the organic department of the science will find this little work exceedingly useful. They will find here instructions which have been verified during long and extended practice in the laboratories of the Universities of Erlangen and Wurzburg. It will be perceived that the substances whose preparation is here described have not been taken at random, but have been selected so as to illustrate the principal operations and the most important methods which are brought into requisition in organic chemistry. It is not too much to say that the student who has worked carefully and intelligently through the operations described in this book will have taken a considerable step towards qualifying himself for original research or for taking part in the industrial preparation of organic compounds.

We have been much pleased with a remark made by Professor Dittmar in his "Introductory Preface." He writes:—"The present book, as a comparison will show, is a close translation of the original; I don't believe in 'adaptations'; if a book is worth translating, translate it as it stands." The writer here lays his finger upon a real evil. We know foreign works which, in the course of translation, have been by no means improved by "adaptation" to British educational prejudices.

Whilst we can conscientiously recommend this book we must admit that it is written for the genuine student, not for the intending examinee. It will surely aid the former to "know," but it will scarcely help the latter to "pass."

**The Proprietor Face to Face with his Forsaken Farm.* Lectures delivered at Brussels at the Request of the Central Society of Agriculture. By M. Georges Ville.

†*M. Georges Ville and Agricultural Belgium.* Lectures delivered at Brussels during the Year 1874 at the Request of the Central Society of Agriculture. By M. Georges Ville. Paris: G. Masson.

Unlike too many chemists, physicists, and engineers of the present day, M. Ville is nobly seeking to increase the productiveness of the soil, so that the agriculturist of Europe, and especially of France, may not be crossed by the competition of America and India, the future of which he views with alarm. But he does not take into consideration a still more serious evil in the background. The time must come when the United States will require their total produce for the support of their own population. Similar will be the case ultimately with India, Australia, the La Plata Regions, &c. The country, then, which cannot grow food for its inhabitants will be in evil plight. But this consideration, far from invalidating the teachings of M. Ville greatly enhances their weight.

The author combats the old prejudice against chemical manures, and the superstition—we can give it no better name—that matter acquires a new value as plant-food by having been passed through the digestive organs of an animal. He does not, as some of his critics have asserted, reject farmyard manure as useless. When produced he would have it turned to full account. But he condemns as unscientific and uneconomical the keeping of stock for the purpose of producing manure. Even in these days we sometimes hear the farmer advised to buy not superphosphate, sulphate of ammonia, nor Bolivian nitre, but "some good feeding stuff!"

The only part in M. Ville's teachings concerning which doubt may be entertained is the great weight which he lays upon lime in the form of gypsum. In all his manurial formulæ, no matter for what crop or on what soil, this ingredient figures largely. Combined nitrogen, potash, superphosphate, and gypsum are his four principles, varying in proportion according to the kind of plant. This certainly seems strange if we reflect that most soils contain lime, often in considerable proportions, and that even the best superphosphates have rarely less than 50 per cent of calcium sulphate. His experiments, we must admit, show somewhat better results in the presence of gypsum then in its absence. But agricultural practice in England does not lead to corresponding results, and our experts generally pronounce gypsum in chemical manures a make-weight. We see that in the grain of cereals, in the seeds of the bean, and the tubers of the potato, *i.e.*, the portions which are most likely to be consumed away from the farm, the magnesia exceeds in the wheat, whilst in the straw, as well as in turnips, hay, and clover, that is to say, in the products which are generally returned to the soil, lime is in excess.

The two works before us may be characterised as forming a popular summary of M. Ville's more extensive treatise on "Artificial Manures," which already exists in an English version.

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* "Le Proprietaire devant sa Ferme Délaissée."
† "M. Georges Ville et La Belgique Agricole."

CORRESPONDENCE.

ACTION OF FERROUS SULPHATE ON SOILS.

To the Editor of the Chemical News.

Sir,—"X" refers me to papers in the *Journal of the Chemical Society*. These to me are inconclusive. Green vitriol was experimented upon a quarter of a century at least before Dr. Griffiths took it up, and he has not added anything to our knowledge regarding it. The late Dr. Voelcker proved that green vitriol was both plant food (indirectly) and plant poison (directly). It is strange that sulphate of ammonia has not gone down to 10s. per ton if we are to credit what "X" says in regard to what Professor Muntz says.—I am, &c.,

John Geddes McIntosh.

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. cviii., No. 11, March 18, 1889.

On the Fixation of Nitrogen during Slow Oxidations.—M. Berthelot.—If an old sample of ether, which has been preserved for months or years in bottles only partially full, is agitated with a small quantity of lime-water absolutely free from nitrates, and if this water is carefully evaporated to dryness, the residue, re-dissolved in a few drops of water and evaporated anew, yields, with strong sulphuric acid and ferrous sulphate, the red colour characteristic of nitric acid. It yields also the blue colouration of diphenylamine, but this colour is not specific, and its use is open to errors which the physiologists have not sufficiently guarded themselves against. The blue is produced by a great number of oxidising bodies, including hydrogen peroxide.

The Formation-heat of Hydrogen Peroxide.—M. Berthelot and P. Petit.— This thermo-chemical paper does not admit of useful abstraction.

Preparation of Cuprous Chloride and Bromide by Means of the Alkaline Haloids and Copper Sulphate.—M. Denigès.—For the preparation of cuprous chloride the author heats to a boil in a flask one part each of crystalline copper sulphate and copper turnings, two parts sodium chloride, and ten parts of distilled water. The solution is filtered into 15 to 20 parts of water acidulated with 1 to 2 parts of acetic acid. If the hot liquid is collected separately after filtration and secluded from air it yields on cooling fine crystals of cuprous chloride. The same liquid dissolves carbon monoxide and hydrogen phosphide.

New and Characteristic Reactions of the Copper Salts.—M. Denigès.—This reaction depends on the easy conversion of the copper salts into cupric bromide under the influence of potassium bromide and on the dehydration of this product by sulphuric acid, which, when dissolved in an excess of the bromide, displays a fine violet red colour.

On the Sugars of Certain Fungi.—Em. Bourquelot. —The sugars found in the fungi in question are chiefly mannite and trelahose. They often exist together in the same species, though some species contain exclusively one or other of these substances.

Moniteur Scientifique, Quesneville.
March, 1889.

Commercial Museum of Turin.—An account of a useful institution, which, however, contains nothing of chemical interest.

Street-pavements in General, and Cement-Pavements in Particular: with Observations made at Grenoble.—G. Arnaudon.—This memoir also has no decided chemical interest.

Ammonia-soda and the Solvay Process.—A summary of the comparative position and prospects of the Leblanc and the Solvay systems.

A new Process for the Manufacture of Soda.—W. W. Stavely.—From the *Journal of the Society of Chemical Industry.*

Industrial Society of Mulhouse; Session of December 12th, 1888.—Camille Schœn sent in a memoir on the fixation of colours by means of tungstic acid.

Solubility of Barium Sulphite in Hydrochloric Acid.—G. Stillingfleet Johnson.—From the Chemical News.

Decomposition of Nitric Oxide in Contact with Water and Alkaline Solutions.—S. Cooke, F.C.S.— From the *Journal of the Chemical Society.*

New Reagent for Iron.—Mr. Venables.—From the Chemical News.

Note on the New Reagent for Iron.—B. Blunt.— From the Chemical News.

On Silicon Hydride.—From the Chemical News.

Crystalline Iron and Nickel Subsulphide.—J. B. Macintosh.—From the Chemical News.

Bulletin de la Société Chimique de Paris.
Vol. i., (Ser. 3), No. 5. March 5th 1889.

On the Use of Oxygenated Water for Determining Metals of the Iron Group: 1 Chrome.—A. Carnot— Already noticed.

On the Use of Oxygenated Water for Determining Metals of the Iron Group: Chrome, Manganese, and Iron.—A. Carnot.—Already noticed.

A New Method of Determining Lithia by Means of the Fluorides.—A. Carnot.—This memoir will appear in full.

Determinations of Lithia in Mineral Waters: Analysis of two Springs of the Côte d' Or.—A. Carnot. —The springs in question, those of Maizières and Santenay, contain respectively, per litre, 0·0240 and 0·0310 grm. of lithia.

On Diastasic Saccharification.—A. Reychler.— Soluble vegetable albumen acts as a diastase, aud its action is intensified by a slight acidity of the solvent.

Transformation of Oleic Acid into Stearic Acid.— P. de Wilde and A. Reychler.—On heating for some hours to 270°—280° oleic acid with 1 per cent of iodine there is formed a mixture of fatty products which after cooling congeal into a solid mass, melting at 50°—55°. From this mixture the authors obtain washings containing about one-third of the iodine used and a watery distillate very poor in hydriodic acid, a distillate of tar, insoluble in alcohol, liquid fatty products, generally very blue, not solidifiable by iodine, and saturating on acidimetric titration only 50 to 60 per cent of the quantity of normal soda calculated for pure oleic acid. A maximum yield of 70 per cent of a solid white acid with a high melting-point. After crystallisation from alcohol this product presents the chemical composition, the melting-point, and all the characteristics of stearic acid. In subsequent operations bromine was substituted for iodine as being more easy of recovery.

Conversion of Erucic Acid into Benic Acid.—A. Reychler.—This conversion has been effected by heating the erucic acid for four hours to 270° in sealed tubes along with 1 per cent of iodine.

Syntheses by means of Cyanacetic Ether, Cyanosuccinic, and Cyanotricarballylic Ethers.—A. Haller and L. Barthe.

Syntheses Effected by means of Cyanosuccinic Ether.—L. Barthe.

Certain Derivatives of Ethyl Acetylcyanacetate.— Alf. Held.—The subject of these three memoirs has been already noticed.

On the Potassium Polysulphides.—W. Spring and J. Demarteau.—The polysulphides K_2S_4 and K_2S_5 cannot be regarded as thiosulphites or thiosulphates.

The Oxidisability and the Cleaning of Tin.—Leo Vignon.—Already noticed.

Some Reactions of the Mercury-Ammonium Chlorides.—In the action of water upon Kane's mercury chloramidide there ensue two inverse reactions, that of the water which tends to produce oxydimercurammonium chloride, and that of ammonium chloride which tends to re-constitute the chloramidide.

Zeitschrift fur Analytische Chemie.
Vol. xxvii., Part 6.

Researches on the Goldenburg Method of Determining Tartaric Acid.—H. Heidenhain.—This bulky memoir is a communication from the laboratory of the New York Tartar Company, and does not admit of reproduction.

The Analysis of Substances Containing Alumina, Lime, and Magnesia.—L. Blum.— This memoir has been already inserted.

Apparatus for the Determination of Carbonic Acid in the Air and in Gaseous Mixtures. — Dr. F. Schydlowski.

Volumetric Determination of Carbonic Acid in Carbonates.—E. Jäger and G. Kruss.—Neither of these papers can be usefully reproduced without the accompanying illustrations.

The Application of Pettenkofer's Bile-Acid Reaction to the Demonstration of Free Sulphuric Acid in Aluminium Sulphate, Alum, &c.—E Egger.—This reaction is obtained when an aqueous solution of cholic acid is heated with sugar and strong sulphuric acid, when there appears a cherry-red solution, becoming purple, and afterwards bluish red. The author finds that 1 c.c. of a mille-normal sulphuric acid=0·00004 grm. SO_3 if heated in the water-bath with a granule of cholic acid and two drops solution of furfurol (1 drop furfurol in 10 c.c. water) leaves a distinct red stain on the sides of the porcelain capsule in which the solution has been heated or evaporated. In applying this test to alum, 50 grms. of the sample in fine powder are put in a flask, moistened with distilled water, let stand for some hours, covered with a mixture of two parts alcohol and three of ether, shaken well, and set aside. After twenty-four hours the liquid is filtered, the filtrate placed in a capsule, and evaporated down to 1 c.c. on a warer-bath, which must be warmed but not boiling. The cholic acid and furfurol are then added and the colouration is then sought for.

Wine Statistics of Germany.—An elaborate paper of great length, but not calculated to interest our readers.

Journal fur Praktische Chemie.
Vol. xxxix., Parts 2 and 3.

Researches from the Chemical Laboratory of Prof. Alex. Saytzeff at Kasan.— These include a memoir on the oxidation of diallyloxalic acid with nitric acid, and one on the action of sulphuric acid upon diallyloxalic acid, both by P. Bulitsch.

On the Acid Character of the Salts of tne Heavy Metals.—Br. Lachowitz.—The author concludes that for salts of one and the same acid, the less heat is liberated during their formation the greater is their capacity for uniting with bases. For the salts of one and the same metal the more heat is evolved during their formation the greater is their capacity for uniting with bases.

The Constitution of the Fatty Diazo- and Azobodies, and on the Formation of Diamide and its Derivatives.—Th. Curtius.—This memoir is not susceptible of useful abridgment.

On Benzoylen-urea and Some of its Derivatives.—W. Abt.—The author here describes the preparation and properties of benzoylen-urea and dimethyl-benzoylen-urea, the preparation of the two monomethyl-compounds, the conversion of α-methyl-benzoylen-urea into dimethyl-benzoylenurea, the action of phosphorus pentachloride upon benzoylen-urea and γ-methyl-benzoylen-urea, and the preparation of dimethoxylquinazoline from $\beta\,\delta$-dichlorquinazoline.

The Chemical Constitution of Cyanethine and Similar Compounds.—E. von Meyer.—In this preliminary notice the author states that the so-called oxybase of cyanethine formed by the substitution of amide can also be produced by the condensation of equal mols. of propionamidine and α-propionyl-propionic ether. Hence this compound is oxymethyl-diethyl-miazine.

Journal de Pharmacie et de Chemie.
Vol. xix., No. 6.

Syntheses and Reactions of Thiophene.—G. Denigès.—If we wish to reprodnce the well-known reactions of thiophene with isatine, phenanthrene, quinone, alloxane, &c., it is necessary to dissolve these reagents in strong sulphuric acid. A good method for recognising the presence of thiophene in any liquid is to take a glass stirring-rod, with a ball at the end, steep it in the sulphuric solution of one of the reagents, and move it about in the vapour of the liquid under examination. Under these conditions the isatine becomes blue, the phenanthene quinone an intense green, shading into blue, and the alloxane blue. Another reagent, which does not seem to have been noticed, is nitrous sulphuric acid. If benzene, free from thiophene, is added to pure, strong sulphuric acid no colour is formed; with commercial benzene, which always contains thiophene, we have a more or less intense yellow colour, which may pass into brown. In either case, if we add to the acid a trace of a nitrite in solution we obtain on stirring a red colour, much deeper in presence of benzene containing thiophene. But what, above all, distinguishes these two reactions is that on adding water very gradually, and stirring after each drop, the liquid of pure benzene does not change colour, but merely becomes paler. With benzene containing thiophene the colour turns to a violet and even to an intense blue. On adding an excess of water it passes to a brownish green, with a brown precipitate.

Reagents for the Mercaptan Function.—G. Denigès.—Already noticed.

The Assimilation of Milk Sugar.—MM. Bourquelot and Thoisier.—Lactose in the animal economy is converted into glucose. Whether this is directly effected in the digestive channel is not proven.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. iii., No. 34.

Report Presented by Z Roussin on behalf of the Committee of the Chemical Arts, on a Work Entitled "Manufacture of Colours," by M. Guignet.—The colours spoken of in this work are those used in the various kinds of painting, and in the pigment style of tissue-printing. The work treats more especially of white lead, artificial ultramarine, Guignet's green, and on the use of colours in the different kinds of painting.

Vol. iii., No. 35 and 36.

In these issues there is no chemical matter.

Series 4, Vol. iv., No. 37, 1889.

This number is occupied with an account of the prizes awarded by the Society.

Revue Universelle des Mines et de la Metallurgie.
November and December, 1888.

These numbers contain no original chemical matter.

January, 1889.

Experiments on Grisoutite.—E. Braive.—According to these experiments grisoutite—the composition of which is not given—can be safely used for blasting in "fiery" coal mines, where it neither ignites marsh-gas nor suspended coal-dust.

On the New Hydrocarbon Explosives—J. Henrotte.—An account of the Favier powder of bellite, securite, and roburite.

Vol. v., (3rd Series), No. 2.

This issue contains no chemical matter.

Archives Neerlandaises des Sciences Exactes et Naturelles.
Vol. xxiii., Part iii.

This number contains no chemical matter.

MISCELLANEOUS.

Detection of Tartaric Acid in Citric Acid.—M. Salzer.—If a solution of citric acid is coloured yellow with a drop of solution of yellow potassium chromate the colour remains unchanged for some days at common temperatures, even if a few drops of sulphuric acid are added. Under the same conditions a solution of tartaric acid converts the yellow chromate into a violet salt of chromic oxide. In cours of a few hours ½ per cent of tartaric acid may thus be recognised in citric acid.—*Revue des Falsifications.*

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Estimation of Glycerin.—(Reply to "Glycerol)."—As nobody else appears to have answered your correspondent's question I beg to refer him for information on quantitative examination of crude glycerin, and detection of impurities objectionable for the manufacture of dynamite, to Sulman and Berry's article in *Analyst*, vol. xi. (1886); Allen's "Commercial Organic Analysis," 2nd Edition, vol. ii.; and Otto Hehner's article in *Journ. Soc. Chem. Ind.*, Jan., 1889 (Quantitative Examination only).—Edward E. Berry.

MEETINGS FOR THE WEEK

Monday, 8th.—Medical, 8.30.
— Society of Arts, 8. Cantor Lectures. "Instruments for the Measurement of Radiant Heat," by C. V. Boys, F.R.S.
Tuesday, 9th.—Institute of Civil Engineers, 8.
— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
— Sanitary Institute, 8. "Nature of Nuisances, including Nuisances the Abatement of which is Difficult," by J. F. J. Sykes, B.Sc.
— Society of Arts, 8. "Architecture in Relation to Landscape," by H. H. Statham.
— Royal Medical and Chirurgical, 8.30.
Wednesday, 10th.—Society of Arts, 8. "The Sanitary Functions of the County Council," by Sir Douglas Galton.
— Pharmaceutical, 8.
— Microscopical, 8.
Thursday, 11th.—Royal, 4.30.
— Royal Institution, 3. "Houses and their Decoration from the Classical to the Mediæval Period," by Prof. J. Henry Middleton, M.A.
— Royal Society Club, 6 30.
— Institute of Electrical Engineers, 8.
— Mathematical, 8.
Friday, 12th.—Royal Institution, 9. "On Iridescent Crystals," by Lord Rayleigh, F.R.S.
— Sanitary Institute, 8. "Sanitary Law—General Enactments, Public Health Act 1875, Model Byelaws," by A. Wynter Blyth, M.R.C.S.
— Astronomical, 8.
— Quekett Club, 8.
Saturday, 13th.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.
— Physical, 3. "A Lecture Experiment illustrating the Effect of Heat on the Magnetic Susceptibility of Nickel," and "An Experiment Showing an Effect of Light on Magnetism," by Shelford Bidwell, F.R.S. "On the Dark Flash seen in Some Lightning Photographs," by G. M. Whipple. "On Quartz as an Insulator," by C. V. Boys, F.R.S. "On a Refraction Goniometer," by A. P. Trotter. "Apparatus to Illustrate Crystal Forms," by Prof. R. J. Anderson, M.D.

THE CHEMICAL NEWS.

Vol. LIX. No. 1533.

ON THE

BEST METHOD OF PREPARING NITROGEN FOR LECTURE PURPOSES.

By CHARLES R. C. TICHBORNE, LL.D., F.I.C., &c.

An article called "A Select Method of Preparing Nitrogen Gas" appeared in the Chemical News, vol. lix., p. 135, and suggested to me the writing of the following communication.

The best method of preparing nitrogen for lecture experiments, or when required in a pure form, is unquestionably (in my opinion) based upon the decomposition of ammonium nitrite. That process possesses numerous advantages over all the others. It is sufficient to enumerate the simplicity of the reaction, the purity of the product, and the ease with which the experiment is performed. The apparatus required is a retort of the right size and a bent tube.

For the last ten years I have been in the habit at my lectures of falling back upon this method when I came to the subject of the oxygen compounds of nitrogen. The symmetric manner in which this reaction harmonises with the production of laughing gas is most instructive, and is a special inducement to use it as a lecture illustration. Here we have the production of a molecule of nitrogen by the splitting up of the nitrite, whilst the nitrate gives us a molecule of the monoxide.

$$NH_4NO_2 - 2H_2O = N_2.$$
$$NH_4NO_3 - 2H_2O = N_2O.$$

A statement in the article (Chemical News, vol. lix., p. 135) runs as follows :—" The action of potassium nitrite, when heated in a suitable apparatus in admixture with ammonium chloride, produces, when prepared cautiously, a moderately pure gas, but, owing to the inconsistence of the reaction, the same is rendered considerably tedious and unprofitable.

As this is contrary to my experience, I think it desirable to give the *modus operandi* which I have adopted, presuming that if the modifications and precautions which I indicate be strictly carried out the experiment will turn out satisfactorily.

Ten grms. of ammonium sulphate and ten grms. of sodium nitrite are mixed in a capacious retort with 40 c.c. of glycerin and 60 c.c. of water. The retort should be of the capacity of half a litre, or about 16 ounces. The retort is placed with the neck elevated to an angle of about forty degrees, so that the water may condense and fall back into the retort. A bent tube is fitted with a cork into the neck, and conducts the gas into a wash-bottle; or it may be collected at once for general purposes without washing.

100 c.c. of water may be used in place of the mixture of glycerin and water, but it does not seem to work quite so regularly. Heat is applied directly to the retort, and the disengagement of free nitrogen begins at a temperature a few degrees below the boiling-point of water. It steadily but rapidly proceeds—the temperature generally rises a few degrees above the boiling-point, but after a little time again begins to fall. A gentle but constant heat will, however, keep up the disengagement of gas until the nitrite is all decomposed. It is desirable to slightly increase the heat towards the end of the reaction.

There is nothing specially new in this process, except the substitution of the sulphate for the chloride, and in the determining of the exact conditions under which the experiment may be carried on successfully for class illustrations, or for the purposes of procuring pure nitrogen with the least expenditure of trouble. If the reaction is pushed on very rapidly ammonia will be evolved, and this phenomenon is most marked when using the chloride in place of the sulphate. If carried on slowly with the sulphate no ammonia is evolved, but a trace of nitrogen dioxide is produced, which may be easily removed by washing with a dilute solution of permanganate of potassium. By carefully regulating the temperature almost pure and neutral nitrogen will be evolved.

A NEW METHOD OF DETERMINING LITHIA BY MEANS OF FLUORIDES.

By A. CARNOT.

The presence of lithia has been recognised in a consider able number of mineral waters, especially in those rich in alkaline chlorides and carbonates. The methods used to effect its determination leave much to be desired, some on account of their inaccuracy and others on account of the complication and length of the analytical operations. The spectroscope furnishes most valuable indications for the qualitative detection of lithia on account of the extreme sensitiveness of the reaction ; but a comparison of the intensity of the spectral rays gives only a doubtful approximation as to the proportion of the metal, especially when it exceeds a few milligrms. per litre.

The reagent which the author employs is ammonium fluoride. It is found in commerce, but it requires to be purified, as it contains silico-fluoride in considerable quantity. For this purpose a few grms. of the salt are dissolved in a small volume of water, a double volume of ammonia is added, the mixture is heated to a boil for a few seconds, let cool, filtered, and washed with ammonia. The silica is thus eliminated, and we have the fluoride in a strong ammoniacal solution. It is kept either in a covered platinum crucible or in a stoppered glass, where it may be left some days without undergoing any change. If there are in solution at most some decigrms. of a lithium salt, with quantities of other alkaline salts not more than ten or fifteen times greater, the author proceeds as follows :—The solution is reduced to a few c.c. in a tared platinum capsule, ammonium fluoride is added, and an excess of ammonia up to 15 to 20 c.c., according to the quantity of the salts. It is well mixed and let settle. There is formed a white gelatinous precipitate of lithium fluoride, scarcely visible and adhering in part to the bottom of the capsule. This is complete by the next morning. Almost all the liquid is decanted through a very small filter and replaced by a few c.c. of ammonia-water with ammonium fluoride. It is stirred up with a platinum spatula and let settle. Soon after a second and a third decantation are made in the same manner and the filter is washed with a few drops of the same reagent. All the soluble alkaline salts are thus removed, and we have, in part on the filter and in part in the capsule, all the lithium salt contaminated merely with ammonia and ammonium fluoride.

The volatile matters are expelled by heating very gently, the filter is burnt, its ash is treated with a few drops of dilute sulphuric acid, and all the liquid is collected in the tared capsule. It is evaporated and gently heated until acid vapours cease to appear, and the neutral lithium sulphate is weighed.

To take account of the solubility of lithium fluoride in the ammoniacal liquid we measure the total volume of the filtrate, which generally ranges from 30 to 50 c.c. We may admit, in accordance with experiments, that 7 c.c. of the liquid contain approximately 2 milligrms. lithium fluoride, corresponding to 4 milligrms. lithium sulphate or 1 milligrm. lithia. The quantity thus calculated is added to that found on weighing.—*Bulletin de la Soc. Chimique de Paris.*

NOTES ON OCHRES, SIENNAS, AND UMBERS.

By GEORGE H. HURST, F.C.S.
Lecturer on Painters' Oils and Colours at the Manchester Technical School.

The literature on these natural and very valuable pigments is very defective, and consists mostly of vague statements concerning their composition and origin, all evidently copied from one original source which I have not been able to trace. The published analyses of ochres are also vague, and are all more or less variations of one original analysis, and generally take the following form:—Clay 69·5, peroxide of iron 23·5, water 7; and they have led to the erroneous idea that ochres are clays coloured with oxide of iron. Very little attention seems to have been paid by chemists to ochreous colours in general.

Recently I have made several analyses of various ochres, siennas, &c., both as extracted from the earth and as prepared for the market, and it seems to me that these analyses are of sufficient interest to warrant their publication.

Ochres are yellow-coloured earthy pigments, varying in shade from a pale yellow of a brownish hue to a reddish yellow. Siennas are all of a more or less brownish yellow tone. Umbers are of a deep warm brown, ranging from yellowish to reddish shades. They are found naturally associated with gangue, from which they are separated and prepared for use as pigments by a process of grinding, levigating, and drying.

The following fourteen analyses will give some idea of the variety in their composition, due to the differ kinds of rocks in which they are found:—

1. *Oxford Ochre.* Crude, from Shotover Mine.

Hygroscopic water	6·887	per cent
Combined water	8·150	,,
Lime, CaO	0·998	,,
Sulphuric acid, SO_3	1·321	,,
Alumina, Al_2O_3	6·475	,,
Oxide of iron, Fe_2O_3	12·812	,,
Silica, SiO_2	63·478	,,
	100·121	

2. *Welsh Ochre.* Crude, unlevigated.

Hygroscopic moisture	2·000	per cent
Water of combination	12·500	,,
Sulphur trioxide, SO_3	1·315	,,
Silica, SiO_2	29·725	,,
Alumina, Al_2O_3	33·315	,,
Oxide of iron, Fe_2O_3	20·705	,,
Copper sulphide, CuS	0·515	,,
	100·075	

Of the sulphur trioxide, 0·555 exists as sulphates soluble in water, and of the iron, 0·7655 per cent is soluble in water in the form of ferrous sulphate.

3. *Irish Ochre.* Crude, unlevigated.

Hygroscopic moisture	9·050	per cent
Water of combination	12·000	,,
[*]Insoluble SiO_2 and gangue ..	32·502	,,
Sulphur trioxide, SO_3	2·685	,,
Alumina, Al_2O_3	16·770	,,
Oxide of iron, Fe_2O_3	26·381	,,
Lime, CaO	0·258	,,
Copper oxide, CuO	0·630	,,
	100·260	

Of the sulphur trioxide 0·33, of the oxide of iron 0·191, of the lime 0·118, and of the copper oxide 0·228 are soluble in water as sulphates. These are the first recorded analyses of ochres where copper is given as a constituent; to my mind this has a bearing on the question of the origin of these ochres, as I will point out further on.

4. *Derbyshire Ochre.* Levigated.

Water of combination	6·100	per cent
Barium sulphate, $BaSO_4$	20·946	,,
Silica, SiO_2	4·530	,,
Calcium sulphate, $CaSO_4$ . ..	2·516	,,
Calcium carbonate, $CaCO_3$ ..	2·755	,,
Alumina, Al_2O_3	10·655	,,
Oxide of iron, Fe_2O_3	33·498	,,
Magnesia, MgO	trace	
	100·000	

5. *Derbyshire Ochre.* Crude.

Hygroscopic moisture	5·400	per cent
Water of combination	6·000	,,
Alumina, Al_2O_3	1·040	,,
Oxide of iron, Fe_2O_3	76·081	,,
Lime, CaO	0·561	,,
Sulphur trioxide, SO_3	1·744	,,
Pyrites, FeS_2	4·783	,,
Silica, SiO_2 Barium sulphate, $BaSO_4$ } ..	4·394	,,
	100·000	

This is a very red ochre, as might be surmised from the large proportion of iron oxide in it.

6. *Sienna.* Italian.

Hygroscopic moisture	8·250	per cent
Combined water	11·000	,,
Silica, SiO_2	17·406	,,
Calcium carbonate, $CaCO_3$ ..	1·075	,,
Manganese, MnO_2	0·627	,,
Alumina, Al_2O_3	5·177	,,
Oxide of iron, Fe_2O_3	57·032	,,
	100·567	

This is a very light sienna, almost approaching ochre in tint, much lighter than might have been expected from the amount of iron in it.

7. *Raw Sienna.* Italy.

Hygroscopic water	17·550	per cent
[*]Water of combination	9·000	,,
Silica, SiO_2	22·656	,,
Calcium carbonate, $CaCO_3$ ..	0·960	,,
Manganese, MnO_2	1·190	,,
Alumina, Al_2O_3	2·840	,,
Oxide of iron, Fe_2O_3	45·820	,,
	100·016	

Raw siennas are brownish yellow in colour, and differ from ochres, which are yellow or reddish yellow, in yielding orange-red pigments on calcining, whereas ochres yield deep reds.

8. *Burnt Sienna.* Italy.

Hygroscopic water	9·450	per cent
[*]Water of combination	3·275	,,
Silica, SiO_2	36·912	,,
Manganese, MnO_2	traces	
Calcium carbonate, $CaCO_3$ ..	1·233	,,
Alumina, Al_2O_3	3·480	,,
Oxide of iron, Fe_2O_3	45·650	,,
	100·000	

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[*] This is almost entirely gangue, and can be separated from the ochre proper by levigation.

[*] See note, next page.

9. *Raw Sienna.* Probably Italian.

[*]Water of combination	9·400	per cent
Hygroscopic water	12·400	,,
Silica, SiO_2	5·016	,,
Calcium carbonate, $CaCO_3$	4·460	,,
Alumina, Al_2O_3	7·265	,,
Oxide of iron, Fe_2O_3	59·695	,,
Manganese, MnO_2	1·465	,,
Magnesia, MgO	trace	
	99·701	

10. *Umber.* From Cyprus.

Hygroscopic moisture	4·325	per cent
Water of combination	8·450	,,
Silica, SiO_2	29·564	,,
Calcium carbonate, $CaCO_3$	5·560	,,
Manganese, MnO_2	12·285	,,
Alumina, Al_2O_3	2·735	,,
Oxide of iron, Fe_2O_3	36·475	,,
	99·394	

11. *Umber.* Derbyshire, Crude.

Hygroscopic water	13·475	per cent
Water of combination	5·175	,,
Barium sulphate, $BaSO_4$	30·105	,,
Silica, SiO_2	4·430	,,
Calcium sulphate, $CaSO_4$	2·153	,,
Calcium carbonate, $CaCO_3$	2·607	,,
Alumina, Al_2O_3	8·078	,,
Oxide of iron, Fe_2O_3	22·500	,,
Manganese, MnO_2	11·530	,,
Phosphoric acid	trace	
	100·053	

12. *Umber.* Probably English.

Hygroscopic water	6·612	per cent
Water of combination	10·250	,,
Calcium sulphate, $CaSO_4$	2·137	,,
Calcium carbonate, $CaCO_3$	6·090	,,
Alumina, Al_2O_3	12·802	,,
Oxide of iron, Fe_2O_3	29·983	,,
Manganese, MnO_2	7·110	,,
Silica, SiO_2	24·518	,,
	99·502	

13. *Ochre.* Cornwall.

Hygroscopic moisture	1·40	per cent
Combined water	10·00	,,
Silica, SiO_2	59·67	,,
Alumina, Al_2O_3	9·72	,,
Oxide of iron, Fe_2O_3	18·54	,,
Lime, CaO	0·23	,,
	99·56	

14. *Ochre.* French.

Hygroscopic moisture	1·80	per cent
Combined water	9·20	,,
Silica, SiO_2	54·00	,,
Alumina, Al_2O_3	13·75	,,
Oxide of iron, Fe_2O_3	20·73	,,
Lime, CaO	0·19	,,
	99·67	

These last two analyses are not original, but are quoted from recently published results.

Terra Verte is a natural green-coloured pigment of which, also, but vague descriptions are to be found in text-books. A sample which was recently sent me had the following composition:—

Hygroscopic moisture	1·450	per cent
Combined water	3·650	,,
Oxide of iron, Fe_2O_3	26·870	,,
Alumina, Al_2O_3	3·165	,,
Manganese, MnO_2	trace	
Lime, CaO	2·065	,,
Silica, SiO_2	52·120	,,
Magnesia, MgO	10·665	,,
	100·000	

It was very hard, broke with a conchoidal fracture, of a waxy lustre and soapy feel. Acids had but slight action on it. From its physical properties and chemical composition I consider it to be the mineral bronzite, and is essentially a ferrous magnesium silicate.

It would be of interest to ascertain the origin of ochres, siennas, and umbers. On this point nothing, or but little, is definitely known, and it can only be arrived at by ascertaining the conditions in which deposits of ochres are found, knowledge which we are not yet possessed of. I cannot myself add much on this point, but from my examination of the ochres—the results of which are recorded above—I am of opinion that they must be classed as alteration-products consisting of earthy substances coloured to a more or less extent by hydrated peroxide of iron and manganese, which latter bodies have been produced by the oxidation and hydration of other iron ores or minerals, such oxidation-products having become incorporated by some means with the earthy bodies. That this may be the origin of ochreous deposits is in my opinion indicated by some of the analyses of ochres I have made. The crude Welsh and Irish ochres both contain copper, the former in the form, I think, of sulphide, the latter in the form of sulphide and sulphate. Both contain ferrous sulphate in small quantities, which lead me to think that these ochres have been formed by the oxidation and hydration of cupreous iron pyrites. In the case of the crude Derbyshire ochre No. 5 I have recognised pyrites in this, and I know that this ochre to prepare it for the market, undergoes a process of levigation, during which much pyrites is separated. The combination of the oxide of iron with the other constituents or earthy matter of the ochre is almost always a physical one, and not a chemical combination. By treatment of many crude ochres with acid the oxide of iron can be dissolved, leaving the earthy matter behind very often in the form of small fragments of mineral, which can be recognised as the basic rock of the district wherein the ochre was found. The Irish ochre No. 3 is one of this character.

In the case of the Italian siennas and ochres, I have information that they are found in basins which have evidently been filled at some period with water, and that into these basins have flowed streams of water carrying down a quantity of ferruginous matter derived from deposits of hæmatite iron ore situated above the deposits of ochre. Along with the ferruginous matter there have also been carried down by the same streams the debris of the rocky base and other products of the destructive action of the weather on the rocks and soil immediately above the basin; these were gradually deposited, and the deposit in time filled up the basin and formed the sienna and ochre which is now quarried. These deposits are not pre-human, for in them have been found arrow-flints, bronze idols, products of the industry of some bygone races of men.

Besides the points of distinction between ochres and siennas above pointed out there seems to be another one. While siennas are invariably, as stated above, found in large masses of a homogeneous structure, all of which

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[*] This includes small quantities of organic matter which are present in siennas, and to which their peculiar brownish yellow colour and their yielding orange-red pigments on calcining is probably due. The amount of this organic matter has not been separately determined. Siennas also contain small quantities of manganese, which also will influence the shade of the pigment.

is utilised for pigment purposes, and which have been formed of the debris due to the denudation of rocks and mineral masses not immediately surrounding the deposit of sienna, ochres seem to have been formed *in situ* by the oxidation of iron pyrites and other iron minerals, the products of such oxidation impregnating the surrounding rock masses to form the colouring-matter as we know it, and which has to be separated by lixiviation and levigation to fit it for pigment purposes.

Of umbers I am unable to bring forward anything bearing on their origin, but I am of opinion that in this particular they resemble the siennas rather than the ochres.

I trust that the little I have been able to add to the knowledge of these valuable pigments will induce some one to come forward with other facts of interest about them, and I for one will be only too glad to welcome such contributions.

Chemical Laboratory,
22, Blackfriars Street, Manchester.

THE EFFECTS OF VOLTAIC ELECTRICITY TOWARDS GERMINATION.

By H. N. WARREN, Research Analyst.

The following effects of voltaic agency towards germination were observed:—

During the previous summer, in my laboratory, four constant ferric chloride cells were arranged, with their respective wires terminating in thin platinum plates of about four inches in length by two wide. Over these was spread, about two inches in thickness, cotton soaked in a dilute solution of salt water, and, sprinkled over the surface of the same, common mustard seed (*Sinapis alba*). In less than twenty-four hours germination over the positive plate was distinctly visible. At the end of three days this was much more distinct, and after a week's duration it had assumed an altitude of upwards of one inch in height and of an intense green colour, whilst those confined to the negative plate, and which, up to this period, had only commenced germinating, and which were possessed of an almost pure white colour, and far more backwards as regards growth. At this period the current was now reversed, that which had previously been the positive plate becoming the negative, and *vice-versâ*. After the further lapse of a few days exactly a reverse phenomenon presented itself; those which had apparently flourished so well when influenced by the positive current, now gradually became bleached of their colour, and speedily withered, whilst the opposite seeds, invigorated by the removal of the opposing current, gradually assumed a green tint, and rapidly commenced to flourish, which nevertheless, together with those on the opposite plate, speedily afterwards withered, and refused to be stimulated on renewing a more intense current.

The rapid bleaching of those situated in the neighbourhood of the negative plate may, I think, be accounted for by the small but constant liberation of chlorine gas, thus enveloping them in an atmosphere of the same, or otherwise retarding germination when in a nascent state.

The experiment becoming terminated, the two platinum plates, in connection with their respective electromotors, were next introduced into a tank containing pond water, having been previously examined microscopically. After the current had been maintained for about six hours, on again presenting it before the microscope for further examination, several living organisms were observed, which increased in kind and number as the experiment proceeded. A few grains of salt were now introduced into the water in order to render it still more able to conduct the current. On a powerful secondary charge being now transmitted into it by the aid of a large induction coil, and a re-examination made, no living organisms were observed, and the experiment was allowed to proceed as before, re-producing further quantities of living organisms.

The experiments were here interrupted, and are now under further investigation.

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

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1889.

Mr. William Crookes, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. John Kitchen, Beech Grove, Ulverston; John Edmund Legg, Elm House, Great Berkhamstead, Herts; Walter J. Sykes, 47, Ouseley Road, Balham, S.W.; William Virtue, The Laboratory, Crosswells Brewery, Oldbury.

26. "*The Molecular Weights of the Metals.*" Preliminary Notice. By William Ramsay, Ph.D., F.R.S.

The molecular weights of a number of metals have been determined by Raoult's vapour-pressure method, viz., by ascertaining the depression of the vapour-pressure of the solvent produced by a known weight of dissolved substance. The connexion between osmotic pressure and depression of vapour-pressure has been shown by van't Hoff, and in a recent number of the *Zeitschrift für Physikalische Chemie*, by Arrhenius; the method of the latter is characterised by great simplicity. It has also been mathematically developed by Planck (see also *Zeitschr. f. Phys. Chem.*, 1888, 405).

The relation between molecular weight and depression is expressed by the equation—

$$W = \frac{W' \times P \times p}{100 \times d},$$

where W is the molecular weight to be found; W' the molecular weight of the solvent; P/100 the percentage weight of the dissolved substance in solution; p the vapour-pressure of the solution; and d the depression in the vapour-pressure of the solvent produced by adding the substance dissolved. It will be noticed that the relation is independent of temperature.

The solvent employed was liquid mercury; the temperature 260° and 270° for a few substances, and the boiling-point of mercury for most. The apparatus, of which a description will appear in the complete paper, is of the simplest description, and lends itself to the

Element.	Atomic weight.	Molecular weight.		Molecular formula.
		Found.	Calulated.	
Lithium	7·02	7·00	7·02	Li_1.
Sodium	23·04	12·1	11·52	$Na_{\frac{1}{2}}$.
Potassium.. ..	39·14	28·57	?	K_1 (?).
Silver	107·93	109·0	107·93	Ag_1.
Gold	197·22	204·3	197·22	Au_1.
Barium	137·0	74·45	68·5	$Ba_{\frac{1}{2}}$.
Magnesium ..	24·3	20·33	24·3	Mg_1.
Zinc	65·34	60·85	65·43	Zn_1.
Cadmium	112·1	100·0	112·1	Cd_1.
Gallium	69·9	68·1	69·9	Ga_1.
Thallium	204·2	183·5	204·2	Tl_1 (?).
Tin	119·1	114·9	119·1	Sn_1.
Lead	206·93	204·1	206·9	Pb_1.
Antimony	120·2	134·2	120·3	Sb_1.
Bismuth	208·1	209·2	208·1	Bi_1.

determination of molecular weights of all substances soluble in any pure menstruum; no knowledge of the vapour-pressures of the solvent being required. The method is much more generally and easily applicable than the alternative method of Raoult, whereby the molecular weight is deduced from the depression of the melting-point of a solvent due to dissolved substance.

The results obtained are given in the Table (see preceding page).

These numbers represent some of the actual results. Nevertheless, they must not be taken as absolute; although in many cases they are conclusive as to the molecular weight of the metal, still further experiments are needed. As an instance of what occurs, the metals thallium and antimony may be chosen. With thallium, for example, the following results were obtained :—

Percentage of thallium. in amalgam.	Molecular weight.	
	Found.	Calculated.
0·8191 p. c.	157·4	204·2
1·666 „	183·5	204·2
2·894 „	174·3	204·2
3·290 „	183·9	204·2

No appreciable change is produced on concentration. But with antimony the molecular weight increases proportionately to the amount present, thus—

Percentage of antimony in amalgam.	Molecular weight.	
	Found.	Calculated.
1·117 p. c.	134·2	120·3
1·526 „	155·4	120·3 to 240·6
2·257 „	193·4	120·3 to 240·6
3·289 „	294·6	240·6 to 481·2 ?

Here an association of atoms is evidently in progress.

It may appear startling that the molecular weight of the metals sodium, potassium, and barium are given as half their atomic weights. From the formula employed in calculation it will be seen that this is on the assumption that the molecular formula of mercury is Hg_1. There are strong reasons in favour of this supposition, and the whole question will be discussed in the complete paper. But at present it may be taken as the most convenient way of stating results. The author would not wish to commit himself to any positive assertion on the point, except in so far as the accuracy of the experimental data are concerned. The numbers have been amply confirmed by repetition, and must be taken as accurate within from 1 to 5 per cent of the quantity measured.

The author is now occupied in extending these results, and in confirming them by the depression of the melting-point method.

27. "*The Application of Raoult's Depression of Melting-point Method to Alloys.*" By C. T. HEYCOCK, M.A., and E. H. NEVILLE, M.A.

The result of Raoult's investigations on the lowering of the freezing-points of solutions, "that one molecular proportion of any substance dissolved in 100 molecular proportions of any solvent whatever lowers the freezing-point of that solvent 0·62 C.," has not apparently been tested by the dissolution of metals in metals.

The authors therefore present the results of some preliminary experiments on the change in the solidifying point of tin caused by the addition of small quantities of other metals. From repeated experiments they have confidence that the numbers obtained are approximately correct, though they reserve for a future paper details of the method of experiment and the conclusions which may be drawn from the results. For the present, it is sufficient to state that the dissolution of a metal in tin appears to follow the same laws as that of compounds in other solvents, *i.e.*, (1) That the fall in temperature of the solidifying point is directly proportional to the weight of metal added. (2) That the fall of temperature is inversely as the atomic (molecular ?) weight of the metal added. The experiments were conducted by melting a mass of 400 grms. of tin, and by means of a mercury thermometer, using a reading telescope, the solidifying point was determined whilst the mass was kept rapidly stirred. Slight surfusion, usually three or four-tenths of a degree, was generally noticed. The tin was then remelted, and from one to three grms. of metal added, and the solidifying point again determined. In some cases where the metals alloy with difficulty, portions of the 400 grms. of tin were withdrawn, and, whilst fused under borax in a gas furnace, known weights of the other metals were added, and then this concentrated alloy was added to the bulk of the tin. Another grm. or two of the metal was then added, and the experiments repeated. The average melting-point of the tin used was 226·4° C. Working as above described, the authors find one atomic proportion of each of the following elements dissolved in 100 atomic proportions of tin causes the following falls of temperature :—

Zn	2·53°
Cu	2·47
Ag	2·67
Cd	2·16
Pb	2·22
Hg	2·3
Al	1·34
Sb	2·0 (rise).

The facts that aluminium produces a fall only one-half that of the other elements, and antimony produces a rise, are they think of especial importance.

They hope shortly to communicate a more complete paper to the Society, and intend using other solvents such as Na, Cd, Pb, Hg, &c. They also propose to investigate the behaviour of those alloys which appear to be true compounds, and to find out to what extent of concentration the fall of temperature remains proportional to the weight of metal added, &c.

DISCUSSION.

Dr. ARMSTRONG said that notwithstanding the apparent regularity and simplicity of the results, he was not prepared to accept them as in the least degree final. There was not sufficient evidence in his opinion that the effect observed was not in part at least the outcome of a change in the molecular composition of the solvent; this objection had already been formulated by himself as well as by Professor J. J. Thomson, and no one had as yet replied to their criticisms (*cf. Brit. Ass. Report*, 1888; *Report of Electrolysis Committee*). The question was one of fundamental importance in relation not only to the determination of molecular weights of dissolved substances, but also to the interpretation of the phenomena of electrolysis and chemical change generally. The results obtained by Raoult's methods were, he thought, comparable with those obtained by determinining the specific heats of elements; in the latter case the observations were undoubtedly made with masses of molecules, which probably were of varying degrees of atomic complexity (*cf. Brit. Ass. Report*, 1885, p. 962), and yet the results were found to be such as to justify conclusions being drawn as to the relative magnitudes of their fundamental constituents—the atoms. In the same way it was possible that the results obtained by Raoult's method by means of observations on the behaviour of molecular complexes might afford the means of deducing the relative magnitudes of the fundamental molecules comprising the complexes, but not of the actual complexes operated with. The formation of compounds which undoubtedly took place in the case of sodium, for example, must influence the results.

Mr. CROMPTON asked Professor Ramsay whether he had examined solutions of strengths other than those given. He drew attention to Beckmann's recent experiments on the lowering of the freezing-point; these show that the true molecular weight was only obtained when solutions were used the concentration of which was allowed to vary only within certain narrow limits; and that if the solutions were too dilute the molecular weight obtained from the lowering of the freezing-point was too low, while, if the solutions were too concentrated, it was too high. In some cases the variation of the number obtained with the concentration was enormous. The same would probably be the case for the reduction of the vapour-pressure. The results brought forward were undoubtedly of the greatest interest, but he thought that the method had not been so thoroughly investigated as to give them an absolute value as molecular weight determinations.

Mr. Pickering said that when the freezing-points of mixtures of sulphuric acid and water were plotted out in a form which should, according to Raoult, give a straight line, they gave a most irregular figure. Between 0 and 100 per cent the solidifying point sunk twice below $-40°$, and rose twice to $+10°$. The extreme end of the figure (for weak solutions) is, no doubt, irregular and curvilinear like the rest of it, and can be called straight only because the irregularity and curvature are lost in the comparative magnitude of the experimental error. It was not fair to consider evidence deduced from such a source in the same light as that deduced from gaseous densities, where any appreciable deviation from straightness is found only at the extreme ends of the figure, and where the deviation is of the same regular character in every case.

Mr. Groves suggested that although compounds of the metals and mercury could be formed, it was possible that these underwent dissociation when dissolved in mercury.

Professor Carey Foster remarked, that in the case of weak solutions the temperature at which ice forms is determined; but in the case of stronger solutions the temperature is often that at which a hydrate forms: this probably was the explanation of the peculiar curve described by Mr. Pickering. Much depended on the definition given of a molecule, whether it is defined as that smallest quantity capable of existence *per se*, or as that quantity which produces a given effect in depressing vapour-pressure, or freezing-point, &c. The two magnitudes were not necessarily the same. The relation observed could hardly be accidental; yet he thought that the value obtained might be a quantity connected with the molecular weight, but not necessarily identical therewith.

Mr. Howard said the main question was, did compounds of mercury with the metals exist at the high temperatures at which the observations were made.

Professor Ramsay, in replying, argued that the existence of a compound of the metal with the solvent—in this case mercury—would give an increased molecular weight; and that, although such compounds existed in many cases at low temperatures, yet, at the boiling-point of mercury, they appeared to be decomposed. The compound of copper and mercury, however, was an exception, inasmuch as it was not dissolved to any great extent by boiling mercury. Hence experiments with copper could not be carried out.

Substances in dilute solutions must be regarded as in the gaseous state, their molecules being so far distant from each other as not to exert appreciable attraction on each other; and as occupying but a small portion of the space they inhabit. It has long been argued that the molecular complexity of the gases, hydrogen, oxygen, and nitrogen, must be the same, inasmuch as these elements have equal coefficients of expansion within the widest limits of temperature. A similar argument applies to substances in dilute solutions; it is much more probable that they have a simple and similar molecular structure than that the molecules, if complex, dissociate to an equal extent on equal rise of temperature or on equal alteration of concentration.

As regards the empirical nature of Raoult's laws, it is paralleled by the empirical nature of Boyle's and Gay-Lussac's laws, that is, such laws are merely approximations to truth, and depend on the fact that the molecules are sensibly beyond the sphere of each other's attraction, and themselves occupy no appreciable space. Hence their inapplicability at high concentrations. Just as gases deviate at high pressures from the laws of elasticity when definite compounds are formed, as instanced by Mr. Pickering in the case of mixtures of sulphuric acid and water, each compound acts as a homogeneous substance—as a solvent of definite molecular weight, with a definite melting-point, which is lowered by the addition of one or other constituent, though probably not to a similar extent, owing to further reactions between the solvent and the added constituent, water or sulphuric acid, as the case might be.

28. "*Some Compounds of Tribenzylphosphine Oxide.*" By N. Collie, Ph.D., F.R.S.E.

Some time ago the author, in conjunction with Prof. Letts, published an account (*Trans. Roy. Soc. Edin.*, xxx., Part I., 181) of the salts of tetrabenzylphosphonium. One of the compounds mentioned, the oxide of tribenzylphosphine, has been further examined. When treated with fuming nitric acid, tribenzylphosphine oxide yields a trinitro-derivative $(C_7H_6{\cdot}NO_2)_3PO$, which is probably reduced by the action of tin and hydrogen chloride to a triamido-derivative. If the oxide be heated at 170° C. with sulphuric acid, a trisulphonic acid results,—

$$(C_7H_6{\cdot}SO_3H)_3PO.$$

In both cases the introduced group takes up the para-position, as on oxidation *p*-nitrobenzoic and *p*-sulphobenzoic acids are obtained. On treatment with acetyl chloride the oxide yields a simple addition product, $(C_7H_7)_3PO{\cdot}C_2H_3OCl$. It also combines with hydrogen chloride and bromide, yielding compounds of a complicated structure agreeing with the corresponding triethylphosphophosphine oxide-derivative, *e.g.*, $5(C_7H_7)_3PO{\cdot}4HCl$.

Tribenzylphosphine oxide therefore differs in several respects from the oxides of the tertiary phosphines of the fatty series. It does not form such stable compounds, neither is the oxide itself capable of resisting oxidising agents to the same extent. On the other hand, however, some of the derivatives, although complicated in their structure, seem to be analogous to the corresponding derivatives in the fatty series.

Discussion.

Professor Ramsay drew attention to the remarkable composition and stability of the malecular compounds obtained by Dr. Collie; he thought it was becoming essential to include and discuss such molecular compounds in a special chapter.

29. "*Contributions to Our Knowledge of the Isothiocyanites.*" By Augustus E. Dixon, M.D.

The author describes a number of compounds obtained from various thiocarbimides by combination with basic substances.

The first two are members of the little known series of benzylated thiocarbamides. *Ethylbenzyl thiocarbamide*, $EtNH{\cdot}CS{\cdot}NHBz$, from ethyl thiocarbamide and benzylamine, crystallises in white needles melting at 102—103°. The corresponding *phenylbenzyl thiocarbamide*,—

$$PhNH{\cdot}CS{\cdot}NHBz,$$

forms short thick prisms; m. p. 153—154°.

The next three compounds are semithiocarbazides, and are obtained by the action of phenylhydrazine on the corresponding thiocarbimides. *Ethylphenyl semithiocarbazide*, $EtNH{\cdot}CS{\cdot}NH{\cdot}NHPh$, forms glassy prisms melting at 121—122° without decomposition. A very delicate test for this substance consists in adding a few drops of ferric chloride to its solution in alcohol; a blood-red colour is produced, changing rapidly to dark green. It is remarkable that the m. p. of a metameric compound, $PhNH{\cdot}CS{\cdot}NH{\cdot}NHEt$, obtained by Fischer (*Annalen*, ccxix., 296) is much lower, viz., 109—110°. *Acetylphenyl-semithiocarbazide*, $AcNH{\cdot}CS{\cdot}NH{\cdot}NHPh$, forms thick white prisms melting at 178—179°, while the analogous *benzoylphenylsemithiocarbazide*,—

$$PhCO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NHPh,$$

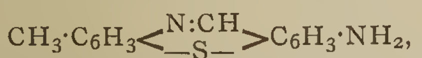
crystallises in silky asbestos-like needles, which do not melt at 220°.

The remaining compounds (together with the two last mentioned) were obtained during an investigation of thiocarbamides containing *acid* radicles, viz., *acetylorthotolylthiocarbamide*, AcNH CS·NHTo, which crystallises in lemon-yellow prisms, m. p. 184°; and *benzoylphenylethylthiocarbamide*, PhCO·NH·CS·NEtPh, which crystallises in yellow prisms melting at 133—134°.

30. "*The Constitution of Primuline and Allied Sulphur-compounds.*" By Arthur G. Green.

The product obtained on heating two mol. props. of paratoluidine with two atomic props. of sulphur until the evolution of hydric sulphide has ceased, chiefly consists of a mixture of Merz and Weith's thiotoluidine (diamidoditolyl sulphide, $(C_7H_6{\cdot}NH_2)_2S$), and a base, $C_{14}H_{12}N_2S$, containing four atoms of hydrogen less, which, as proposed by Jacobsen, may be called "dehydrothiotoluidine." If the amount of sulphur be doubled, thiotoluidine is almost absent, the product containing, together with dehydrothiotoluidine, a more highly condensed base, which probably has the formula $C_{28}H_{18}N_4S_3$. The monosulphonic acid of the latter base possesses the peculiar property of readily dyeing unmordanted cotton in an alkaline bath a pure primrose-yellow, and whilst on the fibre may be converted into a diazo-compound which may there and then be caused to interact with amine and phenols. This product, discovered by the author in February, 1887, was put on the market under the name of "Primuline," and is largely employed by cotton-dyeing on account of the great range of fast shades that may be obtained with it.

Dehydrothiotoluidine, $C_{14}H_{12}N_2S$, is isolated from the melt by boiling with somewhat diluted chlorhydic acid, precipitating with soda, distilling, and crystallising from amyl alcohol. It forms long, yellowish, iridescent needles melting at 191° (uncorr.), and boils at 434° (uncorr., bar. 766 m.m.). It is moderately soluble in hot amyl alcohol, readily in acetic acid. Its alcoholic solution exhibits a violet-blue fluorescence, which also characterises all its derivatives. By diazotisation, and by the constitution of the acetyl-derivative, it is shown that one of the nitrogen atoms is in the form of NH_2, whilst the other is nitrilic. By boiling with zinc-dust and HCl it is reduced to a base of quite different properties. On distillation with zinc-dust it yields paratoluidine. From these and other facts the author deduces the formula—



$$CH_3{\cdot}C_6H_3{<}\begin{matrix}N{:}CH\\ \text{—}S\text{—}\end{matrix}{>}C_6H_3{\cdot}NH_2,$$

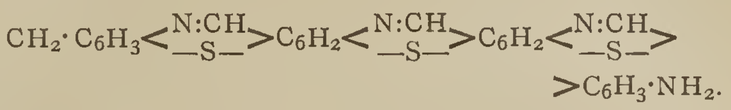
which represents dehydrothiotoluidine as derived from thiotoluidine by removal from a CH_3 and an NH_2-group of four atoms of hydrogen.

The *acetyl-derivative*, $C_{14}H_{10}SN(NH{\cdot}CO{\cdot}CH_3)$, forms white prisms which melt at 227° (uncorr.). It combines with bromine. The *dimethyl-derivative*,—

$$C_{14}H_{10}SN{\cdot}N(CH_3)_2,$$

crystallises in yellowish plates melting at 195—196°. The *trimethylammonium* salts are easily soluble in water and have strong tinctorial power, dyeing silk a pure greenish yellow with a green fluorescence. The *monosulphonic acid*, $C_{14}H_9SN(NH_2)(SO_3H)$, crystallises from water either in flattened, yellow needles ($+H_2O$), or in orange, aggregated leaflets ($+2H_2O$). The salts of the sulphonic acid are mostly colourless, and have no affinity for cotton. The ammonium and copper salts are very characteristic: the latter is an insoluble reddish brown precipitate; the former crystallises in sparingly soluble, white, crystalline plates.

Primuline-base.—As this compound is also obtained by heating thiotoluidine or dehydrothiotoluidine with sulphur, it would appear that its formation is preceded by that of these compounds. The difficulty of isolating it in the pure state has hitherto prevented the determination of its composition with certainty, but it appears to have the formula $C_{28}H_{18}N_4S$, and hence probably has the constitution—



$$CH_2{\cdot}C_6H_3{<}\begin{matrix}N{:}CH\\ \text{—}S\text{—}\end{matrix}{>}C_6H_2{<}\begin{matrix}N{:}CH\\ \text{—}S\text{—}\end{matrix}{>}C_6H_2{<}\begin{matrix}N{:}CH\\ \text{—}S\text{—}\end{matrix}{>}$$
$$>C_6H_3{\cdot}NH_2.$$

Primuline-base is a bright yellow powder, which is nearly insoluble in all solvents. Its salts are dark-coloured and are decomposed by water, in which they are insoluble. It is an extremely stable compound, and may be heated above 400° C. without decomposing.

Discussion.

Mr. Wynne took exception to the formulæ proposed by Mr. Green, regarding it as improbable that dehydrothiotoluidine contained a closed chain of eight atoms, and that the sulphur-atom should be connected in the ortho-position in the one and the meta-position in the other nucleus.

(To be continued).

NOTICES OF BOOKS.

Cosmic Evolution; being Speculations on the Origin of our Environment. By E. A. Ridsdale, Associate of the Royal School of Mines. London: H. K. Lewis.

We have here a thoughtful and weighty little book, *multum in parvo*, in a very different sense of the words from that applied to waistcoat pocket manuals. The author disclaims the introduction of any novel facts, but hopes, and that with good reason, that he has shown among well-known facts a relation which has been hitherto overlooked. His object is one with which we most thoroughly sympathise. He seeks to prove that Evolution is not merely the law of the heavens, as it has been shown by Kant, La Place, and Herschel; not only of the process by which organic species are formed, according to Lamarck and Darwin, but of the material from which stars and organisms are ultimately composed: of matter itself. The attempt may seem bold, but we are convinced that it will ultimately prove successful. He introduces a capital conception, the "survival of the most inert," which plays in the origin and history of chemical compounds a part very similar to that played by the "survival of the fittest" in the life-history of organisms. We know that among animals and plants such forms as are most in harmony with their surroundings survive, whilst those less perfectly adapted are either modified or disappear. In a very similar manner bodies which, taken as wholes, are most inert, and which conseqnently are least likely to be decomposed by the action of surrounding bodies, will remain. On the contrary, those bodies which are the least inert will gradually tend to disappear, and, unless continually re-created, must in time vanish from the globe. This part of his subject, its chemical aspect, Mr. Ridsdale works out very ably. That such a survival of the most inert is actually taking place he shows by reference to phenomena commonly witnessed:—"In Nature's vast laboratory, as in our small experimental ones, there is a constant tendency for barium salts to form sulphates; magnesium and aluminium salts, oxides and silicates silver salts, chlorides; lead salts, sulphides; &c. The stable or inert salt, when formed, remains—except under exceptional circumstances; but any other salt . . . . is broken up, sooner or later, by contact with some unfavourable environment." We have, he considers, a strong presumption that many, if not all, the so-called "elements" are elemental only inasmuch as we have not yet been able to place them among a sufficiently powerful set of conditions. He considers that the bodies formed earliest must have been the simplest, and that those originating later must have been of a more complex constitution and of greater atomic weight. His views are in harmony with certain well-known facts. Thus, in the groups of the elements the most active are usually those with the lowest atomic weights; that there are greater gaps in the amounts of the later-formed elements than in those of the earlier-formed ones; that the elements with the lower atomic weights are more plentiful and more generally distributed than those with higher weights.

The second chapter takes up the organic aspect of Evolution. Concerning life he remarks:—"How it arose we know not; whether it was latent from the beginning, and, oppressed hitherto by the dominant environments, only awaited a period of quiescence to come into operation, or whether it was induced by a special act of Creation we cannot tell." He holds that the earlier forms of life showed a great similarity to the inorganic, from which it has only been differentiated by slow degrees. He considers that in the organic, as in the chemical sphere, the tendency to variation is now dying out. The fact that we can in no way now produce life from inorganic forms, *because we cannot reproduce* the conditions, just as we cannot transmute lead into gold, is a proof of the correctness of the theory of Evolution.

In the third chapter we have the general aspect of Evolution. He rejects the teachings of those physicists who deny to the sun a birthday more than twenty million years distant, as inadequate to account for the facts of terrestrial geology. In this rejection he will be joined by the majority of biologists as well as geologists, who may at any rate claim the right to wait until mathematico-physicists have learned to bring their discordant conclusions into harmony and to demonstrate their fundamental assumptions.

We cannot further prolong our examination of this interesting little work, but we must strongly recommend it to our readers.

Practical Organic Chemistry; the Detection and Properties of Some of the More Important Organic Compounds. By S. Rideal, D.Sc., F.C.S., F.I.C., F.G.S. London: H. K. Lewis.

This little manual is avowedly written with especial reference to the wants of medical students, and accordingly those compounds are brought into prominence with which he is likely to come most in contact. Under each it is stated whether it occurs in the preparations of the British Pharmacopœia or not, and, in the former case, into what preparations it enters. The most characteristic reactions are marked with an asterisk, and to a few, said to be new to English text-books, the name of the discoverer is added in brackets. Some of these are likely to prove useful. We find no mention of certain artificial alkaloids which—whether permanently or as a transient freak of fashion—are finding their way into medical practice.

The aim of the book, as it will be seen at once from the preface, is distinctly examinational. "The student," we are told, "*reading* for the London University Examinations—B.Sc. and Inst.M.B.—will find all the substances mentioned in the Syllabus of the University discussed at length." We beg to call passing attention to the word we have italicised. Like not a few other persons in these days, we should like to see the highest University honours gained not by *reading* but by *working*—in other words, by the power of origination. We here venture to refer to an instance of the examinational spirit. Two youths, at one of our great public schools, had sent in essays on a certain occasion. The judges did not award the prize to the author of the essay they thought the best, but to his rival, because the latter had quoted thirteen books instead of thinking the matter out independently! We do not think that even the Chinese official examiners could improve upon such a procedure.

The Lixiviation of Silver Ores with Hyposulphite Solutions, with Special Reference to the Russell Process. By C. A. Stettefeldt. New York: Scientific Publishing Co.

The author of this book seeks to expound the so-called lixiviation process for silver ores, as compared with amalgamation. He describes the old method of lixiviation with sodium hyposulphite, as introduced by Von Patera and developed by Kiss and Kuestel, but admits that it was not free from grave defects. Of these, perhaps the most important is its inability to deal with silver glance and the antimonial and arsenical silver sulphides. Hence he recommends the adoption of the lixiviation process as modified by E. H. Russell. This metallurgist employed a double sodium-copper (cuprous) hyposulphite, and thus overcame many of the difficulties which beset Von Patera's original method. Mr. Stettefeldt then gives an elaborate comparison of the two lixiviation processes and of Russell's improved lixiviation as against amalgamation. He contends that the percentage of silver extracted is in most cases higher than that gained by amalgamation; that the chemicals used in the process cost less than the value of the wasted mercury and the wear and tear of the pans; that lixiviation allows of the extraction of copper and lead, and in many cases of more gold than is secured by amalgamation, which latter process is, further, injurious to the health of the workmen. The chief defects of lixiviation here recognised are that the precious metals are obtained as sulphides, which require a more difficult and costly treatment than does amalgam.

The author considers that all silver ores which do not contain a large percentage of lead or copper can be successfully dealt with by lixiviation.

In describing the chemicals used in the lixiviation process Mr. Stettefeldt explains the different manners in which the strength of alkali is expressed in England, France, and Germany. The persistent use in English technical circles of 24 as the atomic weight of sodium in place of 23—a custom utterly indefensible, but against which chemists are powerless—he characterises as "one of the numerous mysteries and humbugs of English commerce." As a metallurgist he might have remembered another: the use of the Cornish assay in the copper-trade. And impartiality might have led him to include under the head "humbug" the retention of Baumé's hydrometer in France and America, seeing that its scale exists in two, if not three different modifications, and that its indication cannot be converted into direct specific gravity by any simple calculation.

After discussing the materials for the process, the author gives a very full account of the reactions of the sodium hyposulphite solutions. Then follow the reactions of "extra solutions," apparently the double hyposulphite of sodium and copper.

The problem of extracting from auriferous silver ores a high percentage of both these precious metals by one process in the moist way the author admits is still awaiting its solution.

The amount of chemical operations requiring daily performance in the laboratory of lixiviation works is considerable. It includes pulp-assay of the ore and salt-mixture, determination of percentage of salt, calculation of value of ore from the two preceding data, pulp-assay of roasted ore and determination of soluble salts present, with calculation of value of roasted ore, assay of tailings, and lixiviation tests of roasted ore with ordinary and extra solutions. The execution of these different determinations is only partially laid down.

The second part of the book is devoted to the practical execution of the lixiviation process. The needful plant is fully described, with the addition of numerous illustrations, exceedingly well drawn.

A special chapter treats of the construction, price of erection, and working cost of a lixiviation works.

Mr. Stettefeldt's treatise may be decidedly recommended to all metallurgists who have to deal with silver ores, though of course much of the information given is specially adapted to circumstances in the United States.

CORRESPONDENCE.

SHEEP DRESSING.

To the Editor of the Chemical News.

Sir,—This is the centre of large wool-producing districts, and many flock-masters use, for dressing sheep, solution of calcic sulphides, made on the spot by boiling sulphur in solution of lime, aiming to get the largest amount of sulphur dissolved by the smallest quantity of lime. The orange solution so made is complex—calcium sulphide of several degrees in sulphur and some hyposulphite is made. If alkali-makers who have large by-products of calcic sulphurets could see their way to make—*fit* for carriage, hard and dry, but soluble in water—a compound of sulphur and lime in which the sulphur was in excess, so as to approach the pentasulphurets, I think a good demand could be found for the same. It is troublesome to make in small quantitities with farmers' appliances, and will not keep in solution long when made. Such a form of sulphur would also find a use in treatment of vines and fruit trees, as the lime and sulphur solution is the best for treating them for insect and fungoid diseases, and is used by syringing. I am aware of recent improvements by which the former waste sulphides of the alkali-maker are now utilised, and sulphur regained. But possibly it might pay to use the sulphur compounds as above indicated, and I shall be glad to be placed in communication with anyone wishing further information, or who may see the way to supply the want here set before them, viz., a cheap form of calcium sulphide with excess of sulphur in form fit for export and soluble in water, to be used as dipping-bath for sheep, &c., against scab and allied diseases.—I am, &c.,

Wm. Roe.

Graaff Rimel, Cape Colony,
South Africa.

OBITUARY.

PROFESSOR CHEVREUL.

We deeply regret having to put on record the death of Prof. E. Chevreul, the senior chemist of the world. Not, indeed, that we can be surprised at the demise of one who had earned a European reputation when our elderly *savants* were still in their cradles, or unborn; nor that anything in the shape of research and discovery could be expected from him, seeing that on August 31st next he would have reached the age of 103 years. But it is painful to see a link broken which connected us to the days of Lavoisier, Gay-Lussac, Berthollet, Davy, and Dalton. Much of the abundant and precious work of his long career is almost too well known to need recapitulation. But we may glance in passing at his wonderful researches on the fatty matters, fruitful alike theoretically and practically, and to his splendid investigations on colouring matters and on light, which for the first time gave the art of dyeing a rational foundation. The *doyen* of the students of France, as the deceased modestly called himself, closed his long and illustrious career on the 9th instant.

The Atomic Weight of Osmium.—Karl Seubert.—The author's experiments lead to the mean value 191·12 (O=15·96).—*Zeit. f. Anal. Chem.*, vol. xxviii., Part 1.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 12, March 25, 1889.

On Cobalt and Nickel Peroxides, and on the Volumetric Determination of these Metals.—Adolphe Carnot.—Inserted in full.

The Limits of Error which may be Committed in the Assay of Fine Gold.—Paul Charpentier.—The assay of fine gold, founded, on the one hand, upon the cupellation of this metal in presence of silver and lead, and on the other hand upon the treatment of the alloy with nitric acid, is capable of a very high degree of accuracy. In general the determination of gold by this method can be guaranteed to about 3-10,000ths. But this result can be reached only by adhering closely to certain experimental necessities which long practice has taught. The author has sought to determine what is the maximum error which may ensue if any one of these rules is neglected, whilst the others are adhered to. If the heat of the muffle is too high there may be a mean loss of gold of 24-10,000ths, and if it be too low an excess of 6-10,000ths. If the maximum quantity of lead has been used the mean loss is 2-10,000ths, and if it is too far reduced the mean excess may be 6-10,000ths. Both an excess and a deficiency of silver show an excess of gold, in the latter case to 100 per cent.

The Initial Phase of Electrolysis.—M. Piltschihoff.—The minimum of the electromotive force necessary to set up immediately a visible electrolysis does not, within certain llmits, depend either on the nature of the salt or on the concentration of the solution. The minimum does not appreciably depend either on the combination-heat of the two metals nor on their electromotive force of contact, but essentially on the physical condition of the surface of the cathode.

The Electric Transfer of Dissolved Salts.—A. Chassy.—A salt of zinc in a mixture of copper and zinc salts is always transported in the direction of the current. If two salts, *e.g.*, sodium or barium nitrates whose weights are in a constant proportion, are placed in a mixture of any number of other salts the quantities of the two former salts transported will vary in absolute value, but their proportion will remain constant.

On Chloral Glycolalcoholate.—M. de Forcrand.

Determination of the Combustion-heats of Metaldehyd, of Erythrite, and of Tricarballylic Acid.—M. Louguinine.—These two thermo-chemical memoirs do not admit of useful abstraction.

Justus Liebig's Annalen der Chemie.
Vol. ccl., Part 3.

Communications from the Chemical Laboratory of the Federal Polytechnicum at Zurich: Researches on the Azoles.—These communications comprise memoirs by A. Hantzsch on alkylised thiazoles from the thiamides; by G. Popp on thiazoles from amido-thiazoles; by H. Zürcher on the action of the metallic sulphocyanides and sulphurea upon chlorised acetacetic esters; and by G. Hofmann on seleno-cyanides and on selenazol compounds.

Researches in the Camphor Series (First Treatise):—E. Beckmann.—This very hypothetical paper does not admit of useful abstraction.

On the Three Isomeric Toluric Acids, and on the Behaviour of Metaxylol in the Organism.—A. Gleditsch and H. Moeller.—The three toluric acids form crystals which melt only at high temperatures, and none of them agree with the liquid toluric acid of Schultzen and Naunyn. Metaxylol, if introduced into the organism of dogs, passes into the same crystallisable metatoluric acid which is obtained from glycocoll and metatoluylic acid.

Moniteur Scientifique, Quesneville.
4th Series, Vol. iii., April, 1889.

On Water Gas.—J. Lange and J. Lunge (*Zeitschrift für Angewandte Chemie*).—Even at 1000° the decomposition of watero vapour by carbon is incomplete. Before water-gas can be commonly used for heating or lighting, like coal-gas, a method must be found of communicating to this gas, which is in itself inodorous, a scent much more penetrating and persistent than that of coal-gas, since, by reason of the large proportion of carbon monoxide which it contains, it is at least five times more poisonous than coal-gas. The deadly character of a gaseous mixture seems to increase much more rapidly than the proportion of carbon monoxide. According to the researches of Dr. Wyss, the dangerous results of the inspiration either of coal-gas or water-gas are due solely to carbon monoxide. During the months of January and February, 1888, seven cases of poisoning from water-gas have occurred in New York. It is proposed that water-gas might be rendered odorous, so that its escape could be at once detected, by means of mercaptan.

Researches on Certain Compounds of Sulphur.—Dr. H. Rebs.—A memoir on hydrogen persulphide, the phosphorus sulphides, the barium ether-sulphates, and sulphuric anhydride.—From *Liebig's Annalen.*

Processes of Alkali Manufacture from a Thermo-Chemical and Electrolytical Point of View.—Dr. F. Hunter.—From the *Journal of the Society of Chemical Industry.*

Presence of Sugar in Cereals.—A. von Asboth.—The author shows that neither saccharose nor glucose is present in cereals. Earlier experimentalists have committed the error of inverting an aqueous or alcoholic extract of the grain by an acid. The author has shown that dextrine and analogous substances are dissolved in the water, or the alcohol is converted into sugar by acids.

Determination of Glycerin in the Lyes resulting from the Manufacture of Soap, and in Crude Glycerin.—Otto Hehner.—From the *Journal of the Society of Chemical Industry.*

On Cryolite, and its Substitution in the Glass Manufacture.—R. Zsigmondy (*Dingler's Journal*).—The price of cryolite having become too high for use in the preparation of opal-glasses, a substitute became necessary. C. Weinreb proposed sodium fluoride mixed with aluminous minerals. To obtain an alkaline fluoride he fused fluor-spar with potassium or sodium carbonate; the former of these compounds is too costly, but the latter appears to give satisfactory results. The author melts fluor-spar with potassium carbonate in presence of silica, lixiviates the mass obtained, and treats the concentrated boiling solution of potassium fluoride with a solution of sodium carbonate saturated at 38°. Potassium carbonate is precipitated and serves for a fresh operation. For determining combined hydrofluoric acid the author employs a modification of Knœffler's method for titrating sulphuric acid. He uses decinormal calcium chloride with phenolphthalein as indicator. The solution of potassium fluoride, containing potassium carbonate and silicate, is neutralised, hot, with hydrochloric acid after the addition of phenolphthalein, and treated with 1 c.c. of decinormal sodium carbonate, when the liquid turns red. An excess of the decinormal calcium chloride is then added until the red colour disappears. When all the potassium fluoride is decomposed the calcium chloride acts upon the sodium carbonate, the liquid becomes neutral and colourless. The excess of calcium chloride is then determined by Knœffler's method for the alkaline earths, *i.e.*, it is precipitated by a decinormal solution of sodium carbonate until the red colour reappears. It is then filtered, and the liquid is titrated with a decinormal solution of hydrochloric acid, after the addition of methyl-orange.

On Castor Oil.—K. Hazura and A. Grüssner (*Zeitschrift fur Angewandte Chemie*).—The authors infer from their experiments that the liquid acid of castor oil is not a single compound as it has been hitherto supposed, but a mixture of two isomeric acids of the composition $C_{18}H_{34}O_3$, one of which, ricinoleic acid, yields on oxidation trioxystearic acid, whilst the other, ricinisoleic acid, yields isotrioxystearic acid. The proportion of these acids is about 1 of the former to 2 of the latter. As no dioxystearic acid has been obtained from the oxidation of the liquid acids of castor oil it may be concluded that of all the fatty oils hitherto examined castor oil is the only one which contains no oleine.

On the Non-siccative Oils.—K. Hazura (*Zeitschrift fur Angewandte Chemie*).—All the non-siccative oils contain along with oleic acid, one or more non-saturated acids; probably linolic or linolenic acid.

On Gum Lac.—R. Benedikt, E. Ehrdich, and F Ulzer (*Zeitschrift fur Angewandte Chemie*).—Lac is a substance of the nature of the fats, and by successive oxidations with permanganate it is converted almost entirely into azelaïc acid and certain inferior fatty acids.

The Fat of Ucuhuba.—E. Valenta (*Zeitschrift fur Angewandte Chemie*).—This fat is of a yellowish brown, very consistent, of a peculiar aromatic odour, becoming disagreeable if heated. It is obtained from *Myristica surinamensis.* It contains about 10 per cent of oleic acid, the other ingredients being myristic acid, wax, resins, &c. It is an excellent material for the manufacture of candles.

Metallic Resinates for the Preservation of Wood.—M. Kretschmar (*Chemiker Zeitung*).—The timber is first immersed in a bath of a salt of copper or zinc and is then coated with an alkaline solution of resin.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 1.

Application of Electrolytic Conductivity in Quantitative Determinations.—E. Reichert.—This extensive memoir requires the four accompanying figures and diagrams. The author considers that the specific conductivity of a natural water is a characteristic and fundamental property which should not be omitted in any analysis.

The Examination of Spirit and Spirituous Liquors, Especially as Effected by Means of the Vaporimeter.—J. Traube.—In this treatise the author discusses the capillarimetric method for the determination of fusel, the stalagmometric method, and the separation of impurities by means of saline solutions. He then examines the method of Röse for the determination of fusel and a vaporimetric method for determining the first runnings and the fusel, as well as the signification of the vaporimeter in the alcohol industry.

Determination of Raffinose in the Products of the Manufacture of Beet-Sugar—Prof. J. W. Gunning.—This paper does not admit of useful abstraction.

Quantitative Determination of Zinc along with Manganese.—G. Neumann.—The author, whilst studying the separation of zinc from other metals in a formic solution, met with an inaugural dissertation by Max Bragard, treating almost on the same subject. The author has reached the same conclusions as Bragard, and confirms his result that the determination of zinc in a formic solution in presence of iron and nickel is very useful. He adds that under the same conditions a quantitative determination of zinc in the presence of manganese can be simply and rapidly effected.

A Source of Error in Determining the Nitrogen of Halogeniferous Bodies, and its Prevention.—Richard Zsigmondy.—In determining the nitrogen of such bodies meta-chlor-α-methyl-cinnamaldehyd-phenylhydrazon by the method of Dumas (using halogeniferous copper oxide and a plug of copper), the author obtained regularly from 1 to 2 per cent of nitrogen in excess. He traced the cause to the presence of chlorine in the copper oxide. He finds that this error may be avoided by passing carbon dioxide over the copper oxide whilst still in a state of ignition, and allowing it to cool in a current of the same gas.

Apparatus for the Electrolytic Determination of Metals.—Dr. L. C. Levoir.—This paper requires the accompanying figure.

The Presence of Arsenic in Bone Meal used for Feeding.—H. Fresenius.—"Feeding bone meal," so-called "precipitated phosphate" has been successfully added to the food of cattle in doses ranging from 2 to 15 grms. daily for young animals and 20 to 50 grms. for adult individuals. If the acid used in the manufacture is arseniferous, calcium arseniate or arsenite will accompany the phosphate. The proportion of arsenic in the samples examined ranged from 0·028 to 0·17 per cent (calculated as metallic arsenic).

Determination of Phosphoric Acid in Sweet Wines and on the Examination of Sweet Wines.—W. Fresenius.—The author recommends that the sugar present should be destroyed by fusion with soda and saltpetre.

Analyses of Pure Sherries.—E. Borgmann and W. Fresenius.—Not adapted for abstraction.

Absorptive Power of Grey Vulcanised Rubber.—G. Hüfner (*Annalen der Physik und Chemie*).—Within the temperatures 5° to 25° there is no defined coefficient of the absorption of atmospheric air. Between 15° and 25° no measurable quantities of nitrogen are absorbed by grey vulcanised rubber. The same quality absorbs its own volume of dry carbon dioxide at about $-2°$. The specific coefficient of absorption decreases with a rising temperature. The rubber is indifferent to hydrogen at temperatures from $-2°$ to $+13°$. Even after the lapse of three months no absorption of gas could be detected.

Solubility of Certain Compounds of Gold.—Th. Rosenbladt (*Berichte Deutsch. Chem. Gesell.*).—The author has experimented with the aurochlorides of sodium, lithium, potassium, rubidium, and cæsium.

Determination of Pressure in Sealed Tubes.—A. Reychler.—The author's method cannot be described without the accompanying figure.

A Projection Saccharimeter.—Leon Laurent.—From the *Comptes Rendus*.

A New Refractometer.—C. Pulfrich.—This instrument consists of a rectangular prism of glass, to the horizontal surface of which is cemented a small glass cylinder for the reception of the liquid to be examined.

Determination of the Thermic Value of Coals.—W. Thomson.—From the *Journal of the Society of Chemical Industry*.

Apparatus for Determining the Fluidity of Lubricating Oils.—L. Barbey.—For the description of the apparatus we must refer to the original.

Areometer with Legible Thermometer Scale.—A. Gawalowski.—The thermometer scale is fixed above the areometer scale in the upper part of the instrument.

Determination of the Specific Gravity of Solids.—L. Brasse and E. Vlasto.—This description is imperfect without the figure.

An Improved Valve-burette.—G. Kroupa.—The valve is opened or closed by means of a glass rod secured to a screw with a fine thread.

A New Screw Pinch-Cock.—B. Proskauer.—This paper requires the accompanying figure.

A Modified Calcimeter.—A. Bernard.—From the *Comptes Rendus*.

Modification of Soxhlet's Extraction Apparatus.—W. H. Kent, O. Grothe, and C. M. King.—From the *Journal of the American Chemical Society* and the Chemical News.

Tube for taking Samples of Fluid and Semi-fluid Substances from Casks.—A. Gawalowski.—The instrument consists in two concentric iron cylinders, closed below.

Purification of Mercury.—B. Karsten.—The author describes the method used in the physical laboratory at Kiel.

Development of Hydrogen in the Kipp Apparatus.—J. Habermann.—The author recommends the use of an alloy of tin and zinc.

The Reddening of Phenol.—A number of authors give a series of different explanations of this phenomena, and W. Hankó considers that possibly all may be right.

Production of Absolute Alcohol on the Small Scale.—J. Habermann.—The author places the lime used for dehydration not in the retort, but in a super-imposed appendage consisting of a cylinder tapering downwards, and inclosing a narrower cylinder of iron wire gauze, closed above.

The Application of Ammonium Dithiocarbaminate in Analysis.—Jos. Klein.—This paper will be inserted in full.

Determination of the Available Oxygen in the Peroxides by Means of Gaseous Hydrochloric Acid.—L. L. de Koninck and Ad. Lecrenier (*Zeitschrift fur angewandte Chemie*).—This paper requires the accompanying illustration.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements after Easter:—Dr. Jean Paul Richter, Three Lectures on the Italian Renaissance Painters: their associations, their education, and their employments (with illustrations); Prof. E. Ray Lankester, Four Lectures on Some Recent Biological Discoveries; Mr. Eadweard Muybridge, of Pensylvania, Two Lectures on the Science of Animal Locomotion in its Relation to Design in Art (illustrated by the zoopraxiscope); Professor Dewar, Five Experimental Lectures on Chemical Affinity; Mr. Joseph Bennett, Four Lectures on the Origin and Development of Opera in England (with musical illustrations); Professor W. Knight, of St. Andrews, Three Lectures on I. The Classification of the Sciences, Historical and Critical; II. Idealism and Experience, in Philosophy and Literature; III. Idealism and Experience, in Art and Life (the Tyndall Lectures). The Friday Evening Meetings will be resumed on May 3rd, when a Discourse will be given by Sir Henry Roscoe, M.P., on Aluminium; succeeding Discourses will be given on May 10th, by Professor Dewar, on Optical Properties of Oxygen and Ozone; May 17th, by Professor Silvanus P. Thompson, on Optical Torque; May 24th, by the Rev. S. J. Perry, on the Solar Surface During the Last Ten Years; May 31st, by Professor Demetri Mendeleeff, on An Attempt to Apply to Chemistry One of Newton's Principles; June 7th, by Archibald Geikie, on Recent Researches into the Origin and Age of the Highlands of Scotland and the West of Ireland; and June 14th, by C. V. Boys, on Quartz Fibres.

MEETINGS FOR THE WEEK

Monday, 15th.—Medical, 8.30.
Tuesday, 16th.—Institute of Civil Engineers, 8.
—— Sanitary Institute, 8. "Sanitary Laws and Regulations Governing the Metropolis," by A. Wynter Blyth, M.R.C.S.
—— Pathological, 8.30.
Wednesday, 17th.—Geological, 8.
Thursday, 18th.—Chemical, 8. "Notes on Naphthalene Derivatives," by Dr. Armstrong and Messrs. Heller, Holding, Percival, Rossiter, and Wynne.

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Fee for the Course—Ten shillings to Elementary Teachers; Other persons will be admitted at a fee of £3.

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UNIVERSITY OF LONDON.

NOTICE IS HEREBY GIVEN, That the next Half-yearly Examination for MATRICULATION in this University will commence on MONDAY, the 10th of June, 1889.—In addition to the Examination at the University, Provincial Examinations will be held at University College, Aberystwith; University College, Bangor; The Modern School, Bedford; Queen's College, Birmingham; University College, Bristol; University College, Cardiff; The Ladies' College, Cheltenham (*for Ladies only*); St. Gregory's College, Downside; New College, Eastbourne; The Heriot Watt College, Edinburgh; The Royal Medical College, Epsom; The Yorkshire College, Leeds; University College, Liverpool; The Owens College, Manchester; The School of Science and Art, Newcastle-on-Tyne; University College, Nottingham; The High School, Oswestry; Firth College, Sheffield; Stonyhurst College: and St. Cuthbert's College, Ushaw.

Every Candidate is required to apply to the Registrar (University of London, Burlington Gardens, London, W.) for a Form of Entry *not less than five weeks* before the commencement of the Examination.

Candidates are particularly requested to notice that the June Examination is, in the present and future years, to be held *a week earlier than heretofore.*

ARTHUR MILMAN, M.A.,
April 10th, 1889. Registrar.

THE LONDON HOSPITAL MEDICAL COLLEGE. The SUMMER SESSION will COMMENCE on WEDNESDAY, May 1.

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THE CHEMICAL NEWS.

VOL. LIX. No. 1534.

ON THE
LOSS OF VOLTAIC ENERGY OF ELECTROLYTES DURING CHEMICAL UNION.*

By G. GORE, LL.D., F.R.S.

IN this research the author has shown by suitable examples of measurement of the voltaic energy of different solutions by means of the "voltaic balance" (see *Roy. Soc. Proc.*, vol. xliv., pp. 151; 294, 300—308), the successive losses of energy which occur with every additional degree of complexity of a chemical compound. The following are some of the instances given :—

Energy.	Energy.	Energy.
$I = 3{,}310{,}985$	$Br = 81{,}022{,}500$	$Cl = 1{,}282{,}000{,}000$
$KI = 16{,}361$	$KBr = 66{,}909$	$KCl = 699{,}803$
$KIO_3 = 468$	$KBrO_3 = 364$	$KClO_3 = 239$
		$+KCl = 53$
		$+Am_2C_2O_4 = 28{\cdot}4$

	Energy.
KCl	699,803
$NaCl$	207,589
„ $+KCl$	5,959
K_2SO_4	2,274
Na_2SO_4	2,020
$+K_2SO_4$	112
$+2NaCl.KCl$	41
$+4K_2CrO_4$.. ..	−225
$+8K_2CO_3$	−11435

In all the cases every addition to the degree of complexity of the definite compounds formed was attended by a large decrease of voltaic energy, and the relative amount of electro-negative energy varied inversely with the degree of molecular complexity of the substance.

ON COBALT AND NICKEL PEROXIDES, AND ON THE VOLUMETRIC DETERMINATION OF THESE METALS.

By ADOLPHE CARNOT.

IT is known that the action of potassa, conjointly with that of chlorine, bromine, iodine, or of an alkaline hypochlorite, gives in solutions of cobalt or nickel black precipitates absolutely similar in appearance, though M. Herrenschmidt has remarked that cobalt peroxide thus obtained presents a brown tint, whilst the tint of nickel remains black if examined under the microscope.

If the precipitation is effected by means of oxygenated water and potassa we obtain with nickel a green precipitate of hydrated protoxide, just as with potassa alone. Cobalt yields a precipitate of a rather light brown, easy to distinguish at sight from the foregoing peroxides.

Being struck with this difference of aspect the author has made a series of experiments to demonstrate the state of oxidation of the metals in these precipitates. This examination presented the greater interest from an analytical point of view, as almost all the text-books recommend a volumetric process (Fleischer's method) founded on the uniformity of the composition of the precipitates obtained with nickel and cobalt by the use of potassa and bromine, or a hypochlorite.

The first results obtained were not in harmony with this view, and it was therefore necessary to renew and to vary the experiments.

After the addition of the oxidising agent and of the potassa the liquid was kept at a boil for some time, and then left to settle; the deposit was washed with pure or alkaline water, first by decantation and then on the filter, or an account was taken of the liquid left with the precipitate on submitting to the same experiment an equal volume of the last liquor decanted.

The weight of the metal taken for the experiment is known beforehand, according to the volume of the standard solution employed. The proportion of disposable oxygen (over and above that of the protoxide) was determined by pouring into the flask containing the washed precipitate an excess of potassium iodide and then rather dilute hydrochloric acid, leaving the solution to be completed in the cold, then determining the free iodine by means of a decinormal solution of sodium thiosulphate, added until the liquid is decolourised, and finally adding starch and running in a centinormal solution of iodine until a blue colour appears. The trials with ferrous sulphate, or oxalic acid, or potassium permanganate in a sulphuric solution are less accurate because the rose colour due to the cobalt prevents that of the permanganate from being distinctly seen.

The results of these experiments may be thus summed up :—

The brown oxide obtained on precipitating cobalt by oxygenated water and potassa at a boil, presents the exact composition of a sesquioxide, Co_2O_3.

The black oxide of nickel, precipitated by hypochlorite or by bromine with potassa, corresponds also exactly to the formula of the sesquioxide, Ni_2O_3.

The oxide of cobalt, nearly black, obtained by the use of hypochlorite, of bromine, or iodine, always contains a proportion of oxygen decidedly greater than that which corresponds to the sesquioxide. In place of $Co_{10}O_{15}$, *e.g.*, experiment gives as a mean $Co_{10}O_{16}$ with hypochlorite, and $Co_{10}O_{16\cdot25}$ with bromine or iodine. If we remark on the one hand that the washings have been effected with care so as not to leave any excess of the oxidising reagent, and on the other hand that the black precipitate appears really to differ from the brown precipitate formed by oxygenated water, we are led to think that there is formed under these conditions a saline compound containing a little cobalt dioxide along with sesquioxide. The composition of the precipitate given by hypochlorite may be represented by the formula $2CoCo_2,4Co_2O_3$; that of the precipitate obtained by means of bromine or iodine would correspond to $2CoO_2,3Co_2O_3$.

From an analytical point of view it is certain that we commit an error if we regard these precipitates as sesquioxides. In place of reckoning for one equivalent of available oxygen two equivalents of cobalt, we can only reckon 1·67 with the hypochlorite and 1·60 with bromine.

Nickel, on the contrary, may be very well determined volumetrically after the use of these same reagents by the method indicated above.

The determination of cobalt can also be effected accurately, but on condition of using as reagents oxygenated water and potassa. The operation is even easier than in the former case, because the excess of the oxidising agent disappears during the ebullition, which is not the case with the other reagents. If the two metals occur together we can determine the cobalt singly with accuracy by the use of oxygenated water and potassa, since the nickel is not peroxidised. Several synthetic experiments have given identical results for the same quantity of cobalt, whether in the presence or the absence of nickel. The author has also proved that boiling with ammonia in order to destroy the nickel peroxide, if any was formed, does not modify the final result.—*Comptes Rendus*.

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[*] Abstract of a Paper read before the Birmingham Philosophical Society.

ON SOME ATTEMPTS TO PREPARE THE OXY-HALOID DERIVATIVES OF CHROMIUM,

WITH ESPECIAL REFERENCE TO THE OXY-CYANIDE.

By S. G. RAWSON, B.Sc.

In the *Philosophical Magazine*, xii., 322, there is a paper by Girard on the preparation of the oxy-iodide of chromium, the results of which seemed to me to warrant further investigation. The product which he obtained was not analysed, but it was assumed to contain chromium, and various properties of the body are given. I have repeated his experiments, using the proportions given by him, but could obtain no compound giving any chromium. I then endeavoured to prepare the corresponding oxy-bromide and oxy-cyanide, and though I did not succeed in isolating the latter body, yet I think I obtained proof of its formation in small quantities. In all probability many attempts will have been made to prepare these bodies, but there seems to be no record of the failures, and hence it may happen that in each fresh attempt many of the old failures are repeated. From this point of view, therefore, it is, that I give briefly my own experiments in this direction.

The body obtained by Girard was described by him as a deep red oily liquid which boiled at 149° C., giving off a dense red vapour, corroded and blackened paper and wood, and imparted a deep brownish red stain to the skin, and which was prepared by the distillation of sulphuric acid with potassium bichromate and potassium iodide. I repeated his experiment, taking exactly the proportions given by him, and did obtain very small quantities of a deep red liquid, but in which I was unable to detect a trace of chromium. In a second experiment a trace was found, but so slight, not exceeding 0·00046 grm., that it probably arose from a little of the finely-divided bichromate which had been mechanically carried over. I determined the amount of chromium present by comparison with standard borax beads, *i.e.*, those containing the same amount of borax and a varying but known amount of chromium until a bead of the same depth of tint was obtained. Incidentally I may mention that I found that 0·000005 grm. chromium colours the bead of a recognisable green tinge, but it must be compared with a bead of pure borax. The red liquid consisted of hydriodic acid, very strongly coloured with free iodine, accompanied by traces of sulphurous and sulphuric acids. It behaved in all respects as Girard stated, with the one exception that it distilled at about 129° (the boiling-point of hydriodic acid) instead of 149° C. I also prepared a strong solution of hydriodic acid with much free iodine dissolved in it; this behaved similarly in all respects, and distilled at 129° C. Giraud used the normal potassic chromate, and in my experiments I used both this salt and also the bichromate.

Having convinced myself that the oxyiodide could not be obtained in this way I tried various other methods for its preparation. I passed the vapour of CrO_2Cl_2 in a current of carefully dried CO_2 over the surface of ethyl iodide. This became at once of a reddish brown colour, which gradually deepened, and finally a reddish precipitate was formed; the whole was then heated, the current of CO_2 still passing. A purplish liquid distilled over, leaving behind in the flask the red precipitate. On analysis the distillate was found to contain ethyl chloride, iodide, and free iodine, whilst the residue consisted of a mixture of iodine and Cr_3O_4.

Owing to the constant separation of iodine in this experiment, it seemed as though the presence of a diluent would be beneficial. The best one I found to be CS_2, the use of such reagents as ether or alcohol being of course precluded in the presence of the oxychloride. In the first experiment made a violent ebullition took place, and part of the contents were ejected from the flask, for, depending on the presence of the carbon disulphide, both the ethyl iodide and the chromium oxychloride were mixed together in considerable quantities. A heavy precipitate formed at the same time. With a large excess of CS_2 the reaction was much less violent, but the precipitate again formed, and was merely a mixture of I and Cr_3O_4. I did not analyse this yellow precipitate, but assumed that it was the yellow oxide of chromium. The liquid was carbon disulphide, containing a large quantity of iodine in solution. I then tried the direct action of fuming hydriodic acid on chromic acid in the presence of solid $ZnCl_2$, but iodine alone separated, with evolution of much heat. A mixture of potassic iodide, chromic acid, and solid zinc chloride was treated with (1) HCl, (2) CH_3COOH, (3) H_2SiF_6, but in all cases, sooner or later, iodine was set free as such. Chromium oxychloride was then heated with calcium iodide in a sealed tube at 140° C. for six hours. On cooling, the tube was cut up and a part of the material was carefully heated in a current of dry CO_2 gas. At first much undecomposed CrO_2Cl_2 came over, and then iodine, leaving behind chromium oxide and a mixture of $CaCl_2$ and CaI_2. The experiment was repeated at a temperature of 125° C. for three hours. In this case, however, much of the CrO_2Cl_2 remained unacted upon. Finally, the action of the oxychloride on silver iodide was tried, the mixture being heated between 100° and 110° C. for nine hours, but the result was similar. On taking some of the residue, however, and cautiously warming it in a closed dry test-tube, beautiful crystals of what I believe to be ICl_3 were obtained, some of them nearly half an inch in length.

In the case of the oxybromide, a mixture of the bromide and bichromate of potassium was treated with sulphuric acid, but nothing but free bromine distilled over. Chromium oxychloride was also heated with calcium bromide in sealed tubes at varying temperatures during varying times, but the results were the same as those obtained in the case of the iodide. In every case the oxychloride is decomposed, but the iodine or bromine does not take the place of the chlorine, but remains in the free state, the chromium becoming converted into an oxide. Another difficulty in the sealed tube experiments lies in the fact that at high temperatures the oxychloride is converted into the trichromyl chloride, whilst at low temperatures very much of it is left unacted upon.

Finally, I endeavoured to prepare the oxycyanide, and though I was unable to isolate it, yet, as previously mentioned, I think I obtained some proof of its formation in small quantities. The first and most obvious method was to treat a mixture of potassic cyanide and potassic bichromate with sulphuric acid, when a violent reaction ensued, but only hydrocyanic acid was produced. On the first addition of the sulphuric acid a small portion of the mass took fire spontaneously and burned for a moment. Hence, owing to the violence of the decomposition, I thought that bettter results might perhaps be obtained if the mixture were kept cool. The next experiment was therefore performed at a temperature of −10° C., but still only hydrocyanic acid was given off. Another attempt with the sulphuric acid slightly diluted also failed. Some pure dry mercuric cyanide was then placed in a porcelain boat and warmed and the vapour of CrO_2Cl_2 in a current of dry CO_2 was passed over it. A little of the oxychloride passed over unchanged, together with a trace of mercuric cyanide, and then the whole mass in the tube glowed with a vivid incandescence and complete decomposition took place. A portion of the residue was then exhausted with ether, but in this extract mercury was found, and hence might itself have been present as the cyanide. Another portion, treated with carbon disulphide, left no residue on evaporation. Some of the oxychloride was then heated with mercuric cyanide in a sealed tube for four hours at 135° C., and as there seemed to be no appreciable change at the end of that time the temperature was raised to 190° for another hour and a half. On cooling there seemed to be a very few reddish yellow crystals, A part of the tube was then exhausted by a Sprengel pump to remove the undecomposed CrO_2Cl_2, and then treated with carbon disulphide and again with ether. In the former solution nothing was found, and in the latter much mercury, chromium, and cyanide, so that again the cyanogen might have been present as the mercury salt. Another portion was then treated successively with CS_2, ether, and alcohol. The alcoholic extract, which was of a deep red colour, was distilled, but very soon the liquid became quite colourless, and a gelatinous precipitate of a yellowish brown colour formed, probably chromium oxide. Another tube was then prepared and the previous treatment repeated.

I had hoped that if, on distilling the alcoholic extract, cyanide was found in the distillate, it might be inferred that some or all of the substance which dissolved in the alcohol was oxycyanide; but though the distillate did give distinct cyanide reactions, yet, when mercuric cyanide dissolved in alcohol is distilled, cyanide is also found in the distillate, and hence the presence of cyanogen under these circumstances could afford no definite proof. I then tried heating silver cyanide with the oxychloride in a sealed tube for six hours at 130°. On cutting up the tube as soon as the mass was exposed to the air a portion at once took fire. The residue was, however, submitted to the same treatment as before. The alcoholic extract was at first deep red in colour, but it rapidly became brownish red, and there was much silver cyanide held in suspension. So fine was the state of division of the silver salt that I found it impossible to filter it off, and though, on adding $(NH_4)_2S$ and filtering, much cyanide was present, yet, if silver cyanide be suspended in water and treated with $(NH_4)_2S$, decomposition also takes place and cyanide can be readily detected in the filtrate. Some of the residue was then heated in a current of pure dry CO_2 and the gas passed into water, which gave very distinct cyanide reactions, whilst AgCy similarly treated, in fact heated until it actually melted, gave none or hardly any. Chromium was also present in the aqueous solution, and as the residue, before being heated in CO_2, had been already exhausted in the pump and the residual chromium oxychloride thus removed, I cannot but think that a small quantity of the oxycyanide had been produced.

It will have been noticed that in every case the ethereal and alcoholic extracts were tinged more or less of a red colour, and this was so well marked that I endeavoured to discover the reason. I prepared some trichromyl chloride and found that this was hardly soluble in carbon disulphide, but dissolved much more easily in ether and in alcohol, the solutions becoming red. In the formation of trichromyl chloride, however, chlorine is produced, and it might be urged that the chlorine thus set free reacted on the silver cyanide, forming silver chloride and cyanogen, and that it was this cyanogen which I had detected. But I do not think that this can be so, because in the first place, on opening the tube, most of the cyanogen would certainly escape in the gaseous state; and again, as the residue was exhausted, this would remove the residual gas. I repeated the experiment, however, in a different manner. In the first place, chromium oxychloride was again heated in a closed tube with mercuric cyanide for fifteen hours at 124° C., this being just about the boiling-point of the oxychloride. The tube was then opened and the residue extracted with carbon disulphide. On shaking the disulphide with water the aqueous extract gave the cyanide reactions, but there was not a trace of mercury. Chromium was also present, but there was much undecomposed oxychloride, and hence some, at any rate, of the chromium will have arisen from this source, but these results would also tend to show that a little oxycyanide must have been formed. I then heated the oxychloride with silver cyanide in a flask furnished with an inverted condenser, the joint between the flask and the condenser being made tight with asbestos and gypsum, and to the free open end of the condenser was attached a calcic chloride drying tube. The whole was then heated to 120^c C. for sixteen hours and kept in a dark place. At the end of that time there was a dark grey-coloured residue, and on warming a little of this in a test-tube it suddenly glowed, leaving behind a greenish mass of Cr_2O_3. There did not seem to be anything dissolved out by carbon disulphide, but an alcoholic extract contained much cyanide. This, as already mentioned, was due, at any rate in great part, to the difficulty of filtering off all the silver cyanide, which as I have shown, is easily decomposed by ammonium sulphide. I then treated mercuric cyanide with the oxychloride in a similar manner, keeping at a temperature of about 124° for eight to ten hours. A part was then treated with CS_2 without previous exhaustion in the Sprengel pump, and in this was much cyanide as well as chloride and chromium, but there was not a trace of mercury, and so once more it would seem as though the oxycyanide was present. The cyanogen was not present as gaseous cyanogen chloride, for this being a volatile substance, would have escaped through the calcium chloride drying tube. The method employed did not lend itself either to the supposition that solid cyanogen chloride had been produced. I then tried to separate the cyanide from the oxychloride by placing some of the material in a porcelain boat and passing over it carefully dried CO_2, whilst the tube was at the same time cautiously heated, the products being passed into water. In the aqueous solution both cyanide and chloride occurred, and hence this kind of fractional volatilisation did not effect the separation. As a last resource I placed some of the mixture in a fractionating flask, hoping to first volatilise the oxychloride and then perhaps some of the oxycyanide would either distil or sublime, but on applying a very moderate heat the whole exploded with great violence, the material being flung in a blazing condition in all directions. Hence, though it seems from various indications as though the oxycyanide had been prepared, yet no method which I have been able to devise has proved effectual in separating it from the other bodies occurring with it.

I may add in conclusion that I found the reaction with $(NH_4)_2S$ and the subsequent addition of Fe_2Cl_6 by far the best method for the detection of a cyanide. In some cases I was unable to detect any cyanide at all with the ferrocyanide tests, whilst the sulphocyanide gave it at once. In all cases where the oxychloride had to be dissolved out I was obliged to use CS_2, this being the only substance which was not acted upon by the oxychloride, at any rate not at once, and it has, moreover, the advantage of not dissolving a trace of $HgCy_2$, which latter body dissolves with considerable ease in both absolute alcohol and ether.

University College, Liverpool.

ON THE
CONVERSION OF SOME OF THE HOMOLOGUES OF BENZOL-PHENOL INTO PRIMARY AND SECONDARY AMINES.*

By RACHEL LLOYD.

Various experiments, attended with but little or no success, have been made by distinguished chemists at different periods of time to convert benzol-phenol into aniline.

Some years since, Professor V. Merz and W. Weith† obtained aniline, together with diphenylamine, by heating benzol-phenol and zinc-ammonium chloride at a tempera- of 280—300°. Later experiments, made in the laboratory of Professor Merz,‡ have shown that the above-mentioned

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* "University Studies, Published by the University of Nebraska,' October, 1888.

† *Berichte der Deutschen Chem. Gesellschaft*, xiii., 1298.

‡ P. Müller: "Inaugural-Dissertation." Aarau, 1886.

changes take place more readily when ammonium chloride is added to the zinc-ammonium chloride and the temperature raised to 330°. Under these conditions the three cresols have been converted into the corresponding mono- and ditolylamines, as well as the xylenes into primary and secondary amines. It has been further proved that zinc-ammonium bromide and ammonium bromide produce similar results to those given by zinc-ammonium chloride and ammonium chloride.

In order to ascertain whether the above reactions are common to the benzol series or not, I have undertaken the conversion of some of the higher homologues of benzol-phenol into primary and secondary amines with the following results:—

ISOBUTYLPHENOL.

Isobutylphenol, prepared by the method given by Liebmann,[*] boiling at 230°, was heated in closed tubes with zinc-ammonium bromide and ammonium bromide in the proportions by weight of 1 : 3 : 1 for forty hours at a temperature of 320°—330°.

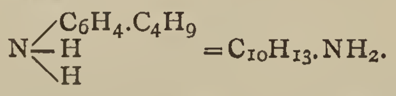
The tube-contents showed indistinct layers: the upper, an amorphous mass of a dark green colour; the under layer, a semi-solid mass of a light green colour, containing an abundance of darker particles. Accompanying these was a quantity of a dark green oily liquid. During the reaction water was formed in abundance in the tubes.

The opening of the tubes showed considerable pressure. The escaping gas possessed an aromatic odour, and burned with a feeble flame.

The tubes were further heated during six hours at the same temperature; the contents showed no special change from the appearances above described, but the oily portions were *darker in colour, and the layers* not so distinctly marked. The treatment of the tube-contents was as follows, and this method, essentially the same as that used by Merz and Müller[†] for the separation and quantitative estimation of monophenyl and diphenylamine, and unchanged phenol from benzol-phenol, was followed in subsequent experiments with other phenols. The reactions-mass was warmed with dilute hydrochloric acid until complete solution took place, with the exception of floating charred particles. Floating on the surface of the green-coloured solution was a dark brown oil. To insure complete separation of the substances, the entire solution was warmed with ether under reversed condenser. The oil dissolved readily in the ether. The primary base was sought for in the acid solution, and the secondary base and unchanged phenol in the ether extract.

The addition of an excess of ammonia to the acid solution caused the separation of a light brown oil, which after extraction with ether and drying over caustic potash was fractionally distilled and weighed.

Phenisobutylamine:—

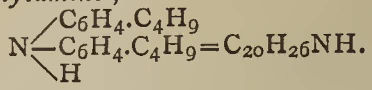


$$N\begin{cases}C_6H_4.C_4H_9\\H\\H\end{cases}=C_{10}H_{13}.NH_2.$$

The larger part of the primary base—a light brown oil—had a constant boiling-point of 230°—231°. The amidoisobutylamine obtained by Studer[‡] from aniline, hydrochloric acid, and isobutyl-alcohol, boiled at the same temperature. The acetyl compound of phenisobutylamine crystallised from warm alcohol in satiny leaflets, which melted at 170°, corresponding in all respects with the amine of Studer. According to the investigations of Pahl[§], it seems evident that Studer's base is a *p*-amidoisobutylamine.

The ether extract, separated from the acid solution by means of a separation funnel, was filtered to remove charred particles (which particles were dried and weighed), then thoroughly shaken with sodium hydrate to free the sought-for secondary amine from any unchanged phenol which might be present.

Diphenisobutylamine;—



$$N\begin{cases}C_6H_4.C_4H_9\\C_6H_4.C_4H_9\\H\end{cases}=C_{20}H_{26}NH.$$

The so-isolated secondary amine—a thick oily liquid of a deep brown colour—was twice distilled with superheated steam. By this means a light golden oil was obtained, which became colourless after distillation in an atmosphere of hydrogen. A small portion distilled over at 290°—305°, a greater amount between 305°—315°; at 315° partial decomposition took place, yellowish white fumes were given off. (Under similar conditions diphenylamine boiled at 297°).

An analysis of the portion distilling between 305°—315° gave the following result:—

I. 0·2176 grm. substance gave 0·6793 grm. carbon dioxide and 0·183 grm. water, corresponding to 0·18525 grm. C. and 0·02033 grm. H.

II. 0·1642 grm. substance gave 8 c.c. of moist nitrogen (thermometer 20° C., barometer 760 m.m.) equal to 0·0090632 grm. N.

III. 0·2737 grm. substance gave 13 c.c. of moist nitrogen (thermometer 21° C., barometer 726 m.m.) equal to 0·0141219 grm. N.

Calculated for $C_{20}H_{27}N$.			Found.	
			I.	II.
		Per cent.	Per cent.	Per cent.
C_{20}	240	85·41	85·13	—
H_{27}	27	9·61	9·34	—
N	14	4·98	5·51	5·51
	281	100·00		

I was unable to obtain the base other than as a thick oil even at temperature of −15° C. A drop of nitric acid added to the light yellow-brown solution of diphenisobutylamine in concentrated sulphuric acid produced a violet tint, which changed rapidly to blue and then to blue-black.

Finally, the unchanged phenol separated from the first ether extract was again set free by hydrochloric acid, isolated with ether, and distilled at 229°—233°. The investigations proved that in its qualitative aspects, at least isobutylphenol is analogous to benzol-phenol, the cresols, and the xylenes. The results of repeated experiments have shown that a better yield of primary and secondary amines is obtained by the action of zinc-ammonium bromide than with zinc-ammonium chloride. With each were used twenty grms. of phenol, sixty grms. of the bromide or chloride of zinc and ammonium, and twenty grms. of ammonium bromide or chloride, and the temperature was maintained at 320°—330° for forty hours.

	Zinc-ammonium bromide.			Zinc-ammonium chloride.			
Isobutylphenol.	I.	II.	III.	I.	II.	III.	
Phenisobutylamine ..	30	34	35	20	30	28	p. c.
Diphenisobutylamine.	25	20	22·5	19	20	18	,,
Unchanged phenol ..	38	40	36·5	45	44·5	44	,,
Carbonised substance.	2	1	1·6	2	2·1	3·9	,,

Derivatives of Diphenisobutylamine.

The platinum double salt—$(C_{20}H_{26}NH.HCl)_2Pt.Cl_4$—was most readily obtained by adding to an alcoholic solu- of the hydrochloric acid salt an alcoholic solution of platinum chloride. An oily salt separated at first, which after standing changed to a granular golden-brown mass.

The mass was with difficulty soluble in water, but dissolved readily in hot alcohol, from which it crystallised in golden needles. The twice crystallised salt was dried over sulphuric acid in vacuum and at 110°, then analysed with the following result:—

I. 0·3300 grm. of the salt gave 0·0670 grm. platinum.
II. 0·3539 ,, ,, 0·0713 ,, ,,

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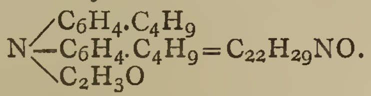
[*] *Berichte der Deutschen chem. Gesellschaft*, xiv., 1842.
[†] *Ibid.*, xix., 2902.
[‡] Studer, *Annalen*, 211, 236.
[§] *Berichte der Deutschen chem. Gesellschaft*, xvii., 1233.

Calculated or $C_{20}H_{26}NH.HCl)_2PtCl_4$.		Found. I.		Found. II.
20·01 per cent Pt	..	20·30	..	20·14 per cent Pt

Acetyldiphenisobutylamine :—



$$N\begin{cases}C_6H_4.C_4H_9\\ C_6H_4.C_4H_9\\ C_2H_3O\end{cases}=C_{22}H_{29}NO.$$

To form this compound, diphenisobutylamine was heated with an excess of acetic anhydride for two hours at a temperature of 130°. The fluid darkened in colour, and upon neutralisation of the free acid with sodium carbonate, a thick crystalline mass of a grey-white colour separated. This mass was thoroughly washed, dried, and crystallised out of benzol by addition of a small quantity of absolute alcohol in glistening white leaflets with 75° as the constant melting-point. The crystals dissolved with difficulty in hot water, readily in alcohol and benzol. Efforts to obtain the base from this compound by heating with sodium carbonate and caustic soda were unsuccessful, the acetyl compound remaining undecomposed. The analysis gave the following result:—

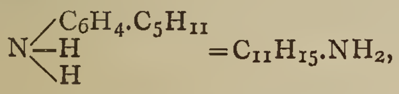
0·2895 grm. substance gave 0·2383 water, corresponding to 0·02647 H, and 0·8640 grm. carbon dioxide to 0·23565 grm. C.

Calculated for $C_{22}H_{29}NO$.				Found.
C_{22}	— 264 —	81·73 per cent	..	81·39 per cent
H_{29}	— 29 —	8·98 ,,	..	9·14 ,,
N	— 14 —	4·34 ,,	..	— ,,
O	— 16 —	4·95 ,,	..	— ,,
	323 —	100·00 per cent		

ISOAMYLPHENOL.

The isoamylphenol, which formed the starting-point of the following experiments, was made after the method given by Liebmann, and distilled at 249°. The experiments were conducted similarly to those with isobutylphenol. With every 20 grms. of phenol sixty grms. of zinc-ammonium bromide and twenty grms. of ammonium bromide were used. The substances were heated in closed tubes for forty hours at a temperature of 330° to 340°. On opening the tubes a very disagreeable-smelling gas escaped, which burned with a feeble flame for a few seconds. The tube-contents were in general appearance similar to those already described. Water was formed in abundance, and the reaction-mass was dark green in colour. The bases were separated by the method used with isobutylphenol.

Phenisamylamine :—



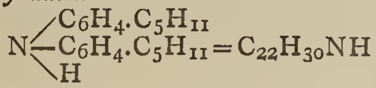
$$N\begin{cases}C_6H_4.C_5H_{11}\\ H\\ H\end{cases}=C_{11}H_{15}.NH_2,$$

a dark brown oil of weak basic character boiled at 259° to 262°. The distillation was continued until the temperature had reached 266°, when only a small amount of carbonised substance remained. It seems probable that the oil distilling between 259°—262° is identical with the amido-amyl benzol prepared by Calm,[*] by the action of chlor-zinc aniline upon fermentation amylic alcohol, of which the boiling-point is given at 256°—258°. It gave upon analysis the following results:—

0·1547 grm. substance gave 0·4566 grm. carbon dioxide and 0·1415 grm. water, equal to 0·12453 grm. C. and 0·01572 grm. H.

Calculated for $C_{11}H_{17}N$.				Found.
C_{11}	— 132 —	80·98 per cent	..	80·50 per cent
H_{17}	— 17 —	10·43 ,,	..	10·16 ,,
N	— 14 —	8·59 ,,	..	—
	163 —	100·00 ,,		

Diphenisamylamine :—



$$N\begin{cases}C_6H_4.C_5H_{11}\\ C_6H_4.C_5H_{11}\\ H\end{cases}=C_{22}H_{30}NH$$

was obtain as a thick dark brown oil, which boiled at 301° to 325°. In order to purify it, it was twice distilled with super-heated steam, then in an atmosphere of hydrogen, when an almost colourless oil distilled over between 319° to 321°.

The analysis confirmed the presence of a secondary amine:—

I. 0·2529 grm. substance gave 0·7925 grm. carbon dioxide and 0·2350 grm. water, equal to 0·21613 grm. C. and 0·02611 grm. H.

II. 0·2291 grm. substance gave 10 c.c. of moist nitrogen (thermometer 22° C., barometer 729 m.m.) equal to 0·010854 grm. N.

Calculated for $C_{22}H_{31}N$.				Found.
C_{22}	— 264 —	85·44 per cent	..	85·45 per cent
H_{31}	— 31 —	10·03 ,,	..	10·32 ,,
N	— 14 —	4·53 ,,	..	4·73 ,,
	309 —	100·00 ,,		

Upon standing, the amine became darker in colour, and in concentrated sulphuric acid dissolved with an exquisite golden colour, which grew darker in the air; the addition of a nitrite or of nitric acid to this solution changed the colour, first to light violet, then to a deep blue. In connection with these bases, a considerable quantity of unchanged phenol was found, which was isolated and distilled. Boiling-point 247°—250°.

The results of corresponding experiments with the bromides and chlorides of zinc and ammonium are here tabulated. Temperature, 330°—340°; time, forty hours.

	Zinc-ammonium bromide.			Zinc-ammonium chloride.			
Isoamylphenol.	I.	II.	III.	I.	II.	III.	
Phenisamylamine ..	35	38	31	25	35	33·2	p.c.
Diphenisamylamine	21	20	25	17·4	19·1	18	,,
Unchanged phenol ..	36	37	35·7	40	32	39·3	,,
Carbonised substance	1	0·5	0·8	3	2·8	4	,,

Derivatives of Phenisamylamine.

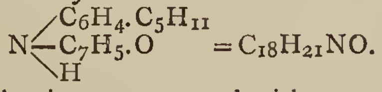
The platinum double salt—$(C_{11}H_{17}N.HCl)_2PtCl_4$—separated as a canary-coloured amorphous mass when to a hydrochloric acid solution of the base platinum chloride was added in slight excess. The amorphous floating-mass was dissolved with difficulty in hot water, more readily in hot alcohol, and was crystallised from a hot mixture of the two in beautiful golden needles.

For the analysis, it was dried at 100°—110°, when it gave the following result:—

0·3464 grm. of the salt gave 0·0912 grm. platinum.

Calculated for $(C_{11}H_{17}N.HCl)_2PtCl_4$.		Found.
26·43 per cent Pt	.. ..	26·33 per cent Pt.

Benzoylphenisamylamine :—



$$N\begin{cases}C_6H_4.C_5H_{11}\\ C_7H_5.O\\ H\end{cases}=C_{18}H_{21}NO.$$

Phenisamylamine was treated with an excess of chlorbenzoyl, and the reaction which commenced at once was fully completed in an hour. During the operation a light brown crystalline mass separated, which was thoroughly washed, made neutral with sodium carbonate, and crystallised from hot absolute alcohol. After a second crystallisation, exquisite crystals of a leaf-like form and a mother-of-pearl lustre shot out from the solution in great abundance. These crystals, which dissolved readily in hot alcohol, and in cold chloroform and benzol, had a constant melting-point of 148·5°. Calm[*] gives the melting-point of the benzoyl compound of his amido-amyl-benzol at 146°—149°.

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[*] Berichte der Deutschen chem. Gesellschaft, xv., 1643.

[*] Berichte der Deutschen chem. Gesellschaft, xv., 1645.

The analysis resulted as follows :—

0·2060 grm. substance gave 0·6101 grm. carbon dioxide and 0·1452 grm. water, equal to 0·16638 grm. C. and 0·01613 grm. H.

Calculated for $C_{18}H_{21}NO$.				Found.
C_{18}	— 216 —	80·89 per cent	..	80·76 per cent
H_{21}	— 21 —	7·87 ,,	..	7·83 ,,
N	— 14 —	5·25 ,,	..	—
O	— 16 —	5·99 ,,	..	—
	267 —	100·00 ,,		

Derivatives of Diphenisamylamine.

The platinum double salt—$(C_{22}H_{30}NH.HCl)_2PtCl_4$.

The salt was best prepared by conducting dry hydrochloric acid gas into an ether solution of the base. The ether was evaporated and an oily compound obtained, which dissolved readily in absolute alcohol.

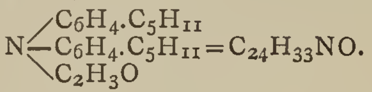
The addition of an alcoholic solution of platinum chloride to this solution, gave, after some days' standing, a compact, dark golden, slightly crystalline body, which difficultly soluble in hot alcohol. After thorough washing with water it was dried over sulphuric acid, and finally at 100°—110°.

The analyses were as follows :—

I. 0·2416 grm. substance gave 0·04450 grm. platinum.
II. 0·3396 ,, ,, ,, 0·06384 ,, ,,

Calculated for $(C_{22}H_{30}NH.HCl)_2PtCl_4$.	Found. I.	Found. II.
18·92 per cent Pt	18·41	18·76 per cent Pt

Acetyldiphenisamylamine :—



$$N\begin{cases}C_6H_4.C_5H_{11}\\C_6H_4.C_5H_{11}\\C_2H_3O\end{cases}=C_{24}H_{33}NO.$$

In the preparation of this substance one molecule of the base was heated with two molecules of acetic anhydride for four hours at a temperature of 130°.

The chocolate-brown resulting-mass became greylsh white after a thorough washing with water and neutralisation of the free acetic anhydride. It was crystallised from hot benzol in shining white leaflets, which melted at 81°, dissolved readily in warm benzol and chloroform, also in hot absolute alcohol.

The analysis gave the following result :—

0·1348 grm. substance gave 0·4056 grm. carbon dioxide and 0·1172 grm. water, corresponding to 0·1104 grm. C. and 0·01302 grm. H.

Calculated for $C_{24}H_{33}NO$.				Found.
C_{24}	— 288 —	82·05 per cent	..	81·89 per cent
H_{33}	— 33 —	9·40 ,,	..	9·65 ,,
N	— 14 —	3·98 ,,	..	— ,,
O	— 16 —	4·57 ,,	..	— ,,
	351 —	100·00 per cent.		

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1889.

Mr. William Crookes, F.R.S., President, in the Chair.

(Concluded from p. 177).

31. "*The Determination of the Constitution of the Heteronucleal αβ- and ββ di-derivatives of Naphthalene.*" (Second Notice). By Henry E. Armstrong and W. P. Wynne.

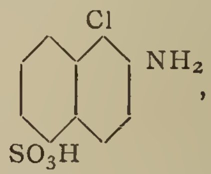
This communication is a continuation of that brought under the notice of the Society at the previous mention (*cf. Chem. Soc. Proc.*, 1889, No. 64, pp. 34—37), and is an account of the constitution of the three isomeric sulphonic acids prepared from 1 : 2 α-chloro-β-naphthylamine in the manner described in the former notice.

In displacing the NH_2 radicle of the amidochlorosulphonic acids by v. Baeyer's hydrazine method (*cf.* Haller, *Ber.*, 1885, 90), the authors were for some time seriously misled, as the products obtained were impure, owing to the extreme sensitiveness of the hydrazines to the action of hydrogen chloride in presence of cuprous salt; they behave, in fact, as diazo-compounds, and it is therefore essential not only to avoid the use of cupric chloride and to employ cupric sulphate, but also to purify the hydrazines.

Constitution of the No. 1 Acid.—As already mentioned, this acid yields the Dahl modification of betanaphthylaminesulphonic acid on reduction. This statement is based both on the study of the properties of the reduction product, and on the further observations that it is converted by Sandmeyer's method into a chloronaphthalenesulphonic acid, yielding a monohydrated sodium salt crystallising in scales, and a chloride which crystallises from a mixture of petroleum spirit and benzene in well-defined prisms melting at 70°; and that this sulphochloride yields on distillation with PCl_5 a dichloronaphthalene which crystallises from alcohol in long, slender needles melting at 48° (*Brit. Assoc. Report*, 1888; Chem. News, lviii., 295).

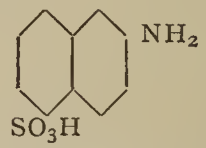
The chlorosulphonic acid obtained from the No. 1 chloroamidosulphonic acid yields a monohydrated potassium salt crystallising in small, elongated plates; a chloride which crystallises from benzene in small, well-defined prisms melting at 95°; an amide crystallising from dilute alcohol in slender needles melting at 225°; and a dichloronaphthalene crystallising from alcohol in scales melting at 107°.

It was pointed out in the previous communication (*cf. Chem. Soc. Proc.*, 1889, p. 35) that γ-dichloronaphthalene must be regarded as the axially symmetric 1 : 4′ αα-heteronucleal dichloronaphthalene; the formula representing the constitution of the No. 1 acid will therefore be—



,

as this results on superposing the formula of the 1 : 4 chloronaphthalenesulphonic acid derived from it and that of the parent 1 : 2 chlorobetanaphthylamine. Displacing chlorine by hydrogen, the formula of the Dahl acid results, viz.,—



;

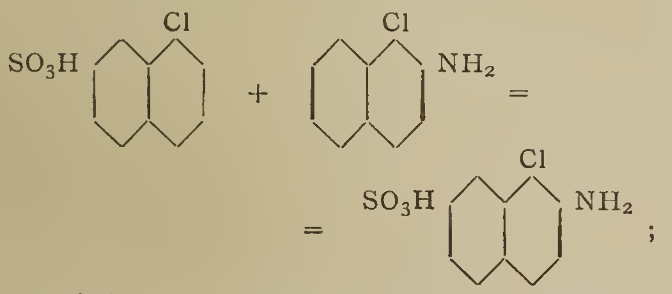
whence it follows that *η-dichloronaphthalene, m. p.* 48°, *is the* 1 : 3′ *dichloronaphthalene.* This result is in harmony with that arrived at by Erdmann and Kirchhoff, and serves to justify the interpretation which they have given of their synthesis of η-dichloronaphthalene.

The No. 1 acid is converted by Sandmeyer's method into a dichloronaphthalenesulphonic acid which yields a potassium salt crystallising in scales; a chloride crystallising from benzene in massive prisms melting at 104°; an amide crystallising from dilute alcohol in slender, elongated plates melting at 218°; and a trichloronaphthalene crystallising from alcohol in long, slender needles melting at 78—78·5°. Dichloronaphthalene melting at 34°, which is obtained by displacing NH_2 in α-chlorobetanaphthylamine by Cl, on sulphonation yields at least two acids (*Brit. Assoc. Report*, 1888; Chem. News, lviii., 295), from each of which the dichloronaphthalene can again be obtained by hydrolysis; one of these acids—the chief product—is undoubtedly identical with that prepared from the No. 1 chloramido-acid, as its chlorine crystallises in massive prisms melting at 105°, its amide in needles or slender scales melting at 216·5—217°, and the trichloronaphthalene prepared from it in needles melting at 78°.

Constitution of the No. 3 Acid.—On reduction this acid yields Bayer and Duisberg's betanaphthylamine-δ-sulphonic acid; the reduction product was converted by Sandmeyer's method into a chloronaphthalenesulphonic acid from which a chloride was prepared crystallising from benzene in prisms melting at 86°, and an amide crystallising from dilute alcohol in minute prisms melting at 175°; on distilling the sulphochloride with PCl_5, δ-dichloronaphthalene, m. p. 114°, was obtained (*cf. Brit. Assoc. Report*, 1888).

The chlorosulphonic acid prepared from the No. 3 acid yields a monohydrated potassium salt crystallising in small, thin scales; a chloride crystallising from a mixture of benzene and petroleum spirit in well-defined, elongated prisms melting at 93—94°; and an amide crystallising from dilute alcohol in long, slender needles melting at 185—186°; the dichloronaphthalene prepared from the sulphochloride, crystallised from alcohol in aggregates of short, slender needles melting at 63·5—64°; it was characterised by the authors' method, by sulphonation—the chloride of the resulting sulphonic acid crystallised in needles which became opaque after some time, and melted at 117—118°. This dichloronaphthalene is obtained, as the authors have shown, from Arnell's β-chloronaphthalenesulphonic acid (*Brit. Assoc. Report*, 1888; Chem. News, lviii., 295); from the Badische betanaphthylaminesulphonic acid (*ibid.; Chem. Soc. Proc.*, 1888, No. 58, p. 105); from parachlorophenylparaconic acid (Erdmann and Kirchhoff; *cf. Chem. Soc. Proc.*, 1889, No. 61, p. 7); and from Cleve's θ-α-nitronaphthalene-β-sulphonic acid (*Chem. Soc. Proc.*, 1889, No. 62, p. 18). As it is a heteronucleal α-β-derivative, it must by exclusion be the 1 : 2'-compound, as the only alternative 1 : 3' formula has been proved above to belong to η-dichloronaphthalene, m. p. 48°.

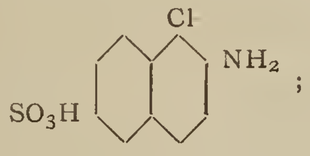
Superposing the formula which expresses the constitution of the new chlorosulphonic acid from the No. 3 acid and that of the parent chloramidonaphthalene, the formula of the No. 3 acid is shown to be as follows:—



whence it follows that Bayer and Duisberg's δ-acid is as more frequently supposed a 2 : 2'-derivative.

The dichloronaphthalenesulphonic acid prepared by Sandmeyer's method from the No. 3 acid yields a monohydrated sodium salt crystallising in elongated, rectangular plates; a chloride crystallising from benzene in small, well-defined prisms melting at 122—123°; and an amide crystallising from dilute alcohol in long, slender needles melting at 225—226°; the corresponding trichloronaphthalene crystallises from alcohol in hemispherical aggregates consisting of microscopic needles melting at 83—84°.

Constitution of the No. 2 Acid.—The chloronaphthalenesulphonic acid prepared from the No. 2 chloramidosulphonic acid yields an anhydrous potassium salt crystallising in small granules; a chloride crystallising from benzene in aggregates of minute diamond-shaped plates which afterwards grew into the form of opaque hemispherical aggregates melting at 112—113°; an amide crystallising from dilute alcohol in small scales melting at 185—186°; and a dichloronaphthalene melting at 48—49°: this acid is consequently identical with that described by Cleve (*Berichte*, 1887, 74), and corresponds with η-dichloronaphthalene in constitution. From this it follows that the constitution of the No. 2 acid is expressed by the formula—



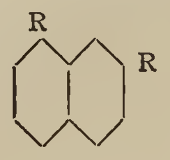
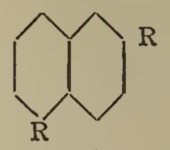
and also that it is derived from the Brönner betanaphthylaminesulphonic acid: that this is the case the authors have been able to place beyond doubt, although owing to its peculiar behaviour on reduction they have not succeeded in converting it directly into the Brönner acid.

The sodium salt of the No. 2 acid is so sparingly soluble in cold water that the reduction has to be effected at a temperature of 50—60°, and then proceeds very slowly: the liquid becomes of a dark brown colour, and yields a very dark coloured sodium salt on evaporation; this salt is soluble in 90 per cent alcohol. On acidulating a solution of the sodium salt, only a relatively very small amount of precipitate was obtained; the acid thus prepared, although evidently very impure, gave on treatment by Sandmeyer's method a chlorosulphonic acid from which a chloride crystallising in small prisms melting at 107°, and an amide crystallising in needles melting at 183° were obtained. The chloride and amide of the chlor-acid prepared by Forsling (*Berichte*, 1887, 80) from the Brönner acid have similar properties to those observed by the authors in the case of their product, and there can be little doubt therefore that the Brönner acid is formed. The chief product of reduction, however, is a very soluble acid—perhaps a hydro-derivative. If placed in contact with sodium amalgam under conditions similar to those observed in reducing the No. 2 acid, the sodium salt of the Brönner acid appears to slowly change, the solution becoming dark coloured.

When the chlorobetanaphthol corresponding to chlorobetanaphthylamine is sulphonated, it yields a sulphonic acid which is undoubtedly a derivative of Schaeffer's betanaphtholsulphonic acid—an acid which itself is convertible into and may be obtained from Brönner's betanaphthylaminesulphonic acid—inasmuch as it yields the same bromhydroxyquinonesulphonate as the Schaeffer acid on treatment with bromine, and may be converted into the Schaeffer acid by reduction with sodium amalgam. An attempt to prepare this naphthol-derivative from the No. 2 acid was unsuccessful, owing to the extreme stability of the diazo-derivative of the latter acid; on the other hand, on heating the chloronaphtholsulphonate with ammonia under pressure, a complex action took place, but a small quantity of an acid was ultimately obtained which, judging from the characteristic appearance of its sodium salt, was the No. 2 acid.

The dichloronaphthalenesulphonic acid prepared by Sandmeyer's method from the No. 2 acid gave a sodium salt crystallising in minute scales; a chloride crystallising from benzene in small aggregates of minute prisms melting at 165—166°; an amide crystallising from dilute alcohol in slender, yellow needles melting at 187—188°; and a trichloronaphthalene crystallising from alcohol in tufts of short, slender needles melting at 92°. A trichloronaphthalene of the same melting-point was obtained by submitting the chlorobetanaphtholsulphonate above-mentioned to the action of PCl_5.

The results obtained in the case of the No. 2 and No. 3 acids prove that betanaphthylamine-δ-sulphonic acid and corresponding di-derivatives of naphthalene (*e.g.*, δ-dichloronaphthalene, m. p. 114°) are 2 : 2'-compounds; and that the isomeric Brönner acid and corresponding di-derivatives (*e.g.*, ε-dichloronaphthalene, m. p. 135°) are 2 : 3'-compounds. They conclusively refute Erdmann's

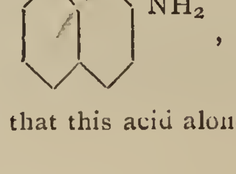
			
2 : 1′	2 : 2′	2 : 3′	2 : 4′
Cl_2. M. p. 63·5°	Cl_2. M. p. 114°	Cl_2. M. p. 135°	Cl_2. M. p. 48°
$NH_2\beta \cdot SO_3H$ (Badische)	$NH_2\beta \cdot SO_3H$ (Bayer and Duisberg)	$NH_2\beta \cdot SO_3H$ (Brönner)	$NH_2\beta \cdot SO_3H$ (Dahl)
$OH\beta \cdot SO_3H$ (Bayer)	$OH\beta \cdot SO_3H$ (Casella)	$OH\beta \cdot SO_3H$ (Schaeffer)	$OH\beta \cdot SO_3H$ (Dahl)
$NO_2\alpha \cdot SO_2Cl$ M. p. 169°	—	—	$NO_2\alpha \cdot SO_2Cl$ M. p. 125°
—	$(SO_3H)_2$ (Ebert and Merz α)	$(SO_3H)_2$ (Ebert and Merz β)	$(SO_3H)_2$ (Armstrong and Wynne)
$Cl\alpha \cdot SO_2Cl$ M. p. 94°	—	—	$Cl\alpha \cdot SO_2Cl$ M. p. 114°
$Cl\beta \cdot SO_2Cl$ M. p. 129°.	$Cl\beta \cdot SO_2Cl$ M. p. 86°	$Cl\beta \cdot SO_2Cl$ M. p. 109°	$Cl\beta \cdot SO_2Cl$ M. p. 70°.

statement (*Berichte*, 1888, 639): "Diese Frage (as to whether the Brönner and δ acids are respectively 2 : 3′ and 2 : 2′ compounds, or *vice versâ*) ist nur durch synthetischen Aufbau dieser oder ähnlichen Verbindungen zu lösen"—indeed notwithstanding it has been their privilege to confirm Erdmann and Kirchhoff's conclusions, the authors remain of the opinion that a synthetic method, such as these chemists have so successfully employed, does not and cannot afford a final solution of the problem, although their results undoubtedly serve to increase our belief in the general trustworthiness in such cases of conclusions based on the application of synthetic methods.

The results also establish the correctness of the opinion, long held and frequently expressed by the authors, based on the higher melting-points of the uniform ε-di-derivatives in comparison with the isomeric δ-di-derivatives, that the ε-derivatives are symmetrically constituted; this conclusion, in fact, is probably the most important outcome of the experiments, as it affords conclusive proof of the influence of symmetry as the determining cause in the case of naphthalene-derivatives of high melting-point and slight solubility, &c.

It has already been pointed out that the dichloronaphthalenesulphonic acid prepared from the No. 1 acid is identical with the chief product of sulphonation of 1 : 2 dichloronaphthalene; the dichloro-acid prepared from the No. 2 acid is found in like manner to be identical with the second acid formed on sulphonating the dichloronaphthalene in question. As the one acid is an alphasulphonic acid and the second a beta-sulphonic acid formed by displacement of the hydrogen-atom contiguous to that which is displaced in the α-sulphonic acid, the authors are of opinion that the beta-sulphonic acid is a product of isomeric change and not a product of initial action; they propose to investigate this question in the manner already adopted with success in the case of the acids derived from β-chloro-, β-bromo-, and β-iodonaphthalene.

Lastly, it may be pointed out that as the Badische betanaphthylaminesulphonic acid is now proved to have the constitution represented by the formula—



the remarkable fact that this acid alone of the our known heteronucleal betanaphthylaminesulphonic acids does not afford azo-colours must be regarded as a result of a "protecting influence" of the amido and sulphonic radicles on the included α-hydrogen atom, and the non-occurrence of the isomeric change which would be involved in the conversion of the diazoamido-compound initially produced by the action of the diazo-compound into the quinonoid azo-colour (*cf. Chem. Soc. Proceedings*, 1888, No. 49, p. 29); it is noteworthy that the isomeric change does take place in the case of the corresponding hydroxy-acid (Bayer's croceinic acid) although the colour is formed but slowly, and it is not improbable that it may be found possible by varying the diazo-compound to obtain colours even from the Badische amido-acid. The authors propose to undertake experiments in this direction.

The constitution of a number of heteronucleal di-derivatives of naphthalene which are of importance as reference compounds is indicated in the table above, the compounds being represented by the symbols of the constituent radicles. The authors take this opportunity of directing the attention especially of Continental colleagues to the desirability of adopting a uniform system of notation; they would advocate that which has long been in use by the Chemical Society, which consists in numbering the positions in the one nucleus 1, 2, 3, 4, and the corresponding positions in the second nucleus 1′, 2′, 3′, 4′. This method they regard as more rational, in view of the fact that naphthalene contains two like nuclei, than the practice now sometimes adopted of numbering the positions 1 to 8.

32. "*Contributions to the Knowledge of Citric and Aconitic Acids.*" By S. Skinner, B.A., and S. Ruhemann, Ph. D., M.A.

The authors have studied the action of phosphorus pentachloride on citric acid, following Pebal's directions (*Annalen*, xcviii., 67). They show that the product is a chloromonochloride formed by the displacement of the alcoholic hydroxyl and one of the carboxylic hydroxyls, it being uncertain, however, which of the three latter in citric acid is affected. The chloride is reconverted into citric acid by the action of water; when heated at 125°, it loses hydrogen chloride, yielding a product which water converts into aconitic acid; aniline transforms it into aconitylanilanilide, and it is similarly affected by treatment with orthotoluidine. The anilanilide yields the anilcarboxylic acid and aniline on hydrolysis, and the toluidine-derivative affords the corresponding toluidcarboxylic acid.

NOTICES OF BOOKS.

A Treatise on Manures, or the Philosophy of Manuring: A Practical Handbook for the Agriculturist, Manufacturer, and Student. By A. B. Griffiths, Ph.D., F.R.S. (Edin.), F.C.S., Principal and Lecturer on Chemistry, the School of Science, Lincoln. London: Whittaker and Co. and G. Bell and Sons.

This manual forms one of the valuable "Specialists' Series," now in course of publication by the two firms above mentioned. The author takes as his motto the saying that:—"There is not a farmer in England, however primitive and however unconscious of the fact, but is now conducting his business more or less on lines emanating from the laboratory." Yet at the same time we find that the failures of the farmer are due to ignorance of the exact nature and requirements of the soils and of the crops he may desire to grow, or to prejudice against the use of artificial manures.

Elsewhere we read:—"The farmer in this country must keep pace with the times if he is to compete with foreign nations who fully recognise the great value of science as applied to agriculture."

Perhaps, however, the most fatal prejudice of the British people is that which leads it, both at home and in the colonies, to devote itself, alike in agriculture and in manufactures, to the production of a few gigantic "staples," neglecting minor industries which, if individually trifling, sum up in their results to an enormous total.

Passing over this consideration as concerning the economist rather than the chemist, we come to the author's elaborate examination of the use of ferrous sulphate as a manure. In the seasons 1883, 1884, and 1886 Dr. Griffiths grew bean crops with and without the application of this salt. On each of two plots, agreeing very closely in the composition of the soil and identical, as we gather, in exposure, texture, and drainage, was planted on the same day an equal number of bean-seeds. The crop grown with the addition of ferrous sulphate at the rate of $\frac{1}{2}$ cwt. per acre yielded 56 bushels of dry beans, whilst the corresponding plots without the copperas produced only 35 bushels. Corresponding experiments in other seasons gave similarly favourable results. With various other crops, *e.g.*, turnips, hay, mangel wurzel, potatoes, wheat, cabbages, and onions, dressings of ferrous sulphate have given advantageous results. The copperas, it will be noticed, is to be superadded to the other manurial agents and not used as a substitute. It is also recommended as an antidote for various microscopic fungi, and it is stated on the authority of MM. Berthelot, Gautier, and Drouin that iron oxides accelerate the process of fixing atmospheric nitrogen in a soil. That iron in certain quantities, *i.e.*, in the neighbourhood of Wellington College, act as plant poisons and sterilise the soils is fully admitted. But the proportion found producing such effects is more than eighty times greater than the dose recommended by the author. The unfavourable results said to have been obtained with the dissolved basic slag, patented by Messrs. Wrightson and Munro, seem to be referrible to the excessive dose, as nearly $1\frac{1}{4}$ cwt. of ferrous sulphate must have been applied to the acre.

Basic slag (Thomas and Gilchrist) finely ground is recommended as a phosphatic manure. The author estimates that the 100,000 tons of this residue annually produced in England would suffice to raise four million tons of hay, and thus feed three quarter million head of cattle. The manure from these cattle would subserve the production of more thon a million tons of grain. "This amount of grain and cattle is more than twice the quantity of these foods we have ever imported, and, according to the smallest calculation, the yearly saving to this country would be $11\frac{1}{2}$ millions sterling. One condition is, however, of importance as regards the grain, that we should not have such summers as those of 1879 and 1888.

M. Ville's system of manuring is pronounced "worthy of the deepest study on the part of British farmers and others." It is remarked that this author, in addition to his four essential constituents of artificial manures, has been led to recognise the value of soluble iron-compounds. Gypsum Dr. Griffiths considers better adapted to the soils—or the climates—of the Continent rather than those of Britain.

As regards the valuation of manures, the author shows that a manure has two distinct values; a *commercial* value, turning solely on supply and demand, and an *agricultural*, which depends on the requirements of the crop to which it is to be applied, and to the deficiencies or redundances of the soils in which they are to be planted. If a manure is to be profitable to the farmer its agricultural value must exceed its commercial value. In other words, it must fetch less money out of his pocket than the value of the produce which it fetches out of the soil.

Other features of this work, which space does not allow us to notice, are the account of the various ingredients used in manures, of the manufacture of superphosphate and other artificial fertilisers, and the directions for the analysis of manures.

The work is indeed a *multum in parvo* of information valuable to the manure-maker and the practical farmer, and must be most strongly recommended.

Nature Series: The Chemistry of Photography. By Raphael Meldola, F.R.S. London: Macmillan and Co.

In the preface to this volume we find quoted an apparently paradoxical but really most significant saying of the late Colonel Russell's, that "Photography would be a most interesting subject *were it not for the pictures.*" It is somewhat curious that in an age when we are literally beset with photographers, amateur and professional, the principles underlying the mere routiue practice of the art should be so generally ignored. To meet this widespread shortcoming Prof. Meldola has delivered at the Finsbury Technical College the course of special lectures which form the subject-matter of the work before us. How fully the author comprehends the necessities of the situation will be at once gathered from the following passage, which, we must take leave to add, might, *mutato nomine*, be applied to not a few other arts:—"I am disposed to believe that the art is in danger of outstripping the Science. This is a state of affairs which we often witness when a discovery of immediate practical utility is made. There are many branches of industry which are now suffering in this country because they have been allowed to go on from the time of their foundation without any attention being paid to the scientific principles underlying them. It has been found by a long course of experience that certain results can be obtained in a particular way, and that mode of procedure has become stereotyped into a kind of article of faith. In such cases no trouble is taken to ascertain *why* the particular mode of operation leads to the desired results—the art has here outstripped the science. But if we thus allow a useful discovery to degenerate into a purely empirical industry we are neglecting our duty to that science which first gave us the discovery; and not only this, but we are running into the danger of seeing the industry taken out of our hands by more scientific competitors, who have no stereotyped formulæ, and who have taken the trouble to investigate the why and the wherefore of the different steps of their processes."

Prof. Meldola, accordingly, does not, in the work before us, attempt to deal with photography as an *art*. He does not even propose to enter upon the chemistry of the *materia photographica*. He is concerned with the chemistry of photographic processes and the principles involved, so that the reader may see what remains to be learnt and in what direction improvement seems necessary and practicable. There are, as the author points, many chemical actions effected by light which cannot be directly brought in connection with the photographic process. These would have proved interesting and apposite subjects in a general work on photo-chemistry, but they lie beyond the scope of the present treatise.

Among the first questions discussed is the action of light on silver chloride. The change which takes place is ascribed in the text-books to the formation of a subchloride, consequent upon the loss of chlorine. But Prof. Meldola, though he admits that the violet chloride contains less chlorine than the unaltered white chloride, shows good reason for questioning the formation of Ag_2Cl, and considering that the compound in question has never yet been isolated, and consequently has not been analysed, he considers that the safest course is to view the violet compound as a reduction-product of unknown formula.

The production of photographic pictures in their natural colours is admitted to be a problem which has never been solved. The author mentions the experiments in this direction of Seebeck, of Sir J. Herschel, Becquerel, Niepce de St. Victor, Poiteven, Carey Lea, and G. Staats. In these experiments variously coloured impressions have been produced. But their fixation has so far not been found practicable. Research in this direction is, however, mentioned as being of interest.

After each chapter we find an appendix describing experiments proving or illustrating the points advanced.

The "Chemistry of Photography" is, in our judgment, a timely production executed by a most competent authority.

Introduction to the Study of the Chemistry of the Ancients and of the Middle Ages ("Introduction à l'Etude de la Chimie des Anciens et du Moyen Age"). By M. Berthelot, Professor in the College of France. Paris: Georges Steinheil.

Men of science, and especially chemists, are generally more concerned with the future than with the present, and still more than with the past. Yet none of us, surely, can read M. Berthelot's work on the infancy of our science without profound interest and without feeling deeply indebted to the writer, who has devoted six years of a busy life to sweeping away certain widespread and deeply rooted errors.

It is commonly said and believed that chemistry had its origin in "alchemy," that word being taken to signify a tissue of mystical dreams on the transmutation of metals and on the elixir of life, diversified with occasional attemps to carry these beliefs into practice. This mistake —for that it is a mistake every reader of the work before us will become convinced—has not been without serious consequences. It has been a main pillar of the heresy that every science must pass successively through three stages—a mystical or mythological, a metaphysical, and finally a "positive." Such, it will be seen, was not the case: chemistry took its rise in the workshops of old Egyptian metallurgists, goldsmiths, and dyers—crafts which were in those days, strangely enough, practised by the same artizans. We find here a curious collection of recipes translated from the "Papyrus X" of the Leyden collection, which, from evidence internal as well as external, dates back to the third century of our era. These recipes show a knowledge of chemistry, certainly limited, but totally free from anything visionary or mythological. Here and there occurs a word which cannot be translated, but in the language and in the purport of these receipts there is no more mysticism than may be found in any modern cyclopædia of chemical recipes. As far as they go they are perfectly matter-of-fact and "positive." We find directions for purifying tin, for hardening lead, for colouring gold, for increasing the weight of gold, for whitening copper, for making a solder for gold, for writing in letters of gold, for giving copper the appearance of gold, for making base metal bear the trial by the touchstone, &c. Not a few of these prescriptions are for objects which cannot be called other than fraudulent. And here we find the transition to alchemy in the ordinary sense of the term. The ancient, adept from deceiving others, was gradually led to deceive himself. Finding that he could apparently multiply gold and silver, the thought dawned upon him that he might do so in reality. He hoped that as a small quantity of yeast vivifies a large volume of saccharine fluid, so a little gold might set up a fermentation in base metal, by which the whole should be ennobled. From this point dates the introduction into chemistry of that mystical element.

M. Berthelot has devoted much patient research to interpreting the peculiar terms and symbols of the old alchemists. All who feel an interest in this portion of the history of our science will find in this volume and in the two preceding works, the "Origines de l'Alchimie" and the "Collection des Alchimists Grecs," a safe guide. We learn that several discoveries supposed to have been made in comparatively modern days may be traced back to a remote antiquity. Thus, cobalt is commonly said to have been first obtained by Brandes in 1742, and its name is connected with certain malignant demons which interfered with the work of the miner. In fact, cobalt was known to the ancients in the days of Theophrastus (though it had not been isolated), and was spoken of as the "male blue," in opposition to the "female blue" derived from the compounds of copper. The very name cobalt is traced to the Greek. Thus in the "Lexicon Alchemiæ Rulandi," we read:—"*Cobatiorum* fumus est kobalt." The expression "fume of cobathia" is to be found in a passage of Hermes, cited by Olympiodorus. Even metallic cobalt seems to have been known as early as 1612. Metallic antimony was also known in ancient Chaldea long before its reputed discovery by Basil Valentine, a semi-mythological personage. The very name "antimony" is derived, not from its legendary poisonous action upon monks, but from the Arabic "athmoud" or "othmoud."

It appears that the autogenous soldering of lead, commonly supposed to be a modern discovery, is described by Vincent de Beauvais in his "*Speculum majus*" as being actually in use. Wood was rendered incombustible, according to Aulus Gellius, by steeping in or coating with alum. The fire-proof textiles of the ancients were woven from asbestos. In fact, in our knowledge of the useful arts, we have not made, in comparison with the days of classical antiquity, such gigantic strides as it is commonly supposed. Had the technical writings of the Egyptians not been destroyed by the Emperor Diocletian and by the ignorant zeal of the early Christians we should doubtless meet with astonishing revelations.

CORRESPONDENCE.

ACTION OF FERROUS SULPHATE ON SOILS.

To the Editor of the Chemical News.

Sir,—Mr. J. G. McIntosh (Chemical News, vol. lix., p. 167) confounds the old experiments with iron sulphate with those of later date.

The old experimentalists used *large* quantities of iron sulphate as a manure, and, in many cases, failed in producing anything like a satisfactory yield; whereas in the experiments recorded in the *Journal of the Chemical Society* during the past few years, only ½ cwt. of $FeSO_4$ per acre were used, with the greatest benefit, for certain crops, proving that it is a *direct* as well as indirect plant food.

Concerning Mr. McIntosh's remarks about the late Dr. Voelcker's experiments, I may say that even Voelcker was preceded by Prince Salm-Horstmar (*Annales de Physique et de Chimie*, 1851).

Mr. McIntosh says:—"It is strange that sulphate of *ammonia* has not gone down to 10s. per ton if we are to credit what "X" says in regard to what Professor Muntz says." I think he must have made a slip of the pen. Ammonium sulphate is a valuable *nitrogenous* manure, and was not included among the sulphates. Even Mr. McIntosh *did not* include it among the sulphates he mentioned in the Chemical News (vol. lix., p. 96).

There are many fresh details recorded in the recent memoirs published in the *Journal of the Chemical Society* (1882—87), or why did the Council of the Society think fit to give them a place in the *Transactions*?

What about (*a*) the displacement of K_2O in the ashes of those plants grown with $FeSO_4$ and, also, an increase of P_2O_5 and Fe_2O_3. (*b*) The increase of chlorophyll, albumenoids, and soluble carbohydrates in those crops grown with $FeSO_4$. (*c*) The increased yield and improved quality of crops grown by its aid?

These details have been confirmed by Muntz, Porion (the *confrère* of Dehérain), Delacharlonny, and others (*La Sucrerie Indigène et Coloniale*, vol. xxxi., p. 571).

Again, what about the germicidal properties of $FeSO_4$, its power for destroying *Peronospora infestans*, *wheat mildew*, *moss* in mossy pastures, &c.? These experiments have also been confirmed in France (*Journal de l'Agriculture*, Sept., 1887, and *Bulletin de la Société d'Horticulture de Soissons*, 1887).

I think it would be well for your correspondent to perform a few experiments on the subject before he criticises the work of others.—I am, &c.,

"X"

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. cviii., No. 13, April 1, 1889.

A Periodic Balance of Precision Admitting of the Direct Reading of the Ultimate Weight.—P. Curie.—This balance cannot be described without the accompanying figure.

The Law of the Solubility of Gases.—M. Woukoloff.—If carbon dioxide does not rigorously follow Dalton's law when it dissolves in carbon disulphide the deviations are very small, and of the same rank as those which it shows as regards the law of Mariotte. At low temperatures its absorption is greater and at high temperatures higher than the law demands.

On Succinamic Nitrile.—René Drouin.—This compound appears in the form of small colourless clinorhombic crystals, scarcely soluble in alcohol, even when hot, insoluble in ethyl ether, chloroform, essence of turpentine, benzene, petroleum, and carbon disulphide, decomposed slowly by cold water and more rapidly by hot water, with escape of ammonia.

Researches on the Alkaloids, Artificial and Natural.—Albert Colson.—The author describes the chlorostannite, the hydrochlorate, and the hexabromoderivative of a base, $C_{22}H_{18}N_2O_3$, and certain bromine derivatives of quinine.

Analysis of the Sewage of Paris.—M. Aymonnet.—The sewage in question was drawn at the outfall of the Clichy sewer. The author has merely determined the nitrogen transformed into ammonia by magnesia and boiling water (method of Boussingault and Schlœsing) and the total nitrogen less nitrates obtained by the Frankland and Armstrong process.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 1.

Separation of Alumina from Ferric Oxide.—Chancel.—From the *Comptes Rendus.*

Determination of Titanium in Iron and Iron Ores.—A. Ledebür (*Chemiker Zeitung*).

Qualitative Separation of Tin and Mercury.—Th. Wilm (*Journal Russ. Phys. Chem. Gesellsch*).—If a mixture of mercury chloride and tin tetrachloride is mixed with yellow ammonium sulphide the mercury remains chiefly in solution along with the tin, as a double compound of the two sulphides soluble in the ammonium polysulphides.

A Rapid Volumetric Method for the Determination of Boric Acid.—Hans Will.

Distinction between Tannin and Gallic Acid.—J. E. Saul.—From the *Pharmaceutical Joürnal.*

Detection of Acetanilide—A number of methods are given by Vulpius, Yvon, Della Cella, Arzen, and Flückiger.

Execution of the Dumas Nitrogen Process.—W. Hankô.—The author proposes a modified apparatus, which is here figured.

Determination of Tannin in Tan and Dye-wares.—The principal processes here described are those of H. R. Procter (*Journal of the Society of Chemical Industry*). Villon, noticed under *Bulletin de la Soc. Chimique de Paris*, and Collid and Benoist (Chemical News).

Detection of Saccharine in Beer.—A. H. Allen.—From the *Analyst.*

Detection of Fusel in Spirits.—E. Sell (*Kaeseil. Gesundheit's Amt.*).—The author's process is not described.

On Cacao Starch.—P. Saltsien (*Archiv der Pharmacie*).—The author shows that, contrary to the common opinion, cacao starch, when pure, gives the ordinary blue colour with iodine.

Adulteration of Tinned Tomatoes.—M. Carles.—From the *Journal de Pharmacie.*

Stability of Explosives on Exposure to Heat.—O. Hagen (*Repert. Anal. Chem.*).—No particulars are given.

Examination of Oil of Almonds.—G. Vulpius (*Archiv der Pharmacic*).—No particulars are given.

Further Test for Aloes.—Messrs. Cripps and Dymond.—From the *Pharmaceutical Journal.*

Reactions of Colours on the Fibre.—R. Lepetit.

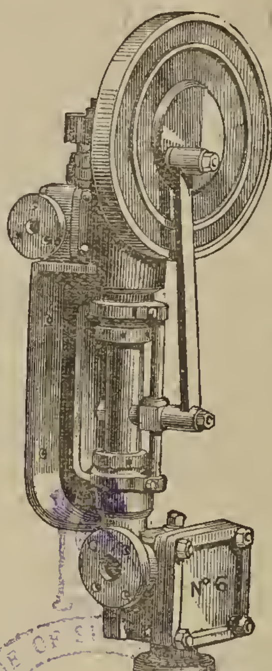
MISCELLANEOUS.

University of London.—We are requested to draw the attention of Candidates for Matriculation to the fact that the June Examination is, in the present and future years, to be held a week earlier than heretofore.

Detection of Resin (Colophonium).—Th. Morawski (*Chemiker Zeitung*).—The author founds a process on L. Storch's reaction for detecting resin-oil by means of acetic anhydride and sulphuric acid. A particle of the substance is dissolved in acetic anhydride at a gentle heat, the solution is cooled, and a drop of sulphuric acid (undiluted) is cautiously let flow down the side of the test-glass. In presence of resin, or resin-oil, there appears an intense red to violet-blue colour, which soon disappears, leaving the liquid brownish yellow and fluorescent.

MEETINGS FOR THE WEEK

Tuesday, 23rd.—Royal Medical and Chirurgical, 8.30.
Thursday, 25th.—Institute of Electrical Engineers, 8.
Friday, 26th.—Quekett Club, 8.



THE CHEMICAL NEWS.

Vol. LIX. No. 1535.

ON THE
CONVERSION OF SOME OF THE HOMOLOGUES OF BENZOL-PHENOL INTO PRIMARY AND SECONDARY AMINES.*

By RACHEL LLOYD.

(Continued from p. 188).

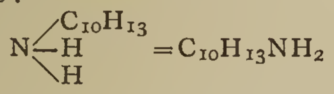
Thymol.

The object of the following research was the study of the action of zinc-ammonium bromide upon some of the phenols of a more complicated chemical structure. To this end thymol was selected as the starting-point.

The thymol used distilled at 230°.

The same proportions by weight of phenol, zinc-ammonium bromide, and ammonium bromide, 1 : 3 : 1, were used as in former experiments, the mixture was heated for forty hours, and the temperature raised to 350°—360°. The tube-contents presented distinctly marked layers. The upper layer, an amorphous mass of a dark brown colour, was intermingled with many lighter particles of an indistinct crystalline form. The under layer, a lighter coloured amorphous mass, was impregnated with a dark oily liquid. Water was formed in abundance. Pressure in tubes, very slight. The contents of the tubes were warmed with dilute hydrochloric acid, then with ether under return-condenser, and the bases separated according to previously described methods.

Thymylamine :—

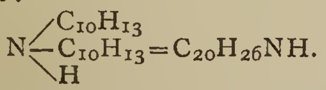


$$N\begin{cases}C_{10}H_{13}\\H\\H\end{cases}=C_{10}H_{13}NH_2$$

separated as a very light coloured oil, which, after two distillations, boiled constantly at 230°.

With sulphuric acid and potassium bichromate it gave the characteristic reaction; in the degree of its solubility in the ordinary solvents and in its compounds it showed its identity with the cymylamine obtained by Widman† from cuminol.

Dithymylamine :—



$$N\begin{cases}C_{10}H_{13}\\C_{10}H_{13}\\H\end{cases}=C_{20}H_{26}NH.$$

The impure secondary amine, a dark smeary mass of indistinct crystalline structure, was purified by repeated distillation with super-heated steam and fractionation in an atmosphere of hydrogen. The greater portion of the oil distilled between 340°—345°; while above 346° partial decomposition took place with evolution of yellow fumes.

The so-obtained almost colourless base, which was not solidified at −18° C., had a pleasant aromatic odour, gave with sulphuric acid a golden-brown colour with a tinge of red: slight fluorescence was noticeable. Nitric acid added to this solution changed the colour at once to dark blue, which remained unchanged. With a nitrite, a greenish blue tint was produced.

The presence of a secondary amine was confirmed by the analysis:—

I. 0·1355 grm. substance gave 0·4264 grm. carbon dioxide and 0·1138 grm. water, corresponding to 0·1163 grm. C. and 0·01264 grm. H.

II. 0·1255 grm. substance gave 6 c.c. moist nitrogen (thermometer 22° C., barometer 727 m.m.), equal to 0·006494 grm. N.

Calculated for $C_{20}H_{27}N$.				Found.
C_{20}	— 240 —	85·41 per cent	..	85·82 per cent
H_{27}	— 27 —	9·61 ,,	..	9·33 ,,
N	— 14 —	4·98 ,,	..	5·17 ,,
	281 —	100·00 per cent		

Accompanying these bases was unchanged thymol, which was isolated and weighed. Corresponding experiments were made with thymol and the chloride of zinc and ammonium. The results of repeated experiment are here given. The proportion of the substances used, as well as the time and temperature, were the same as when the bromides were used.

	Zinc-ammonium bromide.			Zinc-ammonium chloride.		
Thymol.	I.	II.	III.	I.	II.	III.
Thymylamine	25	21·5	29	23	24	22·6 p.c.
Dithymylamine ..	24	30	28·5	20	25	20·5 ,,
Unchanged thymol..	45	40	39	48	26	44·3 ,,
Carbonised substance	1	0·5	0·9	2	1·9	2·3 ,,

Derivatives of Thymylamine.

The platinum double salt—$(C_{10}H_{15}N.HCl)_2PtCl_4$—was prepared by dissolving the base in absolute alcohol, adding a small amount of hydrochloric acid, then an alcoholic solution of platinum chloride in excess. The double salt separated at once in the form of golden needles. These were re-crystallised from absolute alcohol. The crystals warmed with water were decomposed with separation of the base.

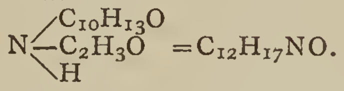
An analysis of the salt dried at 100°—110° gave the following result:—

I. 0·1736 grm. substance gave 0·0476 grm. platinum.

II. 0·6944 grm. substance gave 0·19040 grm. platinum.

Calculated for $(C_{10}H_{15}N.HCl)_2PtCl_4$.		Found. I.		Found. II.
27·48 per cent Pt.	..	27·41	..	27·42 per cent Pt.

Acetylthymylamine :—



$$N\begin{cases}C_{10}H_{13}O\\C_2H_3O\\H\end{cases}=C_{12}H_{17}NO.$$

The compound was formed by heating the base with an excess of acetic anhydride for half an hour at 100°. The solution, which at first was almost colourless, changed to a light brown; upon cooling, a greyish white crystalline mass separated, which was washed and neutralised with sodium carbonate and re-crystallised from absolute alcohol, in satiny white needles which melted at 112·5°, closely agreeing with the melting-point obtained by Widman.*

Derivatives of Dithymylamine.

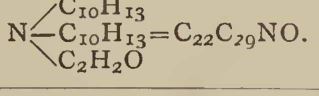
The *platinum double salt*—$(C_{20}H_{26}NH.HCl)_2PtCl_4$—was formed when, to an ether solution of the base acidified with hydrochloric acid, platinum chloride was added in excess. After standing for some days, a thick yellowish brown oil separated, which was thoroughly washed in cold alcohol (in which it was not soluble), dried over paraffin and sulphuric acid, and finally at 100°.

The analysis gave the following result:—

0·1630 grm. substance gave 0·03241 grm. platinum.

Calculated for $(C_{20}H_{26}NH.HCl)_2PtCl_4$.			Found.
20·01 per cent Pt.	..	..	19·88 per cent Pt.

Acetyldithymylamine :—



$$N\begin{cases}C_{10}H_{13}\\C_{10}H_{13}\\C_2H_2O\end{cases}=C_{22}C_{29}NO.$$

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[*] "University Studies, Published by the University of Nebraska," October, 1888.

[†] *Berichte der Deutschen chem. Gesellschaft*, xv., 166.

[*] *Berichte der Deutschen chem. Gesellschaft*, xv., 166.

This body was formed by heating together calculated amounts of the base and acetic anhydride at a temperature of 130°—135°. At the end of an hour the reaction was complete. The product, a yellowish white mass, was crystallised from benzol in white leaflets which melted at 78°, dissolved readily in hot benzol and ligroin, sparingly in alcohol.

An analysis gave the following result:—

0·1929 grm. substance gave 0·5760 grm. carbon dioxide and 0·1589 grm. water, corresponding to 0·15708 grm. C. and 0·1765 grm. H.

Calculated for $C_{22}H_{29}NO$.			Found.
C_{22}	264	81·73 per cent	81·43 per cent
H_{29}	29	8·98 ,,	9·15 ,,
N	14	4·34 ,,	— ,,
O	16	4·95 ,,	— ,,
	323	100·00 per cent	

(To be continued).

ON THE
ANALYSIS OF CINCHONAS,
AND ON THE
RELATIVE SOLUBILITY OF THEIR PROXIMATE PRINCIPLES IN WATER, ALCOHOL, AND DILUTE HYDROCHLORIC ACID.

By ED. LANDRIN.

The type of bark selected for the experiments was the *Cinchona succirubra*, derived from the plantations of the Dutch Government in Java. The author takes 300 grms. of the bark to be assayed and reduces it into powder sufficiently fine to pass through a No. 40 sieve. He prepares a milk of lime with 75 grms. caustic lime, adding 75 grms. of a solution of caustic soda at 40° B. and 1 litre of water. The bark is poured into this mixture so as to be homogeneous, and if it is too thick it may be diluted with a little water. The mixture of lime and soda is very important for liberating the total alkaloids of the cinchona. Since he has used this method his results do not vary by more than 1 part in 1000. He then pours upon the mixture 2 litres of oil of shale, which is raised to the temperature of 100° for twenty minutes, stirring the cinchona and the oil constantly so that all parts may come constantly in contact. The oil saturated with alkaloids is then decanted off, two more litres of oil are then added, and the operation is repeated exactly as before. We have then all the alkaloids of the bark in solution in the four litres of oil. The first treatment carries off, on an average, nine-tenths of the alkaloids. A third treatment with oil would be useless. The four litres of hot oil are then washed, at first with 75 c.c. of water acidulated with sulphuric acid at one-tenth, to which 150 c.c. of water have been added. This washing is continued for ten minutes, and then the acid liquid is poured off. The operation is repeated a second time with the same quantities of the same liquid, and a third time with a quantity one-half less. The two first acid liquids are poured together and neutralised with ammonia at a boiling heat in order to separate resinous matter. The same is done with the third acid liquid, which serves to wash the filter of the first operation. On cooling, the proportion of acid liquid with respect to the cinchona employed is such that the larger proportion of the alkaloid salts, on the mean nine-tenths, crystallise out. These sulphates are separated by filtration and the mother-liquors are precipitated with caustic soda. The alkaloids, drained, dried, and pressed, are taken up in a minimum of acidulated water, so as to transform them into sulphates without acidifying the liquid. The total sulphates are weighed and their separation is effected by known methods. It appeared that the sample of bark examined contained per kilo.—

Total alkaloids..	75·92 grms.
Crystalline salts	51·83 ,,
Quinine sulphate	21·27 ,,

The author finds that water extracts from cinchona bark the chief part of its active principles. Alcohol at 90° extracts from bark approximately the same quantity of alkaloids as water, but dilute hydrochloric acid, contrary to the general opinion, extracts less.—*Comptes Rendus* (vol. cviii., p. 750).

LONDON WATER SUPPLY.

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

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S.,
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 6th, 1889.

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 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 182 samples examined, two were recorded as "very slightly turbid." The remaining 180 samples were clean, bright, and well filtered.

During the month of March, the water furnished to the Metropolis by the seven Companies taking their supply from the Thames and the Lea, has continued to exhibit the wholly satisfactory character commented on in our last month's Report. The mean results afforded by the three different methods of examination employed, namely, the daily estimation of the degree of colour-tint of each Company's water, the daily estimation of the amount of oxygen absorbable from permanganate by each Company's water, and the weekly estimation of the proportion of organic carbon present in each Company's water—the three methods of examination acting as checks upon one another—are, in the case of all three methods respectively, as nearly as possible identical with the mean results afforded by the examination of the previous month's supply.

During the first three months of the year we have examined a total of 537 samples of the water supplied to the Metropolis by the above-mentioned Companies. Seven of these samples were recorded as exhibiting, under careful examination, a "very slight" degree of turbidity or deficiency in absolute clearness. The maximum proportion of organic carbon present in any single sample of water examined (early in January) was 0·197 part—the mean proportion in the Thames derived supply for the three months being 0·164 part—in 100,000 parts of the water. Since January, the maximum proportion of organic carbon present has not exceeded 0·175 part in 100,000 parts of the water. It is to be noted, moreover, that the above are the results afforded by examinations of the water supply conducted during an eminently unfavourable season of the year.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

THE CORROSION AND FOULING OF STEEL AND IRON SHIPS.*

By Professor V. B. LEWES, F.C.S., F.I.C.,
Royal Naval College Associate.

The difficulty of obtaining adequate experimental data, and the fact that nearly everyone who has worked at the subject has had a composition of his own to bring before the public, has so hampered and restrained the free discussion and interchange of ideas on this most important question, that at the present time we have made but scant progress beyond the point reached twenty years ago, and my object in bringing this paper before you is more to excite you to discussion, and to show you the known facts of the case, than to tell you of any very new or startling discoveries.

Corrosion generally precedes fouling on exposed metal surfaces, and it is therefore this portion of the subject that will be considered first, together with the means which have been taken to prevent it, and to protect the plates of our vessels from decay.

In a paper which I had the honour to bring before you two years ago, I pointed out that in all processes of rusting, carbonic acid gas and moisture played an important part, the iron uniting with the carbonic acid and oxygen of the water to form ferrous carbonate whilst the hydrogen was set free, and that the ferrous carbonate then took up oxygen dissolved in the water or present in the atmosphere, as the case may be, and was decomposed into ferric oxide (rust) and carbonic acid, which being liberated in actual contact with the moist surface of the iron, carried on the process of "rusting."

This view of the case was confirmed by a paper read by Professor Crum Brown before the Iron and Steel Institute, at Edinburgh, last autumn, and is generally accepted as the true explanation of the corrosion taking place on iron or steel surfaces exposed to moist air or fresh water; but the rusting of the metal in sea-water has by many chemists been ascribed to a more complex action, in which the salt present plays an important part by first forming oxychloride of iron.

This preliminary stage of corrosion in sea-water is, I am inclined to think, a myth. When iron filings or turnings are exposed to the action of sea-water, hydrogen gas is evolved, and ferrous oxide and carbonate are formed; and this changes, as in air or fresh water, into ferric oxide by taking up dissolved oxygen present in the water. At no time have I been able to detect the presence of oxychloride, and from the fact that a few drops of alkali added to the sea-water stop the corrosion, I am of opinion that the simple rusting of iron in sea-water is due to the same cause as in fresh—*i.e.*, the decomposition of the water by the iron in presence of carbonic acid.

The saline constituents of sea-water, however, do undoubtedly play an important part in a more active form of corrosion, by helping to excite galvanic action between the iron in the plates and any foreign metal or impurities present, an action which is also materially aided by want of homogeneity in the metal, by particles of rust, by mill scale, by wrought and cast-iron or steel in contact with each other; or even by the different amount of work, such as hammering or bending, undergone by different parts of the same plate; and in all of these cases the galvanic action set up causes rapid oxidation of the iron at the expense of the oxygen of the water, hydrogen being evolved.

We may therefore consider that on the skin of a ship two processes of rusting are going on, the one simple corrosion on exposed surfaces of the metal, due to the presence of moisture, carbonic acid, and free oxygen, which forms a fairly uniform coating of rust on the metal, and the more local corrosion due to galvanic action, which results in pitting and uneven eating away of the plates.

As I pointed out in my previous paper, rust cones are due to the most local form of galvanic action, caused by the presence of a spec of deposited copper, lead, or other foreign metal, or even a small particle of rust or mill scale left on the surface of the iron, and covered by the compositions used as protectives and antifoulers; as soon as the sea-water penetrates to these, galvanic action is set up, water is decomposed, rust formed, and the escaping hydrogen pushes up the composition, forming a blister, the hydrogen leaks out, and water leaks in, the action becoming becoming more and more rapid, and the blister gradually filling with the result of the action—rust. The blister bursts, but the cone of rust has by this time set fairly hard, and continues to grow from the base, the layers of rust being perfectly visible in a well-formed cone; and when the rust cone is detached, the pitting of the metal at the base of the cone is, as a rule, found to be of considerable depth.

The spec of foreign matter which has caused this destructive action generally clings to the surface of the iron, and being at the bottom of the pitting escapes detection and removal; and when the vessel, newly coated with fresh compositions, again goes to sea, the corrosion will again probably be set up in the same spot.

The corrosion of the plates in the interior of a vessel is a subject quite equal in importance to the external action of sea-water and dissolved gases on the metal; and from the fact that certain portions of the interior plates from their position escape the frequent examination and attention bestowed upon the exterior, it becomes a still greater source of danger.

Corrosion, like all other forms of chemical action, is much accelerated by increase of temperature; and in the bottom of a ship near the furnace-room and boilers, this has a considerable effect in increasing the rapidity of rusting. Also in the coal-bunkers, the mere contact of moist coal with the iron plates sets up galvanic action, carbon being electro-negative to iron, and the coal dust which sifts down into the double bottoms lends its aid to the destruction of the plates; whilst if the coal contains any "pyrites," which is nearly always the case, these doubles sulphides of iron and copper are gradually oxidised into soluble sulphates of the metals, and these, washing down into the bilge water, would at once cause most serious corrosion, should they come in contact with any bare portion of the plates. Repairs to any portion of the inside plates will loosen rust and mill scale, which, finding its way into the bottom, tends to set up galvanic action; whilst the scale of oxide of copper from copper and brass fittings and pipes is another great cause of danger, as the bilge water would gradually convert it into soluble salts, which will deposit their copper upon the iron wherever a crack or abrasion enables them to come in contact with it; and finally, leakages from stores and cargo are in many cases of a character highly injurious to iron.

In addition to all these sources of danger, we must remember that the interior of the vessel is the part most

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* Read at the Thirtieth Session of the Institution of Naval Architects, April 12th, 1889. The Right Hon. the Earl of Ravensworth, President, in the Chair.

iable to abrasion from shifting and moving of cargo, coals, &c.

The protection of the outsides of the bottoms of our ships from the destructive agencies of sea-water and dissolved gases may be said to have been attempted in two ways, by metallic and by non-metallic coatings.

So far, all attempts at metallic coatings have proved failures, and, as far as it is possible to judge, there is but small likelihood of their ever being made to succeed, because if zinc is used in order to protect the iron of the ship there must be galvanic action, and this action must take place evenly all over the surface of the iron plates, which means that the sheathing must be in uniform metallic contact with the iron, in which case the wasting of the sheathing would be so rapid that it would have to be renewed frequently, which, even leaving out the question of cost, is in many cases impossible.

Zinc is practically the only metal which could be used for this purpose, in order to place the plates of the ship in an electro-negative condition, and it is, therefore, to zinc that inventors have turned from time to time, the chief novelties introduced being the method of attachment. As far back as the year 1835, I believe Mr. Peacock tried zinc plates on the bottom of H.M.S. *Medea*, and in 1867 Mr. T. B. Daft again brought the subject forward: Sir Nathaniel Barnaby, Mr. McIntyre, and others, also suggesting various plans of attachment; whilst as late as last year Mr. C. F. Henwood read a paper at the United Service Institute, again strongly advocating zinc-sheathing as attached by his system.

Where the galvanic contact has been but small there the sheathing has had a certain life, but has afforded but little protection to the iron, and has gradually decayed away in a very uneven fashion; whilst in those cases where galvanic contact has been successfully made the ship has on several occasions returned from her voyage minus a considerable portion of the sheathing.

Another drawback to the use of zinc-sheathing is one which was found when it was used to coat wooden ships, and that is that zinc when in sheets, like every other metal, is by no means homogeneous, and that for this reason the action of sea-water upon it, leaving out of consideration galvanic action, is very unevenly carried on, the sheathing showing a strong tendency to be eaten away in patches, whilst the metal itself undergoes some physical change and rapidly becomes brittle.

Attempts have been made to galvanise the iron before the building of the ship; but Mr. Mallet showed as early as 1843 that this coating was useless when exposed to sea-water, as in from two to three months the whole of the zinc was converted into chloride and oxide, and that when, therefore, galvanising is used, care must be taken to protect the thin coating of zinc. This does not, of course, apply to fresh water, in which galvanised iron would answer very well, the rapid action being due to the salts in the sea-water; but even in this case the galvanising would have to be done after the plates had been riveted together, as any breaking of the surface would set up rapid wasting of the zinc, and it could, therefore, only be used on small craft.

Copper, tin, and lead have been proposed for coating ships, but these metals are electro-negative to iron, and would rapidly destroy the hull should any abrasion of the coating or damage to the insulating material take place.

The non-metallic coatings which are intended to do away with corrosion have been almost endless. At the present moment there are upwards of 30 in the market; whilst the patent list of the last 50 years contains an enormous number which were practically still-born.

They may be divided for convenience into—

(*a*). Oil paints.
(*b*). Pitch, asphalt, tar, or waxes.
(*c*). Varnishes, consisting of resins and gums dissolved in volatile solvents.
(*d*). Varnishes, containing substances to give them body.
(*e*). Coatings of cement.

And, before going into these in detail, it is necessary to consider the condition of the surfaces to which they will have to be applied, and the effect this will have upon them.

Air has the power of holding water vapour in suspension, the amount so held being regulated by the temperature; the higher the temperature the more can the air hold as vapour, whilst any cooling of the air saturated at the particular temperature causes a deposition of the surplus moisture. When a ship is scraped down to the bare iron in the dry dock, we have a huge surface of metal which varies in temperature much more rapidly than the surrounding air, and cools much more rapidly than the stone walls of the dock; as it cools so it chills the layer of air in immediate contact with it, and causes a deposition of the surplus moisture on its surface—a phenomenon known as the "sweating of iron"—and on to this moist surface the protective composition has to be painted. If now a rapidly drying varnish is put on, the rapid evaporation of the volatile solvent causes again another sudden fall of temperature — evaporation being always accompanied by loss of heat—and this fall of temperature again causes a deposition of moisture, this time on the surface of the protective, so that the coating is sandwiched between two layers of moisture, both of them probably acting deleteriously upon the resin or gum in the varnish, whilst the moisture on the iron also prevents adherence of the varnish to the metal. If, instead of a quick-drying varnish, the old-fashioned red lead and linseed oil protector had been used, the second deposition would not have taken place, but the sweating of the iron would have prevented cohesion, and, when dry, any rubbing of the coating would bring it off in strips.

The condition of the outer skin of a ship, when she is being coated with her protective composition, is one of the prime factors in the discrepancies found in the way in which compositions act. It being a very usual thing for a composition to give most satisfactory results on several occasions, and then, apparently under exactly similar circumstances, to utterly break down, and to refuse even to keep on. Too much stress cannot be laid upon the condition of the plates at the time of coating, and it is absolutely essential either to have a perfectly dry ship, or else a composition which is not affected by water.

When an old ship is broken up, you will often see on the backs of the plates the numbers which had been painted on them with white lead and linseed oil before the ship was built, and under the paint the iron in a perfect state of preservation, the secret being that the paint was put on while the plates were hot and dry.

Boiled linseed oil, mixed with red or white lead, is amongst the oldest of the protective compositions in use, but of late years has been but little employed, since it was proved by M. Jouvin, of the French Navy, and also in this country, that compounds of lead, when exposed by the wasting of the vehicle to the action of sea water are converted into chloride of lead, and this is rapidly acted on by the iron, depositing metallic lead and forming chloride of iron, the deposited lead carrying on the corrosion of the iron by rapid galvanic action. The drying of boiled linseed oil is due to the fact that it has in it a certain quantity of an organic compound of lead, and the drying properties are given to it by boiling it with litharge (oxide of lead), so that, even when red or white lead is not mixed with it, still lead compounds are present, and this action will go on to a lesser extent. When the boiled oil dries, it does so by absorbing oxygen from the air and becomes converted into a sort of resin, the acid properties of which also have a bad effect upon iron, so that protectives containing boiled oil are open to objection. Within the last two months a good example of the action of sea water on the botton of an iron ship, coated with red lead, has been afforded by H.M.S. *Nile*, which, after being painted over with coats of red lead, was allowed to remain for some months in Milford Haven, with the result that her bottom is very seriously corroded, and, on examination of specimens of rust taken from her, the crystals of metallic lead are in many cases easily identified.

If red lead is used, it can only form a ground-work for an anti-fouling composition which has to protect the red lead as well as the iron of the ship from the action of sea water, and when the anti-fouling composition perishes then serious corrosion must ensue.

The second class of protectives, consisting of tar and tar products, such as pitch, black varnish, and also asphalt and mineral waxes, are amongst the best protectives, the waxes especially not being affected by the sweating of the plates, and forming admirable coatings for the plates. Certain precautions, however, must be taken in the case of tar and tar products, both of which are liable to contain small quantities of acid and of ammonia salts; but if care be taken to eliminate these, and if it could be managed to apply this class of protectives hot to warm plates, the question of protection would be practically solved, bituminous and asphaltic substances forming an enamel on the surface of the iron which is free from the objections to be raised against all other protectives, that is, that being microscopically porous they are pervious to sea water.

The third class of protectives consists of varnishes formed by dissolving gums or resins in volatile solvents, such as spirit, turpentine, naphtha, fusel oil, &c., and such varnishes are open to several objections—in the first place, they are acted upon by moisture, which causes a deposition of the resins or gums as a non-coherent powder, and destroys the tenacity of the varnish. The amount of action which moisture has on such a spirit-varnish depends to a considerable extent upon the proportion of resin or gum to spirit, when the solvent is present in large quantities, and the resin in comparatively small; then the moisture has apparently little action; but it must be remembered that the drying of such protectives means the rapid evaporation of the solvent and concentration of the resin or gum, whilst the rapid volatilisation which is going on cools the hull of the ship, and causes deposition of moisture on the drying varnish with most disastrous results.

Another point which must be borne in mind is that no such varnish is impervious to gases and liquids. We are apt to think of a coating of varnish as being perfectly homogeneous; but, on examining it through a microscope, it is seen to be full of minute capillary tubes, which become gradually enlarged by the action of water, and finally result in the destruction of the varnish, whilst moisture and dissolved gases find their way to the metal and carry on corrosion. The application of several coats of varnish tends to diminish this evil, as in many cases the holes in the first coat will not correspond with the holes in the second, and so each succeeding coat will tend to make the protective more and more impervious. In using such varnishes, they must only be applied in favourable weather, and must be allowed to thoroughly harden before being brought in contact with the water.

In the fourth class we have varnishes of this kind to which body has been given by the addition of foreign constituents, generally mineral oxides; and this class is far preferable to the last, if the solvent used is not too rapid in its evaporation, and if care has been taken to select substances which do not themselves act injuriously upon iron or upon the gums or resins which are to bind them together, and are also free from any impurities which could do so.

At present the favourite substance used to give colour and body to such varnishes is the red oxide of iron, the colour of which effectually cloaks any rusting which may be going on under it. In using the red oxide for this purpose care should be taken that it contains no free sulphuric acid or soluble sulphates, as these are common impurities, and are extremely injurious, tending to greatly increase the rate of corrosion. The finest coloured oxides are, as a rule, the worst offenders in this respect, as they are made by heating green vitriol (sulphate of iron), and in most cases the whole of the sulphuric acid is not driven off as the heat necessary impairs the colour; this acid is often neutralised by washing the oxide with dilute soda solution, but very little trouble, as a rule, is taken to wash it free from the resulting sulphate of soda, which is left in the oxide.

A sample of exceptionally good colour intended for using in protective compositions was sent me a few weeks ago for analysis, and proved to contain no less than 15·3 per cent of sulphate of soda.

The best form of oxide of iron to use for this purpose is obtained by calcining a good specimen of hæmatite iron ore at a high temperature. When prepared in this way it contains no sulphates, but from 8 to 40 per cent of clay; if the percentage does not, however, exceed 12 to 18 per cent it is perfectly harmless.

Composition manufacturers can easily test their red oxide for themselves, to see if it contains soluble sulphates, by warming a little of it with pure water, filtering through blotting-paper, and adding to the clear solution a few drops of pure hydrochloric acid, and a little solution of chloride of barium (easily obtained at any druggist's). If a white sediment forms in the solution the sample should be rejected.

In a previous paper on the corrosion and protection of iron and steel ships, I pointed out that when such a varnish perished, the oxide of iron being left in contact with the iron plates, increased the corrosion going on at the surface of the metal, all oxides being electro-negative to the metals from which they are produced, and on that occasion I advocated the use of finely divided metallic metallic zinc, which can be obtained as an impalpable powder, in place of the oxide of iron, pointing out that such a composition would last as long as any varnish of this class, and that, when the varnish perished, as it must do after long exposure to sea water, then the metallic zinc would, on coming in contact with the iron, set up galvanic action; but that, instead of being electro-negative, as in the case of the oxide of iron, and causing corrosion of the plates, it would be electro-positive, and in consequence would protect them, being itself slowly oxidised, and so would give a fresh period of protection.

I hoped at the time that I had made it perfectly clear that the zinc would in no way act until both the anti-fouling and protective varnish had perished, and had become spongy and porous, and that the idea was a prolongation of the period of protection, the great point which has now to be aimed at; but the remarks made afterwards in several journals which were kind enough to notice my paper showed me that they had mistaken my intention, and supposed that the zinc was put in to at once create galvanic action, and predicted that if by any chance it did act, the hydrogen generated would blow the composition into blisters, and defeat its own purpose. I need hardly point out that nothing was farther from my intention, as zinc in fine powder would be acted on more rapidly than the dense metal in plates, and I have already pointed out that this is destroyed too rapidly by galvanic action to render it of practical use as a protective *per se.*

As to the hydrogen blowing off the composition, no gas could be generated until both the anti-fouling and protective coatings had been perished and rendered perfectly porous by the action of the sea water, a condition which would have permitted the free escape of the generated hydrogen, which, it must be remembered, will permeate through openings which other gases cannot pass through.

(To be continued).

The Use of Saccharine.—Ph. de Clermont.—The author recommends saccharine as an addition to chocolates, &c., intended for diabetic patients.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 28th, 1889.

Mr. William Crookes, F.R.S., President, in the Chair.

The President delivered an address, of which the following is an abstract:—

The number of fellows of the Society is 1650, of whom 36 are honorary foreign members; at the same period last year there were 1571 Fellows, of whom 37 were honorary foreign members.

140 Fellows have been elected during the year.

23 Fellows have died during the year:—Professor Brazier, R. Cartmell, John Collins, J. J. Coleman, Professor H. Debray (Foreign Member), W. F. Donkin, H. C. Foote, Peter Griess, A. N. Gow, John Horsley, J. M. Kavanagh, J. D. Perrins, Dr. David Price, F. G. Ree, J. Robinson, W. O. Senior, J. Storey, James Taylor, J. S. Topham, Thomas Ward, Dr. W. Wallace, G. J. Wishart, John Williams.

16 Fellows have withdrawn.

21 Fellows have been removed on account of arrears.

In the year 1888 there were 75 original papers published in the *Transactions*, occupying 895 pages, compared with 88 papers of 871 pages in 1887. The Abstracts in 1888 occupy 1351 pages, compared with 1159 in 1887. The number of Abstracts is 2470 compared with 2277 in 1887.

103 papers have been communicated to the Society this session.

The Library continues to increase, and every year is becoming richer in rare volumes and books of reference. The duplicate library for lending is also becoming increasingly useful. The following Table shows the present state of the shelves:—

	March 31st, 1888.	Addition in 1888-89.	Present state.
Volumes of systematic works	2780	142	2922
Volumes of journals ..	5119	355[*]	5474
Volumes of duplicate journals for circulation	941	143[†]	1084
Pamphlets	1410	16	1426
	10,250	656	10,906

The expenditure under this head for the current year is £308 5*s*. 6*d*.

I must now ask your attention to an event of which none of you can be ignorant, which, though not exclusively relating to chemistry, bears closely upon it and upon the future of British Science. I refer to the protest against the examination system in education which appeared in November last. That protest had long been in the air. For years past men who take the trouble to observe and to reflect have come to the conclusion that competitive examination is injurious to the individual, injurious to the race, and that it starves original research at the very root. They have convinced themselves that if we flag in scientific investigation, that if a large and increasing proportion of professorships and of leading positions in industrial establishments, both in the home kingdom and in the colonies, are filled by aliens, the fault lies mainly with our educational system. Men trained chiefly to pass examinations either in theoretical or practical departments cannot equal those who have been schooled in actual research, trained to accurately observe and draw correct inferences from facts. All the earlier protests were desultory, and calculated to produce no lasting impression; but the recent manifesto is the expression of the collective opinion of many earnest representative men and women. Hence it cannot be slighted as the mere outcry of a faction, a sect, a school, or an interest.

A most satisfactory feature is the adhesion to the protest of men who formerly were in favour of competitive examination as the test for entrance into the civil or military service of the State. Prof. Max Müller, of Oxford, frankly admits he now considers competition to be a mistake, and avers that the failure springs not only from the manner in which the system has been worked, but is involved in its very nature. But if this protest is to avail it must be energetically followed up, for I must repeat what I have before declared that the position of science in Britian is far from satisfactory.

Though the number of articles devoted to research in German transactions and journals exceeds those in our own publications, we must remember that the population of the German empire is greater than that of the United Kingdom by at least one-fourth; further, that the *savants* of Russia, of the Austrian empire, of Switzerland, of Holland, and Scandinavia largely select German journals as their medium of publication. Not a few English and American scientific men follow the same course. Hence, as regards quantity, our share in the world's scientific work is more considerable than appears at the first glance. Further, I think that if deficient in quantity English research excels in quality. If we do less detail work we furnish a larger proportion of generalisations and laws than most of our rivals. As the discoverers of laws and generalisations, Black, Boyle, Dalton, Faraday, Graham, Joule, Newton, Wollaston, and Young are household words in the laboratory—yet none of these men were the products of the examination system.

There is another evil against which I must strongly protest. I refer to the system of "sealed papers." Every one knows that on the Continent, more especially in France, it is common for anyone who has, as he thinks, approached the solution of some important question, to deposit a sealed sketch of his incomplete results with the president or secretary of some learned society. The sketch may lie *perdu* for years, until the author requests it may be opened and read before the Society. The practice arose from a desire that the author's priority should be guaranteed against others who might lay claim to his ideas. But priority can be quite as effectually secured by a brief preliminary notice read before some society or sent to some journal, the author thus reserving to himself the further investigation of the subject. Among men of honour such reservations are invariably respected. But the "sealed paper" system lends itself to something which borders unpleasantly upon fraud.

Suppose an investigator takes up some question, sees that it admits of two or more solutions, or that various hypotheses present themselves to him as possible. To work out the matter conclusively might require much time and trouble. He therefore writes out each hypothesis and incloses them separately in "sealed papers" duly numbered, carefully retaining copies. In process of time some other investigator, ignorant of what the first author has done, takes up the subject and works out one of these hypotheses to demonstration. So soon as his supplementary memoir is before the world the first investigator requests that the "sealed paper" No. 2 or No. 3 be opened and read. The new theory, laboriously considered and worked out, is found to have been anticipated, and the man who has really done the work is robbed of much of his credit. The seeming anticipator says nothing about the contents of other "sealed papers," in which he has proposed totally different hypotheses; these he now leaves to oblivion.

I think the Fellows of our Society will agree with me that a system which thus enables a man to reap the fruit

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[*] Including 170 vols. *Dingler's Polytechnisches Journal.*

[†] Including 95 vols. *Dingler's Polytechnisches Journal.*

of another man's experiments does not deserve to be naturalised in England.

There is a further abuse to which attention may usefully be drawn. It sometimes happens a man of science will send an account of researches he has completed to two journals simultaneously, English or foreign, leaving each editor under the impression that he is the sole recipient of the communication. Or, still worse, a man reads a paper before our Society and sends it to some foreign journal, so that it may figure in print before it appears in the Society's *Transactions*.

To this subject I felt compelled to refer when I had the honour of addressing you last year. And you are now aware, your council declines to publish any memoir which has previously appeared in a foreign journal unless specially recommended by the Publication Committee and approved by the Council. The reasons for this resolution are not hard to seek. Not merely is the reputation of the Society, as the original channel of the researches in question, imperilled, or at least obscured, but a serious waste of time and labour is inflicted upon any one who needs to read up the literature of the subject. We, in England, are by no means the only sinners in this respect. It often happens that memoirs which have been read before the Paris Academy of Sciences reappear as "original matter" in certain French journals.

I cannot pass over a discovery made this season by Prof. Krüss concerning nickel and cobalt. As at first reported it seemed that these two metals might be eliminated from our text-books and that two or three new substances would take their place. Had this been the case it would undoubtedly have been one of the greatest steps in pure chemistry taken this century. It now appears that each of the two metals contains a common impurity which Prof. Krüss has been the first to detect and isolate. Nickel and cobalt thus purified will still retain their individuality, though their accepted properties, physical and chemical, will need careful revision.

In any case the discovery is most instructive, warning us how careful we should be to have firm ground under our feet. It is almost humiliating that two metals which have been subjected to infinite research and scrutiny should now be found to contain such a proportion of unsuspected impurity.

You are aware that at the ballots for the election of Fellows half an hour or more of valuable time is thus spent in a manner which, to say the least, is not very interesting. An attempt has been made to save time by taking the ballot in the library, after the meeting, but so many Fellows leave before the end of the meeting that the number remaining has not been found sufficient to meet the requirement of the bye-laws. Your Council have from time to time had this matter under discussion, and at their last meeting, on the 21st inst, it was resolved "that in future the balloting for Fellows be conducted by means of papers." The best manner of carrying out this resolution will be a subject for future arrangement.

A posthumous memoir on the compressibility of hydrogen, by the late Prof. Wroblewski, reminds us of the sad and untimely death of this meritorious and distinguished worker in physical chemistry. His death, as most of us doubtless are aware, was due to the frightful burns which he received from the overturning or explosion of a paraffin lamp. In the memoir in question Prof. Wroblewski treats of the compressibility of hydrogen at 99°, at 0°, at −103·5° (boiling-point of ethylen), and at −182·4° (boiling-point of oxygen) for pressures ranging from 1 to 70 atmospheres. From the results the following data were calculated:—Critical temperature −240°; critical pressure 13·3 atmospheres; critical volume 0·00335. Hence it appears very doubtful whether M. Pictet or M. Cailletet really succeeded in liquefying hydrogen.

Last year I had the pleasure to announce that one of our Fellows, Mr. Newlands, had received the "Davy Medal" of the Royal Society for his splendid discovery of the Periodic Law of the Chemical Elements. I may also be allowed to state that to me, your President, the Royal Society has likewise awarded the same distinction for my Researches on the Behaviour of Substances under the influence of the Electric Discharge in a High Vacuum, with especial reference to their Spectroscopic Reactions.

Hence it has been suggested that I might not unprofitably claim your attention this evening for a History of the so-called Rare Earth, as they have been brought to light and discriminated by the aid of the Spectroscope.

[The continuation of the Address will be inserted *in extenso* in a future number of the CHEMICAL NEWS.]

Professor DEWAR proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed; Dr. GLADSTONE seconded the motion, which was carried by acclamation. The PRESIDENT briefly responded.

Dr. RUSSELL, the Treasurer, then gave an account of the financial position of the Society. The receipts by admission fees and subscriptions had been £3402; by sale of Journal, £365 3*s.* 3*d.*; and by dividends on invested capital, £344 4*s.* 3*d.* The expenses on account of the Journal had been £2350 5*s.* 11*d.*; on account of the Abstracts of Proceedings, £164 4*s.* 7*d.*; on account of the Library, £308 5*s.* 6*d.*; the total expenditure being £3429 18*s.* 3*d.* £500 had been invested in Metropolitan Board of Works 3½ per cent stock, and the balance in hand was £1833 10*s.* 6*d.*, the balance at the corresponding period last year having been £1672 19*s.* 3*d.*

Professor THORPE moved that the thanks of the Society be tendered to the Treasurer for his services during the past session; Dr. PERKIN seconded the motion. Dr. RUSSELL, after replying, proposed a vote of thanks to the auditors, Messrs. R. H. Davies, Friswell, and Rideal; this was seconded by Dr. P. F. FRANKLAND, and acknowledged by Mr. FRISWELL.

Mr. J. NEWLANDS proposed a vote of thanks to the Officers and Council, which was seconded by Dr. J. VOELCKER, and acknowledged by Dr. ARMSTRONG.

Professor CLOWES moved that the thanks of the Fellows be tendered to the Editors, Abstractors, and Librarian for their important services during the year. Dr. COLLIE seconded the motion. Mr. GROVES and Dr. THORNE replied.

Messrs. Foster and E. W. Voelcker having been appointed Scrutators, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session:—

President—W. J. Russell, Ph.D., F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; Warren de la Rue, D.C.L., F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—G. Carey Foster, F.R.S.; J. W. Mallet, M.D., F.R.S.; H. McLeod, F.R.S.; Ludwig Mond; J. Emerson Reynolds, M.D., F.R.S.; Robert Warington, F.R.S.

Secretaries—H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary—F. R. Japp, LL.D., F.R.S.

Treasurer—T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council—Norman Collie, Ph.D.; A. H. Church; Frank Clowes, D.Sc.; Wyndham Dunstan; John Ferguson, M.A.; Charles W. Heaton; E. Kinch; H. F. Morley, M.A.; F. J. M. Page; S. U. Pickering, M.A.; R. T. Plimpton, Ph.D.; Thomas Purdie, B.Sc.

April 4th, 1889.

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

Mr. Alexander Hill was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. William Waters Butler, Crown Brewery, Birmingham; Francis Ransom, Hitchin.

The following were elected Fellows of the Society:—Messrs. John Leigh Hoskyns Abrahall; James Aunal; Richard Douglas Bailey; T. D. Collis Barry; Frederick William Boam; Harry Broadbent; Edward Barnwell Cook; Francis Edward John Cridland; Alexander Archie Cunningham; Thomas Hill Easterfield; Joseph T. Freestone; William Frew; James Hall; Richard Ashworth Hoyle; Henry Richardson Hoyles; Herbert Ingle; Clement Joseph Leaper; George Cannon McMurtry; Christopher J. McNally, M.D.; James Bruce Miller; William Beattie Nesbitt, B.A.; George Thos. Wilkinson Newsholme; John Charles Platts; Charles Proctor; Arthur Avery Read; Ernest Reckitt; Duncan Taylor Richards; Richard Wrightwick Roberts; Thomas Alexander Shegog; Henry Simmonds; John William Slater; Henry Charles Anslie Vine; Walter Arthur Voss; William John Waterhouse; Patrick Alexander Wier, M.B.; John Tsawoo White; Charles Wood; Mortimor Woolf.

The following papers were read:—

33. "*The Rate of Dissolution of Metals in Acids.*" By V. H. Veley.

When the rate of evolution of a gas is taken as the measure of the amount of interaction between metals and acids, the result is due to a variety of causes, each one of which is variable at any moment of time, and its peculiar effect not susceptible of mathematical analysis. Among the varying conditions are the surface of the metal exposed, the local rise of temperature, the rate of diffusion of the metallic salt formed in the acid liquid, and the rate of its removal by the gas-bubbles. In the present research metallic spheres, by various mechanical devices, were rolled about continuously and regularly within the acid liquid, and the products of the changes continuously removed from the immediate neighbourhood of the metal. The dissolution of copper in a solution of potassium bichromate acidified with sulphuric acid was investigated as affording a case in which no gas is evolved as such. The dependence of this action on the conditions of (i.) temperature, (ii.) proportion of sulphuric acid, and (iii.) proportion of potassium bichromate, is illustrated by various series of experiments.

(i.) As regards temperature, it is shown that if this be varied between 21° and 41° in an arithmetical proportion, the amount of chemical action varies in a geometrical proportion: in this respect the change is perfectly analogous to several others quite different from it and from one another. Attention is drawn to this relation as common to a number of chemical changes, and to the causes on which it is probably dependent. (ii.) On varying the amounts of sulphuric acid in an arithmetical proportion within the limits of 41·3 and 23·5 grms. per litre, the amount of change also varies in an arithmetical proportion. (iii.) The amount of change is at first considerably increased by increase of proportion of potassium bichromate, but the effect gradually diminishes almost to *nil*, at which point the bichromate can be considered as so much inert material; the amounts used varied from 22·1 to 66·3 grms. per litre.

34. "*Note on the Interaction of Metals and Acids.*" By Henry E. Armstrong.

When a metal forming an element in a voltaic couple is dissolved, the rate of dissolution is in accordance with Ohm's law, $C = E/R$: and this should apply also to the case in which a metal is dissolved without any precaution being taken to arrange it as an element of a couple, as the action is conditioned by the formation of, and takes place within, "local circuits." The changes attending the dissolution of metals may, therefore, in a certain sense, be said to be purely electrical in the first instance; yet, within recent years, it has been argued by various chemists that the phenomena are only in part electrical and in part chemical—whatever this may mean. The author discusses the various phases of such changes, and criticises the conclusions arrived at by Spring and Aubel and others.

Discussion.

Referring to Mr. Veley's experiments, Dr. Armstrong expressed the opinion that the results were in no way commensurate with the labour expended in obtaining them; although by introducing bichromate polarisation by hydrogen had been prevented, its use had introduced complications which made the analysis of the results impossible; in fact, the information likely to be obtained from such experiments was not of the kind required in the present state of chemical science. Thus, the proof obtained that a copper sphere dissolved uniformly in a mixture of sulphuric acid and bichromate was but a proof of the efficiency of the stirring apparatus: such would necessarily be the case, as the values of E and R remained almost unchanged throughout the experiment, owing to the relatively small proportion of the agents used up.

Mr. Veley, in the course of a reply in which he attempted to justify his position, mentioned that he had had occasion to verify Dr. Russell's observation that silver is not dissolved by nitric acid, to which reference had been made, and stated that in experiments with copper and nitric acid he had observed that the action took place at first more slowly, and only attained a maximum rate when a certain small amount of nitrate was formed.

Dr. Armstrong remarked that this was a really important observation, proving that the dissolution of copper in nitric acid was dependent on the presence of a third substance—perhaps cupric nitrate. The discovery of the exact conditions which determine any particular chemical change is at the present time of great importance, and investigations establishing these were much required; it was useless, however, to study cases in which complications instead of simplifications were introduced, as even the changes which apparently were of the simplest kind, were probably but the end results of more or less complex series of successive or simultaneous changes.

35. "*A Zinc Mineral from a Blast-Furnace.*" By J. Tudor Cundall.

The author has examined a mineral found in cavities of the wall of a blast furnace at Mostyn, in North Wales; it crystallises in white to yellow translucent tufts, of the relative density 5·60. Analysis gave results which show that it is impure zinc oxide:—

	ZnO.	Pb.	S.	SiO_2.	FeO.
I.	97·96	1·02	0·39	0·61	0·39
II.	98·97	0·95	0·10	trace	trace

It was examined crystallographically by Mr. A. Hutchinson, who found that the crystals belong to the rhomboidal system, and exhibit combinations of the hexagonal prism and pyramids with the basal plane; two new forms were also noted, viz., the rhombohedron $r\{100\}$ and the hexagonal pyramid $h\{21, 13, 17\}$.

Faraday Lecture.

The Faraday Lecture will be delivered on June 4, by Professor Mendeleeff, in the Theatre of the Royal Institution. The Fellows of the Society will entertain the Faraday Lecturer at a dinner at the Holborn Restaurant on the following evening.

PHYSICAL SOCIETY.

April 13, 1889.

Prof. Reinold, F.R.S., President, in the chair.

Messrs. J. E. Dowson, W. M. Mordey, E. A. O'Keefe, C. Priest, A. Siemens, and W. B. Willans, were elected members.

Mr. Shelford Bidwell, F.R.S., showed "*A Lecture Experiment Illustrating the Effect of Heat on the Magnetic Susceptibility of Nickel,*" and "*An Experiment Showing an Effect of Light on Magnetism.*"

In the first experiment a piece of nickel was attached to one side of a copper pendulum bob, which was held out of the vertical by bringing the nickel in contact with a fixed magnet. On placing a spirit-lamp flame below the nickel the bob was (after a short time) released, and oscillated until the nickel had cooled, when it was again attracted and the operation repeated itself.

The second experiment had been recently shown before the Royal Society. One end of an iron bar, which had been magnetised and then de-magnetised, was placed near a magnetometer needle. On directing a beam of light on the bar an immediate deflection of the needle resulted, and on cutting off the light the needle promptly returned to near its initial position. The direction of magnetisation induced by the light is the same as the previous magnetisation, and the bar seems to be in an unstable magnetic state. That the effect is due to light and not heat the author thinks is rendered probable by the suddenness of the action.

The President said he had tried the experiment himself, and failed to get any effect, but after seeing the arrangement of apparatus used he believed his non-success due to the comparatively great distance between his bar and needle.

A Member asked if the results were different for different coloured rays, and

Prof. S. P. Thompson enquired whether the magnitude of the effect varied with the intensity of illumination, as in selenium, and also if any change was produced by altering the direction of vibration of the incident light.

Mr. G. M. Whipple wished to know whether any difference was produced by blackening the bars, and, as bearing somewhat on the same subject, mentioned an induction magnetometer in which an iron bar used was demagnetised by plunging in hot water. The results obtained were very irregular after the first magnetisation, and this may have been due to the instability shown to exist by Mr. Bidwell's experiment.

In reply, Mr. Bidwell said red light produces most effect and blackening the bar makes the action much slower. As regards selenium the character of the effect is similar, but he believes the causes to be different. Polarised light produces no change. In answer to Prof. Herschel he said that any part of the bar is sensitive to light, and showed that illuminating both sides of the bar increased the effect.

Mr. G. M. Whipple read a "*Note on the Dark Flash Seen in Some Lightning Photographs.*"

After expressing his dissent from the explanations offered in the report of the Lightning Flash Committee of the Meteorological Society and Prof. Stokes respecting "Ribbon Lightning" and "Dark Flashes," the author described some experiments he had made on the subject. Ribbon lightning he conceives to be an effect produced by taking the photographs through windows, and to test this lines on a blackboard were photographed: 1st, direct; 2nd, through good plate-glass placed obliquely; and 3rd, through window-glass; the result being that double, triple, and ribbon flashes were closely imitated. As regards "Dark Flashes," the author believes the appearance due to the prints being taken in oblique light, and to be produced by successive reflection from the reduced silver forming the dark line on the negative and the upper surface of the glass of the negative.

Prof. Perry suggested that this might be easily proved by examining a negative the prints from which show the dark flash.

Mr. Baily pointed out that if the explanation given was correct the dark one should be parallel to the bright one, and this he understood was not always the case.

Mr. Boys remarked that one dark flash exhibited minute wriggles not seen in the bright one, and

Mr. C. V. Burton thought these might be due to irregularities in the upper surface of the negative.

Dr. Gladstone said he was not satisfied with Prof. Stokes's nitrous oxide explanation, but thought the phenomena may be due to some kind of reversion. He also mentioned that a negative might probably be obtained from Mr. Shephard, of Westbourne Grove.

As regards "Multiple Flashes," Mr. Boys said he had often seen seven or eight flashes traverse the same path in rapid succession.

On the motion of the President the discussion was adjourned until next meeting, when Mr. Whipple hopes to exhibit the negative referred to, together with photographs of his experimental dark flashes.

"*On Quartz as an Insulator.*" By Mr. C. V. Boys, F.R.S.

In making quartz fibres the author observed that the ends of fibres broken during the shooting process coiled up into screws and projected themselves against anything brought in their vicinity. After a short time they released themselves and sprang back to their original position. This could be repeated indefinitely, and the only explanation he could think of was that the fibres were electrified. If so, then to exhibit such phenomena the insulating properties of quartz must be very great, and experiments were shown to demonstrate this deduction. A small pair of charged gold leaves were suspended from a short quartz rod in a moistened atmosphere, and the deflection fell one-fourth the original amount in about five hours. A clean glass rod under the same conditions would discharge the leaves in a few seconds. Dipping the quartz into water did not seem to diminish its insulating properties, and ordinary chemicals produce no permanent prejudicial effect. The author considers that quartz will be very useful in electrostatic apparatus, for the troublesome sulphuric acid may be dispensed with.

"*On a Refraction Goniometer.*" By Mr. A. P. Trotter

The goniometer, which was designed when determining the figure of a refracting surface to effect a special distribution of light, is practically a movable four-bar linkwork representing the figure given in Deschanal, p. 924; two of the bars are parallel to the incident and emergent rays, and the other two normals to the faces of the prism. By its means the angle of a prism to produce a given deviation, when the index of refraction and angle of incidence are known, can be readily found. A series of curves expressing the relation between incidence and deviation for prisms of various angles were shown, and the same curves show the minimum deviation and limiting angle for prisms of all angles represented. The author thinks the instrument will be useful in physical laboratories for adjusting optical apparatus and for the calculation of lighthouse and other polyzonal lenses, Fresnel prisms, &c.

Prof. Herschel said he found a wooden model, illustrating the relations between the angles of incidence and refraction very useful in teaching, and

Mr. Blakesley sketched an arrangement of links and cords devised for the same purpose.

Mr. Boys considered that all such relations were best on a slide rule.

"*A Note on Apparatus to Illustrate Crystal Forms,*" by Prof. R. J. Anderson, was read by Prof. Perry.

The apparatus is constructed of cords, pulleys, and weights, arranged to produce the required figure when in equilibrium. By increasing or decreasing some of the weights the corresponding axes of the crystal forms can be lengthened or shortened, and the passage from one system to another effected. In one arrangement the forces may be divided or united, and the pulleys are carried by rings capable of rotating on different axes. By this apparatus the various conditions are said to be beautifully illustrated, and methods of deriving the oblique from the rectangular systems are shown in photographs which accompany the paper.

NOTICES OF BOOKS.

The Principles of Empirical or Inductive Logic. By John Venn, D.Sc., F.R.S., Fellow and Lecturer in the Moral Sciences, Gonville and Caius College, Cambridge. London: Macmillan and Co.

The work before us, though approximating to the "System of Logic" of John Stuart Mill, differs from it so decidedly, and in many points so advantageously, that it will not be regarded as an *Ilias post Homerum.* Attention must first be called to the introduction of the term "empirical" into the title. By this the author, as he tells us, wishes to "emphasize his belief that no ultimate objective, certainly such as Mill, *e.g.*, seemed to attribute to the results of induction, is attainable by any exercise of the human reason." Dr. Venn aims at being constructive rather than critical, but his treatise will be unavoidably compared with that of Mill, already referred to. It will, we think, be seen that he possesses a mind more imbued with the spirit of scientific inquiry than was that of his predecessor. This statement will doubtless surprise some of our readers. But on careful examination we shall find that Mill was not a man of Science. His own training had been exclusively classical and literary, and to the last he sought to uphold the predominance of literature in education. No man of Science could ever have penned his well-known outbreak against the influence of heredity in the genesis of character.

Like several of his predecessors, Dr. Venn discriminates very closely between Science and Art. As he puts it:—"By Science may be understood a coherent and methodical body of generalisations about matters of fact; by Art, a similar body of rules for securing some end or class of ends. The former deals with what is; with what exists in great part irrespective of our wishes. The latter deals rather with what ought to be, or with what is wished for; wished for, it may be, by the speculator or by others as represented and interpreted by him." We fear, however, that here Dr. Venn will have lost his labour, and we refer to his opinion more in the hope of showing that so judicious a thinker adheres to the protest against the popular abuse of the terms Science and its paronyms, than in any hope of widely influencing the British public.

As inductive methods the author accepts with certain reservations the four processes recognised by Mill, viz., the methods of difference, of concomitant variations, of agreement, and of the joint method of agreement and difference, or, as he more happily calls it, the method of exclusions. Concerning the method of difference, he remarks that it is a means rather of verification than of discovery. He points out, too, the great practical difficulty in its application, that of being certain that no other antecedent save those we have taken into consideration has slipped in. This point requires care, even in physical and chemical inquiries. In biology the method becomes one of grave difficulty, and in social science it is scarcely manageable at all. Another precaution which he justly insists upon is that the step of omitting or inserting some one antecedent shall not involve any collateral effects.

The method of concomitant variations turns, of course, on the partial exclusion of some antecedent which cannot be entirely eliminated. Some of the instances here given of the unsatisfactory character of this method cannot be considered fair. They prove merely its limited applicability. The partial closing of a polluted drain could not be expected to throw any light upon the question whether such drain were a main factor in producing a local epidemic. The method of agreement Dr. Venn considers as merely suggesting the directions for experiment. The method of exclusions deals with cases in which the supposed cause and effect are both absent, and on this, where available, a great weight is laid. The author, however, emphasizes the consideration that the four inductive methods just discussed involve no appreciation of quantity. "Accurate measurement, in fact, forms the essence of true science." If this proposition is correct biology and psychology are not true sciences, and to beings possessing merely human faculties scarcely ever can become so. Who can say whether there then is more or less life in a child than in an adult, in a polype than in an eagle? To such questions diametrically opposite answers, both alike incapable of demonstration, might be given and maintained with profuse inkshed. Considerations relating to measurement have been, it is here pointed out, omitted by Mill and discussed at great length by Jevons.

The chapter on the data of geometry is very instructive. The author does not admit, with Mill, that lines and planes are not mere boundaries, but a something almost approaching material entities, formed by gradually "fining down" a thin sheet of paper or a spider's thread.

Explanation and verification are treated as steps towards the methodisation and establishment of our knowledge of Nature. It is pointed out that a certain satisfaction is reached by the mere taking a fact out of its isolated condition and including it under some general head. This chapter is one of the most valuable in the whole work, and deserves very careful study.

Passing over the section on a universal or perfect language, we come to a chapter on the extensions of our general powers of observation, especially by aiding or intensifying the powers of our own organs, such as in the case of sight, is effected by means of the microscope. Quoting Hooke, he calls attention to the improvement of smell, which is certainly of far greater value than hearing in our inquiries into Nature. What an advance would ensue, both in our chemistry and our biology, if we could gain olfactory powers equal to those of the bee and the wasp, which accept beet-root sugar only as a *pis aller* in the absence of cane-sugar, and which reject Fahlberg's saccharin as an insulting simulacrum!

The work before us must be accepted as preferable to Mill's in every respect save one, *i.e.*, the character of the illustrative examples. Concrete instances would be far more readily grasped than symbolic ones, such as that of the bells ringing in different rooms, A, B, C, D, &c.

Electro-Deposition: A Practical Treatise on the Electrolysis of Gold, Silver, Copper, Nickel, and other Metals and Alloys, with Descriptions of Voltaic Batteries, Magneto- and Dynamo-Electric Machines, Thermopiles, and of the Materials and Processes used in Every Department of the Art, and Several Chapters on Electro-Metallurgy. With numerous Illustrations. Third Edition, Revised, Corrected, and Enlarged. London: Crosby Lockwood and Son.

The number of persons who practise the electro-deposition of metals in the widest sense of the term falls scarcely below those who concern themselves with photography. In addition to thousands of amateurs there are a multitude of manufacturers who have occasion to make use of the art on a more or less extensive scale in the course of their business. And as Mr. Watts's work is undoubtedly the best modern treatise on the subject in the English language we need feel little surprise that the second edition (1886) has been already succeeded by a third.

A very severe critic might take objection to the use of the term "electrolysis" on the title-page. Everyone can understand the electrolysis, *i.e.*, the decomposition by electric action, of the salts or alloys of gold, silver, &c. But the electrolysis of the metals themselves would be indeed a novelty.

We find here three chapters on electro-metallurgy, an art confounded by many persons with electro-deposition, but which the author correctly defines as the extraction, separation, and refining metals from ores by electric action. Among its many and multiplying operations we find here an account of the Cowles electric smelting process as now applied in the production of aluminium and its alloys. It is mentioned that at the Cowles Company's works at Stoke-upon-Trent a dynamo having a guaranteed capacity of 402,000 volts is about to be put down. He suggests that our government might do well to employ aluminium-bronze for heavy artillery. Its tensile strength is to that of steel as tensile strengths of 100,000 and 130,000, as against steel plates 81,000 and cast-steel 63,000.

The most important additions to this edition are compressed in an appendix, and include methods for depositing platinum, aluminium and its alloys, and cobalt; the removal of the tin from waste tinned iron, &c. A section on poisoning includes, of course, merely those substances with which the electro-depositor is likely to form unpleasant acquaintance in his labours. The author mentions that he once "inadvertently swallowed a quantity of old gold solution, which he had placed in a tea-cup for experimental purposes, in mistake for some coffee without milk which it was his custom to drink when at work in his laboratory." We cannot help calling this a most imprudent custom. No liquid should ever be consumed in laboratories, colour-shops, or other rooms in chemical manufactories, dye and print-works, &c. We have observed very serious accidents result from the neglect of this caution.

The table of atomic weights is not free from error, as that of platinum is still given as higher than gold.

There is a useful bibliography of works on electro-deposition, and the index is commendably copious.

CORRESPONDENCE.

ESTIMATION OF COBALT AND NICKEL.

To the Editor of the Chemical News.

Sir,—Referring to the paper "On Cobalt and Nickel Peroxides and on the Volumetric Determination of these Metals," translated from the *Comptes Rendus* into the Chemical News (lix., p. 183), the author, A. Carnot, is evidently unaware that English investigators have preceded him in his subject, and whose results are not wholly in harmony with his. It would not be inferred, for instance, from Bayley's work "On the Higher Oxides of Nickel and Cobalt" (Chemical News, vol. xxxiv., p. 81), that Fleischer's process could, by any practical modification, be adapted to the accurate volumetric estimation of nickel: yet, according to M. Carnot, nickel peroxide precipitated with potash and bromine is of stable and definite composition, and representable by the formula Ni_2O_3. Now Bayley shows—and I have in part corroborated his work (Chem. News, vol. lvi., p. 27)—that nickel peroxide obtained as above may, according to the proportion of chlorine or bromine, the temperature of precipitation, and length of time of subsequent boiling, if any, have any proportion of oxygen from Ni_3O_4 to Ni_3O_5.

To touch on one more of M. Carnot's statements:—"The brown oxide obtained on precipitating cobalt by oxygenated water and potassa at a boil presents the exact composition of a sesquioxide, Co_2O_3." I have not the slightest doubt that the author is in error on this point. Scores of careful experiments have satisfied me that the formula $Co_{13}O_{19}$ is nearer the truth, and that, again, only so far that as a basis for the volumetric estimation of cobalt, the results may differ by four per cent of the quantity of cobalt taken.—I am, &c.,

Norman McCulloch.

Laboratory, Clyde Iron Works
(by Tolcross), Glasgow,
April 22, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Journal de Pharmacie et de Chemie.
Vol. xix., No. 7.

Assay of Smoking Opium (Chandoo).—M. Lalande.—The author finds that the ordinary procedures used for the determination of morphine should be modified for the examination of chandoo. He weighs out 10 grms. chandoo, 4 grms. slaked lime, and mixes them intimately with 100 c.c. of distilled water. He stirs the mixture from time to time and filters after the lapse of an hour. He receives 64 c.c. of the filtrate in a round wide-mouthed stoppered flask, adding 1 grm. ammonium chloride and 10 c.c. of washed ether. The flask is stoppered, carefully shaken to dissolve the salt, and the bases precipitated at the outset, and the whole is set aside for four days. The ether is then decanted, renewed, decanted afresh with a Robiquet's apparatus, and the liquid is filtered through a filter without folds. The crystals, carefully detached from the sides of the flask, are triturated with 20 c.c. of water, which serve for washing the filter, then with 20 c.c. of alcohol at 30 per cent, by means of which they are collected upon the filter. They are dried, washed with 20 c.c. of chloroform in four applications, dried at 100°, and weighed. The weight is the morphine in 6 grms. of chaudoo.

New Process for Detecting the Presence of Foreign Colouring-matters in Wines.—A. Pagnoul.—The author uses as a reagent the standard soap-liquid used in determining the hardness of waters. Of this liquid 5 c.c. are placed in a small test-tube with an equal volume of distilled water. From 10 to 20 drops of the wine in question are added and the whole is mixed by inverting the tube. With a natural wine the liquid remains colourless, but it is coloured if some foreign colouring-matter is present.

Bulletin de la Société Chimique de Paris.
Vol. i., (Ser. 3), No. 6. March 20th 1889.

The Development of Chlorine during the Decomposition of Chlorates by Heat.—W. Spring and E. Prost.—The authors have submitted to the action of heat the chlorates of K, Na, Ba, Al, Ag, Cu, Zn, Pb, and Hg, heating them in boats of platinum or porcelain firstly alone, moist or dry, then in contact with carbonic, silicic, and phosphoric anhydrides and phosphoric acid. In each case the manner of heating has been modified, being either abrupt or gradual, and lastly, currents of dry air have been let circulate slowly or rapidly. The proportion of chlorine evolved varies much with the nature of the chlorate and with the conditions of the experiment. It is larger in case of the chlorates of feeble bases and in presence of an anhydride capable of forming a salt with the base of the chlorate. If we also take account of the notable augmentation of chlorine when the heat is abrupt we are led to think that the chlorine disappears from among the gaseous products only if it has time to react with the base which has been set at liberty for an instant at least. These facts seem to be explained if the production of oxygen is not an immediate but an indirect result of the decomposition of the chlorates. These salts are split up at first, like the carbonates and nitrates, into a base and an anhydride. The chloric anhydride is then decomposed in turn into oxygen and chlorine, which latter reacts upon the base. These facts seem to show that if the salts are not actually formed by the juxtaposition of bases and anhydrides these tend to reappear when the molecule is split up under the influence of heat.

The Trivalence of Aluminium, and on a New Compound of this Metal.—Alphonse Combes.—The author seeks to show that the compounds of aluminium have the general formula AlR_3. The novel aluminium compound is the acetylacetonate, $Al(C_5H_7O_2)_3$.

Colouring-matters derived from the Tetrabenzylic Ether of Benzidine.—Albert Colson.—M. Colson describes the isolation of the dibenzylic ether of hydroquinone and the formation of the nitro-derivative. If this substance is reduced by zinc in an alkaline solution it gives a yellow compound, fusible at 140°, and a small quantity of a base soluble in alcohol, which, in contact with dilute hydrochloric acid, deposits the hydrochlorate of a benzidine which takes a red colour in the air. This benzidine, if transformed into a tetrazo-derivative, combines in the cold with salicylic acid, sulphonaphthol, and other phenols, yielding colouring-matters which combine direct with cotton in an alkaline bath. But these colours have not the brightness of the dyes obtained with the tetramethylic or tetraethylic ether of benzidine.

The Danger of Using White Lead in Lace.—Ph. de Clermont.—The author mentions that certain kinds of lace ("Point d'Angleterre") are got up with lead carbonate to an extent calculated to injure the health of the wearers, and to be completely spoiled on contact with any gas or vapour containing sulphuretted hydrogen.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 1.

The Degree of Accuracy of the Tests for Silver.—H. Rossler.—For the particulars of these two papers the reader is referred to the *Zeitschrift fur Angewandte Chemie.*

Systematic Procedure for Examining Quinine Sulphate on Hydrochlorate.—C. Hielbig.—This paper will be inserted in detail as early as possible.

Determination of Resin Oils in Mineral Oils.—H. Demski and Th. Morawski.—The authors reject the methods of E. Valenta (optical dextro-rotatory power, high iodine values, and solubility in glacial acetic acid) as not suitable for quantitative determinations. They find that in American and Gallician oils an admixture with resin oil exceeding 35 per cent may be detected by the complete miscibility of the sample with acetone. In Wallachian and Caucasian oils this phenomenon does not occur with less than 50 per cent of resin oil.

Bunsen's Determination of Urea, with Reference to the Nitrogenous Extractive Matters, and to the Salts of Ammonium.—K. Bohland.—The author proposes a modification of the improvement on the Bunsen process as suggested by himself and Pflüger.

Detection of Indican in Urine by Means of Chloroform and Chloride of Lime.—L. Renault (*Archiv der Pharmacie*).—In presence of iodides the reaction may be masked, but, in such cases, a subsequent addition of sodium thiosulphate converts the iodine into hydriodic acid and allows the colour of the indigo to be distinguished.

The Application of the Furfurol Reactions for the Detection of Biliary Acids and Carbohydrates in Animal Fluids.—This memoir does not admit of useful abstraction.

Determination of Albumen in Urine.—Ch. Lecerf (*Archiv der Pharmacie*) boils 50 c.c. of the sample with sodium sulphate and acetic acid, and determines nitrogen in the precipitate by Kjeldahl's process. He calculates the albumen by multiplying the nitrogen by 6·24.

Examination of Flesh for Caustic Alkalies.—Vitali.—The author digests the masses under examination with eight volumes of absolute alcohol, and washes out the residue with alcohol. A small quantity of the alkaline liquid is tested for caustic alkali with mercurous chloride.

Detection of Oxalic Acid in Cases of Poisoning.—D. Vitali (*Annali di Chimica*).—Absolute alcohol extracts part of the acid out of a mixture of flesh and oxalic acid. It may then be precipitated as ammonium oxalate by adding ammonia. This deposit is dissolved in water, precipitated with lead acetate, the precipitate of lead oxalate is decomposed by sulphuretted hydrogen, and free oxalic acid is crystallised out of the solution.

A Conspectus of the Ptomaines and Leukomaines at Present Known.—The reader is referred to the *Pharm. Central Halle* (29, 336).

Reactions of Physostigmine (Eserine).—W. Eber (*Pharm. Zeitung*).—The most sensitive reactions are with gold chloride (reduction), and potassium-bismuth iodide, and potassium-zinc iodide, the latter of which indicates 0·000001 grm. of physostigmine. Platinum chloride does *not* give a precipitate.

The Atomic Weight of Silicon.—T. E. Thorpe and J. W. Young.—From the *Journal of the Chemical Society.*

MEETINGS FOR THE WEEK

Monday, 29th.—Medical, 8.30.
Tuesday, 30th.—Royal Institution, 3. "The Italian Renaissance Painters; their Associations," by Jean Paul Richter.
— Society of Arts, 8. "The Northern Waterway to Siberia," by Capt. Wiggins.
— Institute of Civil Engineers, 8.
Wednesday, May 1st.—Society of Arts, 8. "Secondary Batteries," by W. H. Preece, F.R.S.
— Royal Institution, 1,30. Annual Meeting.
Thursday, 2nd.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Science of Locomotion in its relation to Design in Art (illustrated by the Zoopraxiscope," by Eadweard Muybridge.
— Sanitary Institute, 8. "Rural Epidemics, by Dr. Bushell Anningson.
— Chemical, 8. "Thiophosphonyl Fluoride," by Prof. Thorpe, F.R.S., and Mr. Hambly. "The Boiling-point of Potassium and Sodium," by G. P. Penman, B.Sc.
Friday, 3rd.—Royal Institution, 9. "On Aluminium," by Sir Henry Roscoe, F.R.S.
— Society of Arts, 8. "The Karun as a Trade Route," by Major-Gen. Sir R. Murdoch Smith.
— Geologists' Association, 8.
Saturday, 4th.—Royal Institution, 3. "The Origin and Development of Opera in England," by Joseph Bennett.

THE CHEMICAL NEWS.

Vol. LIX. No. 1536.

EXAMINATION OF FEED WATER FOR STEAM-BOILERS.

By THOMAS T. P. BRUCE WARREN.

Although water used for any special industry may require peculiar methods of treatment to render the same better adapted for certain manufactures, the same latitude cannot be extended to a boiler-supply. In this case the main points to be provided for are the prevention of scale and corrosion. Scale, resulting from carbonates of lime and magnesia, may be guarded against by the ordinary process of softening by means of lime. Sulphate of lime cannot be removed in the same way, but by using caustic soda and lime together its removal may be made complete. Corrosion arises from the liberation of hydrochloric acid from magnesium chloride, and is quite as serious as scaling. Magnesium chloride may not exist as such in the water, but we cannot be sure that by heating a soluble magnesian salt with a soluble chloride in a steam-boiler we do not bring about a reaction which results in its formation.

Great stress is laid on the hardness of water, but it seems to me that if the excessive hardness of water is due to freely soluble salts of lime and magnesia which cannot result in scaling or corrosion, we are scarcely justified in condemning it as a boiler supply, where we have not the choice of a supply of a purer type of water, unless at a great cost.

Assuming that we have a water yielding a large total, in the way of soluble solids, free from magnesium chloride and calcium sulphate, it would be interesting to know what is the extra consumption of fuel required to hold a large quantity of soluble substances in solution. I am not aware that this subject has been considered by any writer on water analysis, whilst to a manufacturer, the capacity for heat of his boiler supply when concentrated by the evolution of steam, is of paramount importance. We know that concentrated saline solutions have a boiling-point considerably over 100° C.; the temperature of the escaping steam is 100° C. Admitting the principle of the conservation of energy, there must be a consumption of heat which is not refunded in the dynamical form of work by the engine. No doubt this is a simple problem in chemical physics; the mere fact of a substance dissolving absorbs energy, and the recrystallisation again absorbs energy. It does not follow that the total energy in each case is additive, but in striking a balance as to the consumption of fuel, we can hardly come to the conclusion that we entail no loss. The higher the temperature is above that required for solution the less is the loss of heat relatively, but on cooling down we probably cannot recover the total energy given out by the coal in burning.

In examining a water for steam boilers, the temporary hardness is of great importance, as it furnishes us with the data for roughly calculating how much lime is required to take up the carbonic acid, so as to render the carbonates of lime and magnesia insoluble. According to Prof. Frankland, one ounce of lime to 700 gallons of water for each degree of hardness will, *approximately*, do all that the lime economically can perform. It is perfectly true that lime will precipitate many salts of magnesia, but it is tedious and troublesome to deal with in practice. It is better to do this by means of sodic hydrate or carbonate; the hydrate may be used with the lime at one operation; the carbonate, if used, should be added after the lime has well acted upon the water. We may thus make sure of removing magnesium chloride. The water residue is carefully heated in a platinum dish to 127° to 130° C., covered with a watch glass which has been moistened with a little acidified nitrate silver solution, which will become rapidly turbid if any hydrochloric acid is given off. More soda is to be added to the water, until no turbidity is detected.

The estimation of the chlorides may be made in the ordinary way with the hard or softened water. A measured quantity of the water is evaporated to dryness, and the residuum heated to 127°—130° C. for some time; the residuum is dissolved, and the chlorine again estimated. The loss of chlorine will show that magnesium chloride has not been totally removed. If the chlorides of lime and magnesia have been removed the dry residuum will be considerably less hygroscopic.

It is an important matter to be able to find out readily how much lime or soda has been added in excess. A measured quantity of the softened water is coloured with a few drops of solution of phenolphthalein; the hard water is then run in until the colour barely vanishes; the free carbonic acid is taken up so long as lime or soda is in excess, and consequently does not mislead in the colour reaction.

ON THE INFLUENCE OF COPPER UPON THE DETERMINATION OF IRON IN FERRO-ALLOYS.

By T. W. HOGG.

The ease and rapidity with which most iron alloys are decomposed by dilute hydrochloric or sulphuric acid and then oxidised by means of a standard solution of bichromate of potash, render such a method for the direct determination of iron of considerable technical importance, and it is well known that as a general rule the results so obtained are fairly accurate.

As our standard text-books do not caution the operator against any occasional source of error it is very important to remember that when examining strange alloys, if any of them should contain copper, the results obtained by the above method become quite erroneous. When such an alloy is decomposed by the dilute acid the whole of the copper remains behind in the metallic state and does not pass into the solution, as might be supposed. It is now that the accuracy of the process begins to be seriously interfered with, for as soon as the standard solution of bichromate is added and there is present iron in the ferric state, then the finely-divided copper gradually reduces this back to the ferrous condition; the iron determination will thus come out too high, and the extent of the error will depend upon the quantity of copper present and the rapidity with which the titration has been conducted.

That the error so introduced may sometimes be a serious one will at once be evident when it is remembered that there are many published analyses of spiegeleisen showing considerable quantities of copper, and I have myself in one case found as much as 0·65 per cent. I have also met with several specimens of foreign tool and casting steels and other special iron alloys containing large quantities of copper, in some cases occurring as an impurity and in others no doubt added intentionally.

It has also been pointed out that the direct determination of iron in spiegeleisen is influenced by the unexpelled hydrocarbons (Riley, *Proc. Chem. Soc.*, vol. ii., 1877), an objection which will obviously apply to most of the iron alloys.

Small quantities of organic matter or copper do not interfere with the results obtained by the following method:—

A weighed portion of the alloy is dissolved in dilute hydrochloric acid, a slight excess of potassic chlorate is now added, and the liquid well boiled to expel the chlorine compounds. By this treatment the small quantity of organic matter is decomposed, and the copper passes into the solution. The iron is now reduced by means of a solution of sodium sulphite, and after the excess of sulphurous acid has been expelled by boiling, the standard solution of bichromate is added in the usual manner.

Newburn Steel Works,
near Newcastle-on-Tyne.

THE SEPARATION OF COBALT AND NICKEL AFTER OXIDATION IN AN AMMONIACAL LIQUID.

By ADOLPHE CARNOT.

The problem of the separation of cobalt and nickel has been the subject of many researches. Among the methods proposed the author refers only to those which depend on the differences of the properties of the two metals when they have been submitted to peroxidation in an ammoniacal solution.

Such a process was proposed by M. Terreil (*Comptes Rendus*, lxii., p. 139, 1866). After boiling with permanganate in slight excess the solution is acidified with hydrochloric acid. On cooling a sparingly soluble purpureo-cobaltic chloride is deposited, but a portion of the cobalt escapes precipitation. The process is not available in analysis, but it may serve for the preparation of cobalt salts perfectly free from nickel.

M. Delvaux (*Comptes Rendus*, xcii., p. 723, 1876) also proposes to peroxidise with permanganate and to precipitate the nickel from the ammoniacal solution by caustic potassa. The bulk of the cobalt remains in solution, but an important quantity is found in the precipitate with the nickel and manganese oxides. Even after a second repetition it is too important to be neglected.

M. Vortmann (*Monatshefte für Chemie*, vol. iv., p. 1, 1883) takes as oxidising agent hypochlorite of soda, and heats the ammoniacal solution for some minutes to transform the cobalt salt into purpureo-cobaltic and luteo-cobaltic salts. After cooling and an addition of pure water he precipitates nickel monoxide with an excess of potassa. The ammonio-cobaltic salt gives the liquid a red colour if there is an appreciable quantity or yellow if there are merely traces. This method gives very distinct indications for qualitative research, but it has not apparently been used for quantitative separations.

The author has studied the effects of bromine and of oxygenated water upon cobalt salts in presence of ammoniacal salts, and sought if the use of the reagents could furnish an effective means of separating the two metals.

For the use of bromine the metallic solution must be cold and acid or contain ammonium chloride. There takes place a brisk escape of gaseous bubbles, and the solution turns to a rose colour if it contains cobalt alone, but violet if nickel also is present. A roseo-cobaltic salt is formed.

Oxygenated water may be added either before or after supersaturation with ammonia. In the cold it produces at first a brown colour, which in a few minutes turns to a purple-red or a rose according as there is more or less cobalt, but to a violet-rose if the proportion of nickel is considerable. In heat the same change takes place in a few moments. But it is in the cold that the colouration should be observed, for if the blue tint of nickel remains on heating that of cobalt diminishes much in intensity, and may even cease to become appreciable to the eye. These points constitute good qualitative characteristics for cobalt.

The ammoniacal solution may be heated and kept for some time at 100° without losing its limpidity, but ultimately it turns reddish brown and becomes turbid. The cobalt is in the state of a purpureo-cobaltic salt in the purple liquid, and it is converted into a luteo-cobaltic salt if the boiling is continued. The final decomposition gives rise to a deposit of cobalt sesquioxide, but this deposit is incomplete and contains nickel. Hence this process cannot be used for the separation of the two metals.

The addition of caustic potassa to the cold liquid determines the complete precipitation of the nickel as monoxide, provided there is a sufficient excess of potassa, depending on the quantities of ammonium chloride and of free ammonia. A pure solution of the purpureo-cobaltic salt gives no precipitate under the same conditions. In a mixture of the two salts there is produced a greenish deposit which we might believe composed exclusively of nickel, but when it is received on the filter it is easily seen to be of a darker green, and if treated with very dilute nitric acid it leaves a yellowish brown, and the solution is tinged of a yellowish rose or brownish by a little of the cobalt salt. If we dissolve the precipitate entirely and repeat the same operations we obtain a rose liquid and a green deposit which still contains a small quantity of cobalt. A third operation leaves merely an imponderable quantity of cobalt. We may therefore thus determine nickel in the precipitate by converting it into peroxide or sulphide in order to free it from alkalies. As for the cobalt, it is obtained entirely either by boiling the alkaline solution, which leaves a light brown deposit of cobalt sesquioxide, or by precipitating the black sulphide with a current of sulphuretted hydrogen or with ammonium sulphide.

The author has attempted in vain to obtain at once a precipitate of nickel free from cobalt, both by varying the state of combination of the latter metal, by effecting the peroxidation in heat, or by heating the ammoniacal solution for a longer or shorter time with hypochlorite, bromine, or oxygenated water. The best results have been obtained by leaving the solution for a few moments at 100°, cooling, adding much water, and then pouring in a solution of potassa. But they have never been quite satisfactory at the first precipitation, the operation having to be repeated twice more. Still the method may be recommended, because it has the great advantage of showing clearly the presence of the cobalt by the rose colouration of the liquid as long as any traces of it remain.

In the course of these researches the author has repeatedly observed that on dissolving in hydrochloric acid the precipitate produced by potassa and then treating the liquid with oxygenated water and ammonia there remained a slight brown precipitate, which, on furthur submission to the same treatment, turned to a rose. It seemed to present some novel reactions, and the author thought he had met with the new metal the discovery of which has been announced by MM. Krüss and Schmidt. On closer examination the precipitate was found composed of alumina with small quantities of iron, cobalt, and nickel.—*Comptes Rendus*, vol. cviii., p. 741.

LECTURE EXPERIMENTS WITH NITRIC ACID.*

By PETER T. AUSTEN.

Nitric acid, when in the state of a gas, makes an admirable subject for lecture experiments. A number of experiments with the liquid form are given in Heumann† and other books on experimental chemistry, but the following experiments with the gaseous form I have not been able to find described. A flask can be filled with nitric acid gas by placing in it some strong pure nitric acid and

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* Communications from the Chemical Laboratory of Rutgers College. From the *American Chemical Journal*, March, 1889.

† "Anleitung zum Experimentiren," p. 125.

boiling. This operation, however, takes some little time and is not always satisfactory, as the flask at first becomes filled with a mist. The better plan is to pour into a quart flask having a neck wide enough to admit a deflagration spoon, some commercial concentrated sulphuric acid in sufficient amount to cover the bottom of the flask about half an inch, and add to it ten to twenty grms. of potassium nitrate. The potassium salt is better than the sodium salt, as it is less liable to contain nitrites, which will discolour the gas by the liberation of N_2O_3. The nitrate should be added in the form of crystals of about one-quarter of an inch in size. If added in a powdered condition, the mass cakes, and requires considerable shaking to disintegrate it. The coarser kind behaves admirably, and on heating the mixture the gas is liberated quickly and evenly.

The flask is hung free on a stand and a small naked flame applied. The nitric acid gas is liberated in large amounts, and expels the air at once. This operation should be done under a hood, although, by regulating the heat carefully, it is easily possible to fill the flask and yet not drive off enough gas to cause discomfort. If the filling is done under a hood, the flask and stand are placed, when needed, on a lecture-table; heat, sufficient to prevent the condensation of the gas, being kept under the flask. The sulphuric acid solution on the bottom of the flask is practically invisible, and does not in any way interfere with the experiments.

Nitric acid acts in all of these experiments, except the last, as an oxidising agent, viz:—

$$2HNO_3 = H_2O + N_2O_4 + O.$$

It will therefore serve as a source of oxygen, and its reduction will be indicated by the formation of the red N_2O_4. The strong colour of this gas makes some of the experiments very striking. In fact, several of them are worthy of performance in the regular lecture course. The temperature of the gas lies between 90°—100°. To get the full effect of the phenomena, the experiments should be performed in a partially darkened room, which, while permitting the details of the experiments to be observed, makes the combustions appear more brilliant.

Candle.—A lighted candle continues to burn, giving a brilliant flame surrounded by a large pale halo. The peroxide, N_2O_4, as in all of these experiments, forms at first in a large halo about the flame, and eventually fills the flask. As this phenomenon occurs in every case, it will not be mentioned again. Owing to the heat of the gas, the candle melts rapidly. The dropping wax soon sets up an action with the mixture of sulphuric and nitric acids on the bottom of the flask. The experiment should be stopped before this begins.

Wood.—An ignited splinter of wood (a splinter fastened to an iron wire is best) burns energetically. A spark bursts into flame as in oxygen.

Charcoal burns brilliantly. If bark-charcoal is used, the scintillations in the red gas produce an unusually fine effect.

Steel Watch-spring.—The spring should be not over 1½ m.m. wide, and should be detempered. By winding sulphur-string about the end, igniting and introducing quickly, the steel soon ignites and continues to burn brilliantly, but with an effect quite different from the combustion in oxygen. In this case it is well to put a layer of sand half an inch deep in the flask to prevent fracture of the bottom by the falling globules of fused iron.

Phosphorus burns with an intensely bright light as in oxygen. It soon volatilises and fills the flask with flame. Here again the tinging of the light by the red peroxide, N_2O_4, produces a peculiar effect.

Sodium takes fire without preliminary heating, and burns with an intense yellow light. A small piece and a deep spoon should be used so as to avoid any chance of the melted sodium falling into the sulphuric acid, as such an occurrence is dangerous.

Magnesium when ignited burns with its characteristic white light.

Copper, zinc, and antimony I have been unable to make burn.

Illuminating Gas.—A flame of gas, issuing from a bent-up glass tip, when inserted, continues to burn with a brilliant white centre surrounded by a large red halo. At first the flame becomes musical, degenerates into a series of rapid slight explosions, and is extinguished. The tone varies with the size of the flame. After a certain amount of peroxide, N_2O_4, is formed, the flame is not extinguished, and the musical tone also soon ceases.

Hydrogen sulphide burns with a bright yellow flame. The flask becomes filled with thick vapours—probably a cloud of chamber-crystals arising from the action of the sulphur dioxide and water (which result from the combustion of the hydrogen sulphide) on the nitrogen tetroxide.

Hydrogen burns with an intensely white flame resembling the flame of illuminating gas just described. It does not become musical.

Caoutchouc.—A piece of black rubber tube, introduced in a deflagration-spoon, soon fuses and evolves gas, which ignites and burns with a large flame having a bright core and a pale halo. It the caoutchouc is ignited in the air, it burns with a white smoky flame. When now introduced, the flame entirely loses its luminosity and becomes as described.

Turpentine boils violently and emits white fumes, which soon ignite with a gentle explosion and burn with a luminous flame.

Carbon disulphide does not ignite spontaneously, but when ignited and introduced it continues to burn energetically. It soon volatilises and fills the whole flask with flame.

Benzene does not ignite spontaneously, but when ignited and introduced it burns quietly with a white flame.

Ether evaporates and reduces the nitric acid gas to the tetroxide, N_2O_4. When ignited and introduced it soon volatilises and fills the flask with luminous flame.

Hydrochloric Acid Gas.—A stream of the gas issuing from a turned-up tip did not react, nor could the gas be ignited by applying a flame at the point of mixture between the gases. Heating the tube through which the hydrochloric acid was delivered also failed to effect a decomposition.

Hydrobromic acid gas could not be made to react, although a slight decomposition occurred.

Hydriodic acid gas could not be made to ignite. On passing it into the nitric acid gas, however, decomposition and liberation of iodine gas took place. It is a difficult matter to regulate the evolution of hydriodic acid, so that my failure may have been caused by the irregularity of the pressure. Hofmann* has shown that drops of hot fuming nitric acid falling through an atmosphere of hydriodic acid produce a large red flame and deposition of iodine crystals. I shall make another attempt to ignite the gas, using a different form of apparatus.

Ammonia.—This experiment requires a little skill, but is not difficult. Ammonia is evolved in a six-ounce flask by heating a mixture of ammonium chloride, slaked lime, and water. The flask is clamped to a stand and heated with a small flame. The stop-cock to this burner must be accessible without leaving the experiment, for by it is controlled the evolution of the ammonia gas. The success of the experiment depends on getting the right-sized jet of ammonia gas. The ammonia gas is led into the nitric acid gas by means of a glass jet, the tip of which turns up. This jet is connected with the evolution flask by a sufficiently long rubber tube. The orifice of the jet should not be less than one-eighth of an inch in diameter; a small jet rapidly clogs and closes. The jet-tube should be about sixteen inches long, so that the

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* *Ber. der chem. Gesell.*, iii., 658.

rubber connection may not be attacked by the nitric acid gas issuing from the flask. The tube is grasped with a pair of tongs, and lowered into the mouth of the flask. As the gases mix, a dense cloud of ammonium nitrate is produced. As soon as the jet is on a level with the mouth of the flask, it should be ignited by means of a wax gaslighter, and at the same instant the jet is lowered into the centre of the flask. If the jet is of the right size and the pressure is neither too great nor too small, the ammonia will ignite easily and, on lowering into the flask, will continue to burn with a fine yellow flame. When once in position and burning evenly, the flame can be considerably enlarged by increasing the heat under the ammonia flask. The evolution must be regular, and to this end the flame under the ammonia flask should be protected against draughts.

The flame is a peculiar one, consisting of a yellow centre, then a greenish yellow envelope, and then a carmine-red envelope. As the colour of the peroxide, N_2O_4, gets deeper the flame becomes unusually handsome. The products of combustion are presumably oxides of nitrogen, perhaps free nitrogen, although I have not yet established this. It is a more striking experiment than the combustion of ammonia in a current of oxygen.

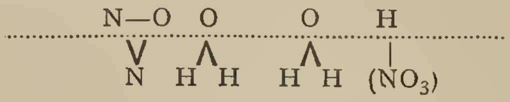
This experiment can be performed in a large oxygen globe. In this case the flask from which the ammonia is evolved must be provided with a trapped stand-tube filled with ammonia water to give a pressure. In this way, or by using a large jet and carefully manipulating a clamp on the rubber supply pipe, a large flame may be easily obtained.

Nitric Oxide.—A jet of nitric oxide, N_2O_2, introduced into nitric acid gas, reacts with it, the mixture turning at once red. The product of the reaction is probably nitrous acid,* $N_2O_2+2HNO_3=2HNO_2+N_2O_4$.

Nitrous Oxide.—A jet of moist nitrous oxide, prepared by heating ammonium nitrate, refuses to ignite in the nitric acid gas. I was surprised to observe, however, the formation of dense white clouds, which on examination proved to be ammonium nitrate. The reaction here is a synthesis of ammonium nitrate,—

$$N_2O+2H_2O+HNO_3=NH_4NO_3+HNO_3.$$

The molecule of nitric acid which appears on both sides of the equation is not an instance of chemical tautology, but is demanded since the rest, NO_3, that appears in the new molecule of NH_4NO_3 is not derived from the $2H_2O$ and the N_2O, but from the HNO_3; for water and nitrous oxide do not unite at a moderate heat. If I interpret the mechanism of this reaction correctly, it should be represented by the following diagram:—



$$\begin{array}{cccccc} N\text{—}O & O & & O & & H \\ \vee & \wedge & & \wedge & & | \\ N & H & H & H & H & (NO_3) \end{array}$$

THE CORROSION AND FOULING OF STEEL AND IRON SHIPS.†

By Professor V. B. LEWES, F.C.S., F.I.C.,
Royal Naval College Associate.
(Concluded from p. 199).

ONE of the largest firms of composition manufacturers had enough curiosity to try the effect of zinc *versus* oxide of iron, and painted a patch of it upon a ship coated with his composition, and after a long voyage she returned with her protectives in perfectly good order, and had it not been for the patch containing zinc having had its position fixed by careful measurements, its whereabouts could not have been discovered. This is exactly what one would have expected; as long as the varnish remains intact oxide of iron, zinc, or, indeed, any substance which will not damage the varnish, does perfectly well; but had the vessel been allowed to continue until the varnishes had perished, then I venture to say that the patch containing the zinc would have shown better protection than those parts containing the oxide of iron. My ideas have undergone considerable modification during the past two years, but I still consider the views I put forward in my last paper were perfectly sound, and I am every day more and more convinced that the great object the composition maker has to aim at is the prolongation of the life and the effectiveness of the compositions, and not the multiplication of short-lived devices, however admirable in their action.

In the fifth class of protectives we have cement coatings; but these, together with such schemes as the covering the hull of the vessels with vitreous glazes, glass, &c., have of late years, as far as I know, entirely been abandoned. The action of cement on iron, however, must later on be discussed in its important bearing on the protection of the interior portions of the hull, for which it is largely employed, its weight and the difficulty of attachment rendering it unfitted for outside work.

In selecting a protective composition for the bottom of a vessel, one of the second or fourth class should be chosen, attention being given to the points I have indicated, which are that in the bituminous and asphaltic compositions all the original acids must be eliminated, and that in the varnishes of the fourth group quickly evaporating solvents should be avoided, and, if possible, zinc substituted for oxide of iron.

The vessel should have her plates as dry as possible during the application of the protective, and, if feasible, days on which the air is fairly dry should be chosen. The protective should not be too thick, as, if it is, it does not readily fill into inequalities in the plates; and, if in this way any air is enclosed, change of temperature will cause it to expand or contract, thus causing a blister to form, which will fill with sea water and set up rapid corrosion. The composition must either be elastic or else have the same rate of expansion and contraction as the iron; for, if not, the change of temperature will cause cracking and tearing of the composition, with disastrous results. The vessel, if she has to be scraped down to the bare metal, must be scrubbed free from all traces of rust, and where a well-adhering coating of composition exists, it should be painted over and not disturbed. In the case of a new ship, she must be pickled with dilute acid, to get rid of every trace of mill scale, and then washed down with some slightly alkaline liquid to neutralise every trace of acidity, the alkali in turn being removed by clean water. Under these conditions, and given a composition with good adhering properties, but little apprehension need be felt as to the ravages of corrosion on the metal of the ship's bottom, the chief risk being from abrasion and other mechanical injury to the composition, coupled with improper constituents in the anti-fouling compositions. The protection of the interior portion of the vessel, where the plates are exposed to the corroding action of bilge water, rendered more active by a high temperature, leakage from cargo, acids and sulphates from wet coals, and the presence of such electro-negative factors as coal-dust, scale, and rust, is a matter of quite as great importance as the exterior protection; whilst the great chance of mechanical abrasion during coaling and shifting of cargo, as well as the difficulty of getting at the lower portions of the hold to examine the condition of the plates, renders it a question of the gravest consideration. The corrosion found in the portions underneath the engine-seats, the bunkers, and the water-ballast chambers, especially near the engine-room, is often very serious, and needs most careful watching, which, from the position of these parts of the vessel, it is very hard to bestow upon it.

It must also be remembered that the bilge water in a

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* Nitric oxide when led through concentrated nitric acid forms nitrous acid.—Gmelin-Kraut, 6 ed., i., 2 Aufl., 454.

† Read at the Thirtieth Session of the Institution of Naval Architects, April 12th, 1889. The Right Hon. the Earl of Ravensworth, President, in the Chair.

vessel is in constant motion, and that the air in these parts of the vessel may be expected to be exceptionally rich in carbonic acid gas, which, as I have before shown, is the most important factor in corrosion. Under these conditions any abraded portion would probably be continually washed over, and then exposed to the foul air, a condition of things most conducive to rapid rusting. There are three main classes of protectives for the interior of a ship—

1. Cements.
2. Bituminous coatings.
3. Paints.

The first of these, the cement coatings, have many good points to recommend them, but they also have many serious drawbacks.

The rigidity, firmness of adherence and endurance, are all of them points of the greatest importance, and there is no doubt but that the silicates present in the cement in time, not only bind the cement into a mass of wonderful hardness, but also bind the cement to the iron. A point to which I should like to draw your attention, however, is that a thin coating of Portland cement is highly porous, and that it can be permeated by liquids and gases. Suppose, now, that some copper scale from the interior fittings had fallen into the bottom of the vessel, and had been converted into soluble salts of copper by the saline bilge water, this solution would soak through the capillary orifices in the cement, until it came in contact with the iron below, when the copper would be deposited on the iron, and rapid galvanic action set up, the cement being loosened, and to a certain extent lifted, by the formation of rust, whilst corrosion would gradually extend under the cement, giving on the outside of the coating but little sign of the damage taking place below it.

Also the hardness and rigidity of the cement gives it a tendency to crack away from the metal when any strain is thrown on the plates, or during any expansion or contraction of the metal; whilst any repairs on the outside of the ship, such as making a boring to test the thickness of plate, replacement of rivets, &c., would undoubtedly cause a loosening of the cement coating within, and, wherever a loosening takes place, the space between the cement and the plate will quickly be found to become a starting-point for corrosion, which quickly spreads and loosens the cement, and will only be discovered by chance.

It is for this reason that I consider bituminous or asphaltic varnishes, freed from any trace of acid, and applied hot, or sound, tough paint, preferable to cement; as, although they are not so hard, yet if serious corrosion should be set up, it is easily discovered and stopped before much damage results, whilst, being impervious to moisture, deleterious solutions, either from the coal bunkers or cargo, would be prevented from acting upon the skin of the ship.

In approaching the subject of fouling, one is impressed with the apparent hopelessness of obtaining any reliable information from the successes or failures registered by the bottoms of the vessels in the Service, or in the Mercantile Marine. Hundreds of ships may be examined, and their condition and the nature of the compositions used upon them registered, and just as one begins to feel that the key to the mystery is within one's grasp, a whole series of results so abnormal suddenly comes to light that it seems impossible to reconcile them with one's previous experience. A ship may sail half a dozen times to the same waters, coated with the same composition—on four occasions she will come home clean, and in good condition, whilst on the other two voyages she may accumulate an amount of weed and animal life sufficient to knock down her speed from nine knots to five. Moreover, if the compositions with which she was coated be examined, and scrapings taken from her on her return, no cause will present itself that can in any way explain the great difference in her condition. After several years' close observation, however, certain factors begin to make themselves apparent. Ships at sea from March to August show a worse average than those afloat from August to March; one also begins to realise that the amount of fouling increases enormously if the ship has been long at anchor—ships which have been lying at the mouths of rivers, although quite clean in the brackish water, foul much more rapidly on going to sea than vessels which have been cruising, or even at anchor for the same time, in salt water; and, finally, certain ports and certain seas seem to exercise a deleterious effect, both as regards corrosion and fouling, which is not to be found elsewhere.

Turning back to the naval history of the past, we find that fouling is no new trouble born with the advent of our present iron monsters; but that it has been the one trouble that the combined engineering and scientific skill of many centuries has been unable to overcome.

With our wooden ships, metallic copper sheathing, if it were of the best kind, answered the purpose fairly well; but then the copper wasted so fast that inferior kinds and alloys were substituted to prevent the rapid loss, and, with the slowing down of the destruction of the copper, at once the trouble of fouling returned.

When iron ships began to replace the wooden ones, as was only natural, attempts were made to utilise the metal which had before given relief; but it was quickly found that the effect of the galvanic action set up by the copper was fatal to the iron plates of the ship, and attempts were then made to sheathe the ship with copper plates in such a way that they should be insulated from the iron of the vessel, a condition almost impossible to attain, and attended with great risk should any accidental injury to the insulation take place. Early in the history of iron shipbuilding the idea was started of using coatings of paint, so prepared as to fulfil the same functions as the copper plates had done; but from 1840, when the first paint of this kind was patented, down to the present day, when there are upwards of thirty-two different compositions in the market, very little progress has been made in their manufacture, and the best of the present compounds cannot be relied upon for keeping a ship's bottom even fairly free from fouling for periods extending beyond nine months, and I am personally convinced that the reason of this is to be found in the fact that a start was originally made in a wrong direction.

The idea which originally led to the present class of anti-fouling compositions was that the copper salts formed by the action of the sea-water on the metallic sheathing owed a considerable portion of their value as anti-foulers to the poisonous action they exerted upon marine animal and vegetable growths; but, when an observer comes to study the natural history of these lower forms of animal life and vegetation, it is gradually forced upon one that it is only in the early stages of their growth—the germ period—that metallic poisons can affect them. Seaweeds do not take in the constituents they require for their growth by means of their roots, as is, to a certain extent, the case with ordinary plants, but absorb them by means of their pores from the water itself, the root only serving to attach them to the solid they choose for their resting-place; and it is also well known that when once a marine plant which has passed the first stages of existence is dislodged or torn from its support, it cannot re-attach itself to anything else, whilst most of the mineral poisons have little or no effect upon their life and growth.

In the same way we find that, with the animal life found on a ship's bottom, the under side is used to cling on with only, and not as an extractor of nourishment, and that, therefore, after the seeds and germs have once obtained a foothold on the side of the vessel, no amount of poison which can be put into a composition will have any effect upon them. Metallic poisons undoubtedly do exert an influence upon the germs in their earliest stages; but after that they are perfectly useless as anti-foulers, and only imperil the plates of the vessel.

The germs of both kinds of growth are of necessity more abundant in the surface-water near shore than in deep water, and, therefore, the period when the ship is in port is the time when the germs are most likely to make good their attachment, after which their further development is, unless other methods of getting rid of them are employed, merely a matter of time.

On examining the conditions under which a vessel is placed when coated with a composition which relies, for its anti-fouling powers, on metallic poisons only, we at once see the reasons which must make such a coating of little or no avail. In the composition we have drastic mineral poisons, probably salts of copper, mercury, or arsenic, which have been worked into a paint by admixture with varnishes of varying composition, and each particle of poison is protected from the action of the sea-water by being entirely coated by this vehicle; that this must be so is evident, or the composition would not have sufficient cohesive power to stick on the ship. As a rule, care is taken to select fairly good varnishes, which will resist the action of sea-water for, perhaps, two or three months, before they get sufficiently disintegrated to allow the sea-water to dissolve any of the poison; whilst, even with the accidental or intentional use of inferior varnishes, three or four weeks will pass before any solution can take place, and any poison be liberated to attack the germs. A ship is dry-docked, cleaned, and, her anti-fouling composition having been put on, she goes probably into the basin to take in cargo. Here she is at rest, and, with no skin friction or other disturbing causes to prevent it, a slimy deposit of dirt from the water takes place, and this, as a rule, is rich in the ova and germs of all kinds of growth, whilst the poisons in her coating are locked up in their restraining varnish, and are rendered inactive at the only period during which they could be of any use. After a more or less protracted period the ship puts to sea, and, the perishing of the varnish being aided by the friction of the water, the poisonous salts begin to dissolve or wash out of the composition; but the germs have already got a foothold, and with a vessel sweeping at a rate of, say 10 to 12 knots through the water, the amount of poison which can come in contact with their breathing and absorbing organs is evidently so infinitesimally minute that it would be impossible to imagine it having any effect whatever upon their growth. If the poison is soluble, it is at once washed away as it dissolves; if it is insoluble, then it is also washed away, but there is just a chance that a grain or two may become entangled in the organs of some of the forms of life, and cause them discomfort. As the surface varnish perishes, the impact of the water during the rapid passage of the vessel through the water quickly dissolves out or washes out the poisonous salts, and leaves a perished and porous, but still cohesive, coating of resinous matter, which forms an admirable lodgment for anything which can cling to it; and by the time the vessel lays-to in foreign waters, teeming with every kind of life, the poison, which would now again have been of some use, is probably all washed away, and a fresh crop of germs are acquired, to be developed on the homeward voyage, and a "bad ship" is reported by the person who looks after her docking. It is evident that a poison, even if it had the power of killing animal and vegetable life in all stages, could only act with the vessel at rest, unless it were of so actively corrosive a nature as to burn off the roots and attachments of the life rooted to it, and if it did this, what, may I ask, would become of the protective composition and the plates of the vessel? And I think it is also evident that any poison so used must be under conditions in which it is very unlikely to be in a position to act when it might do good.

The lamentable failure of composition after composition of this kind has gradually reduced them in number to some ten or twelve at the present time, and in most cases it is low price alone which keeps them in the market.

The practical proof, given by experience, that poisons alone are unable to secure a clean bottom soon led many inquirers to the conviction that it was the exfoliation in the case of copper which had acted in giving fairly good results, and in many compositions the attempt has been made to provide a coating which shall slowly wash off, and, by losing its original surface, shall at the same time clear away germs and partly developed growths, and so expose a continually renewed surface, in this way keeping the bottom of the vessel free from life. There is no doubt that when this is successfully done, a most valuable composition will result, but the practical difficulties which beset this class of anti-foulers must not be overlooked. In order to secure success the composition must waste at a fairly uniform rate, when the ship is at rest, and also when she is rushing through the water; and this is the more important in the case of service vessels, as in many cases they spend a large percentage of their existence at anchor, or in the basins of our big dockyards. If a composition is made to waste so rapidly that it will keep a vessel clean for months in a basin, then you have a good composition *for that purpose*; but send the vessel to sea, and under conditions where you have a higher temperature, and the enormous friction caused by her passage through the water exerting its influence upon the composition, and you will find that the coating, which did its work well for six months at rest in the basin, will, in the course of one month under these altered conditions, be all washed away, and fouling will be set up. Noting this result, the manufacturer renders his composition more insoluble—less wasting—and so obtains a coating which, when the vessel is in motion, scales just fast enough to prevent fouling, and good results at once follow; the composition is then put on the same or other vessels, and they take a spell of rest in the basin, and bereft of the aid of the higher temperatures, and the friction of the water, the composition ceases to waste fast enough, and bad results at once have to be recorded.

There is no doubt that this is the true explanation of the wide discrepancies which are found between the compositions in the Navy and in the Mercantile Marine—take any of the big lines, their steamers are running at a fairly uniform rate of speed, and the periods of inaction are as short as the desire not to waste the charge on the capital they represent can make them, and under these conditions, by varying the constituents in the varnishes used for anti-fouling purposes, it is fairly easy, given the necessary data, to so constitute a composition as to secure admirable results; but when you come to apply this same coating to an ironclad, running at various speeds, and as often at rest as in motion, then you at once find that the composition you before imagined to be all that could be desired fails just as lamentably as the tribe of anti-foulers which preceded it. It is not so very long ago that I had the honour to serve on an Admiralty Committee under the able guidance of Admiral Colomb, and after inspecting many vessels in the Mercantile Marine, and watching all the dockings of service vessels over a considerable space of time, we were forced to the conviction that it was only in very rare cases that the condition of the bottoms of Her Majesty's ships at all approached the freedom from fouling to be found in the ships belonging to the big companies, with the result that some of the most successful of the compositions in the Mercantile Marine were brought into use in the Navy, and I believe the reports of the dockings since they have been adopted will amply prove the existences of the difficulties I have mentioned.

Another factor which is often overlooked, and which tends to give misleading results, is the action of brackish water, which, in many cases, seems to exert a special action in keeping the bottom of a vessel clean, the fresh water having a tendency to disagree with certain forms of marine growth, whilst the salt water is apparently equally unpalatable to the fresh-water forms of fouling.

In most of the compositions now in use attempts are made to combine strongly poisonous substances with exfoliating and wasting coatings, and this is done by either using metallic soaps, the basis of which is, as a rule, copper, or else by charging a perishable and easily washed off varnish with poisonous salts, consisting as usual of compounds of either copper, mercury, or arsenic, and in some cases all three.

As I have before pointed out, I do not think the presence of these substances exerts any deterrent action upon the fouling, save perhaps when the vessel is at rest; but they exert undoubtedly an important influence upon the rate of exfoliation, as when the perishing of the varnish exposes them they dissolve, or are washed out, and in this way tend to disintegrate and clear away the surface more rapidly, an important and decidedly useful function, but one which might be more cheaply performed by substances other than high-priced metallic poisons.

The use of metallic poisons of the character indicated throws an increased burden upon the protective composition, as, should the latter become abraded by friction of chain cables, barges alongside, or any other cause, the iron of the vessel will be attacked by the metallic salts, either present in the soluble form in the anti-fouling composition, or rendered so by the solvent action of the saline constituents of the sea-water, the action of the metallic salts being to rapidly dissolve portions of the iron, and to deposit the metal which they contain upon the surface of the plates, and these deposits, exciting energetic galvanic action, cause corrosion and pitting to go on with alarming rapidity. Both mercury and copper salts are offenders in this way, but copper is by far the most objectionable, from the fact that the salts formed by the action of the sea-water upon the compounds used in the compositions are far more soluble than the corresponding salts of mercury, and are, therefore, liable to be present in much larger quantity, and so exert comparatively a much more injurious action on the plates.

As an illustration of this, two equal portions of sea-water were saturated, the one with copper chloride, the other with mercuric chloride, and into each a piece of steel, planed upon one side, and of about equal weight and size, was placed, and left for four days. At the end of this period the two plates were removed, and after being cleaned and dried were again weighed, when it was found that the one exposed to the copper saturated sea-water had lost 22·2 per cent in weight, while the plate exposed to the mercurial solution had only lost 3·6 per cent, this being due to the much larger amount of the copper salt soluble in the sea-water.

On now placing these plates in clean sea-water, corrosion went on in each case with extreme rapidity, and after being exposed for a month they had both wasted to about the same extent, that is to say, when once deposited on the iron, mercury is practically as injurious as copper.

I am quite aware that this experiment is not at all likely to be carried out in practice, and none can have a greater conviction of the inutility of small laboratory experiments than I have, as they lack all the factors of mass of material and atmospheric influence which play so important a part in a question like the presence; but such an experiment gives one a definite and fairly correct idea of the relative rate of action of the two poisons upon the plates.

All the time the ship is in motion the wash of the sea-water will prevent the metallic poisons doing the plates or the marine growths much harm, but there is one phase of this question which I think has been overlooked. I need not point out that in certain ports there is a fashion in compositions, and that most of the homes of the Mercantile Marine have some pet local composition which is largely used at the particular port. If, now, many ships are laying in a basin, taking in and discharging cargo, and if the prevalent compositions contain copper, it is evident that a certain quantity will go into solution in the water, which often does not undergo frequent or rapid change, and under these conditions every ship in the basin will be exposed to the same danger, and wherever an abrasion has taken place in the protectives, there copper will be deposited on the iron, causing corrosion and destruction of the plates; and it must be remembered that when the vessel is next docked and coated no amount of scraping will remove the fine particles of copper deposited in the pitted and corroded portions of the plate, and so finely divided as to be invisible to the eye, but that it will remain and carry on its destructive work under the new coatings of protective.

It is, I think, a well-recognised fact that, when a vessel coated with a copper compound has become corroded from failure of her protective, or from abrasion, even an entire change of composition does little or no good in stemming the tide of corrosion, until after some considerable period has elapsed, a result which is due to the same cause; and, inasmuch as copper compositions are a source of danger, not only to the ships coated with them, but to any others which may be at rest in the same basin, I do strongly urge upon the manufacturers to abandon the use of these deleterious compounds, and to use others equally efficacious and free from the grave objections I have enumerated.

At the present time 15 out of the 32 principal compositions rely upon copper in some form or other as the basis of their anti-fouling composition, and in one which has enjoyed considerable favour finely divided metallic copper itself is used, and should a vessel coated with it, after the varnishes had commenced to disintegrate, be moored alongside an iron ship by a chain cable, or even by a wet hawser, a big galvanic couple would be formed at the expense of serious damage to any exposed iron.

In the history of anti-fouling many attempts have been made to obtain highly glazed and glass-like surfaces which it was hoped would withstand the action of sea water, and afford no lodgment to marine growths; but even glass itself is slowly acted upon by sea water, and, when once roughened on the surface, will foul, whilst the rigidity of such coatings, and the straining and cracking consequent on unequal expansion and contraction of the plates and their coating, offers a serious obstacle to any such scheme.

In concluding this long paper, I wish to point out that in the present phase of the anti-fouling question, and until some new principle for preventing marine growth has been advanced and successfully adopted, satisfactory results can only be insured by an intelligent use of the existing compositions.

The protective composition is the important composition, and care must be taken to obtain the best in the market, as, if the protection is good, the plates remain uninjured even if fouling take place. The anti-fouling composition to be used with it must either be elastic, or have the same rate of contraction and expansion as the protective, and must—at any rate in the Navy—be chosen to suit the work to be done, such as contain copper compounds being carefully rejected, whilst preference should be given to those which rely on exfoliation rather than mineral poisons. If a vessel is to remain at rest for a considerable period, an anti-fouling composition which exfoliates rapidly, and which also contains poisons known to act on germ life, must be used, the amount of such poison depending on the seasons and the waters in which the ship is to be; whilst if a vessel is to be continually running, then a slowly exfoliating composition must be employed, and a very small percentage of poison is all that is required, as skin friction and the comparative absence of the germs and spores in deep water will do the rest.

Our ships represent an enormous capital, and any trouble or care which will prolong their existence is well worth taking and will be amply repaid, and at the present time a heavily corroded and foul vessel means either ignorance or negligence on the part of those who have the responsibility of deciding on the composition to be used, and, finally, it must be clearly borne in mind that there is no anti-fouling composition which ever has been made, or probably ever will be made, that will answer for all cases, and that until this is clearly recognised, the present unsatisfactory condition of the question will exist.

ON THE

BEHAVIOUR OF PHENOLPHTHALEIN WITH AMMONIA.

By J. H. Long.

The peculiar action of ammonia on phenolphthalein was first pointed out by Beckurts, I believe, in a paper in the *Pharmaceutische Centralhalle*.[*] Soon after the experiments of Luck[†] were published, showing the great value of this substance as an indicator, it came into general use in Germany, and was even incorporated among the tests of a new edition of the German Pharmacopœia then published. Schlickum, in his "Commentary on the German Pharmacopœia," 2nd Ed., states in one place that the behaviour of litmus and phenolphthalein in the titration of acids with ammonia water is the same, while in another place he remarks that the presence of ammonium salts interferes somewhat with the delicacy of the titration when phenolphthalein is the indicator. Beckurts shows the error into which a number of writers had fallen in this regard, by giving a series of tests carried out with different indicators. In the following year Flückiger[‡] published experiments on the sensitiveness of phenolphthalein, leading to the conclusion that it could not be employed with ammoniacal solutions. In the excellent papers by Thomson,[§] a similar conclusion is reached.

In the *Pharmacist*[||] I published the results of a long series of experiments on the action of phenolphthalein, and, among other points, I touched on the want of delicacy with ammonia. In that paper I offered an explanation of this behaviour, suggested in part by a remark of Baeyer[¶] on the formation of phenol-di-imido-phthalein, and partially confirmed this explanation by a number of experiments. Since then I have again taken up the subject, repeating the old experiments and adding new ones, which I think afford a full confirmation of my former suggestion. It is this later work which I wish to present here in detail.

When a few drops of an alcoholic solution of phenolphthalein are added to a strong solution of soda, the deep red colour which forms at first vanishes in a short time—within a minute, if the soda is sufficiently strong. The colour can be restored by partial neutralisation with acids. When the indicator is added to strong ammonia solution (26 per cent), a red colour is produced which is more permanent, fading completely only after hours or days.

In this case, that is, after the *complete* disappearance of the colour, addition of acid produces no change. If the acid is added before the colour is fully discharged it becomes much brighter.

When phenolphthalein is added to a very weak soda solution, the red colour produced seems to be indefinitely permanent; but with weak ammonia it vanishes sooner or later, the interval between the mixing of the solutions and the disappearance of colour depending on several factors, as dilution, temperature, and strength of indicator.

There are, therefore, important differences between the action of soda and that of ammonia on phenolphthalein. If to a definite amount of a standard solution of hydrochloric acid containing a few drops of the indicator, standard ammonia solution be added, something more than the theoretical amount of the latter must be used to give the permanent red colour. However, by increasing the amount of indicator added, or by cooling the solutions, the colour can be obtained by nearly or quite the equivalent number of c.c. of ammonia.

A similar result is obtained by adding soda solution to a solution containing, along with free mineral acid, some salt of ammonium and the indicator. The effect of temperature was shown by the following experiments. I prepared half normal solutions of hydrochloric acid and sodium hydroxide and a solution of ammonium chloride containing 100 grms. in one litre. I took now 25 c.c. of the acid, 10 c.c. of the ammonium chloride, 65 c.c. of water, and a few drops of the indicator. To the mixture, slightly less than 25 c.c. of the sodium hydroxide was added, the whole was cooled to the desired temperature, and then more sodium hydroxide was run in to colouration. The results obtained at various temperatures are given in this Table :—

Temperature.	C.c. N/2NaOH.
6·5	26·2
13·5	27·0
22·5	27·6
30·0	28·1
38·0	28·7
49·5	29·9
62·0	31·0
69·1	32·0
76·0	32·8

The final reaction was in no case as sharp as in a titration between the alkali and acid alone, but the results are close approximations. Something similar is shown in the following experiments, which disclose likewise the effects of excess of ammonium chloride. Here I employed normal solutions of hydrochloric acid, sodium hydroxide, and ammonium chloride, and for each experiment took 25 c.c. of acid, a definite quantity of ammonium chloride, and added enough water to make 100 c.c. In each case 1 c.c. of a one-tenth per cent solution of phenolphthalein was added, and then caustic soda from a burette to colouration.

The solution in the beaker was kept at a temperature of 0° C., and that in the burette as near this as possible. The experiments were repeated for each mixture three times, and gave closely agreeing results, the end reactions being quite satisfactory and sharp. In the following table the mean of the results from the three tests is given :—

No	HCl. C.c.	NH_4Cl. C.c.	H_2O. C.c.	NaOH required. C.c.
1.	25	5	70	25·
2.	25	10	65	25·08
3.	25	15	60	25·20
4.	25	25	50	25·28
5.	25	30	45	25·37
6.	25	50	25	25·68

These experiments show clearly that with the temperature sufficiently low, the disturbing action of small amounts of ammonium salts is very slight. They show also at what rate the disturbance increases with increasing amounts of ammonium chloride.

At a temperature of 20° C. I obtained the following results, working with the same solutions :—

No.	HCl. C.c.	NH_4Cl. C.c.	H_2O. C.c.	NaOH required. C.c.
1.	25	5	70	25·22
2.	25	10	65	25·38
3.	25	15	60	25·61
4.	25	20	55	25·82
5.	25	25	50	25·98

We find here differences in the amount of alkali required, varying between 0·2 c.c. for the weakest solution to 1 c.c. for that containing 25 c.c. of ammonium chloride, which amounts to an error of 4 per cent. In all these

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[*] 1883, p. 333.
[†] *Ztschr. anal. Chem.*, 1877, 332.
[‡] *Ber. d. chem. Ges.* xvii., 592. Ref.
[§] Chem. News, xlvii., 125, 135, and 184.
[||] 1885, 43; also Chem. News, li., 160.
[¶] *Ber. d. Chem. Ges.*, xi., 1297.

cases the error is so large that it could not be neglected in any kind of practical work. However, by employing a larger amount of indicator, the error can be almost entirely corrected, as shown by the following tests:—

I used here 25 c.c. of the acid and 5 c.c. of the ammonium chloride solution at a temperature of 20° C.

1. With 2 c.c. of indicator required 25·12 c.c. NaOH.
2. With 4 c.c. of indicator required 25·02 c.c. NaOH.
3. With 6 c.c. of indicator required 25·00 c.c. NaOH.

By using larger amounts of the indicator, the final reaction is obtained with satisfactory sharpness.

In another series of experiments, ammonia was run into the solution containing hydrochloric acid and different amounts of the phenolphthalein. Where but a few drops of this were taken, the end reaction could not be observed accurately; with larger amounts the reaction was sharper, but only came after addition of an excess of alkali.

1. With 25 c.c. of acid and 5 c.c. of indicator I used 25·57 c.c. of NH_4OH.
2. With 25 c.c. of acid and 10 c.c. of indicator I used 25·28 c.c. of NH_4OH.

In presence of alcohol the reaction was always less distinct than with water, and more alkali was required to bring it.

The above results seem to indicate that ammonia combines with phenolphthalein, forming, to some extent, a colourless compound, besides forming a coloured one as does sodium hydrate; and also that this colourless body is produced more quickly as the temperature is higher or the ammonia stronger.

I expressed the opinion in my former paper, referred to above, that the phenol-di-imido-phthalein discovered by Baeyer is the compound formed here, and that this explains the peculiar reaction.

The experiments given below seem to confirm fully this view. Baeyer* states that phenolphthalein and aqueous ammonia heated to 160°—170° in sealed tubes for some hours react on each other in this way:—

$$C_{20}H_{14}O_4+2NH_3=C_{20}H_{16}N_2O_2+2H_2O.$$

The phenol-di-imido-phthalein is a colourless body soluble in alkalies without colour, but which dissolves at a high temperature in acids, with formation of an ammonium salt and phenolphthalein:—

$$C_{20}H_{16}N_2O_2+2H_2O+2HCl=C_{20}H_{14}O_4+2NH_4Cl.$$

I prepared the product by the following methods:—

1. Three grms. of phenolphthalein and 30 c.c. of strong ammonia were heated during three hours in a sealed tube to 160° C. The tube was then opened and the contents neutralised with hydrochloric acid. This precipitated a gummy mass, which was washed thoroughly with water, and finally dissolved in 90 per cent alcohol. The solution, after filtration through bone charcoal, was evaporated to dryness. The residue left was dissolved in a mixture of equal parts of benzene and alcohol. The solution was allowed to evaporate spontaneously, leaving a residue, which was heated to 120° C. to completely remove all traces of the solvent. The product then remained as a colourless mass of fine needle-shaped crystals.

2. Ten grms. of phenolphthalein were treated with 200 c.c. of strong ammonia solution in a flask kept hot on a water-bath during fifteen hours; at the end of that time the solution was neutralised with hydrochloric acid, and an insoluble gummy mass formed was treated as under 1.

3. Ten grms. of phenolphthalein were dissolved in 200 c.c. of strong ammonia water (26 per cent) at the ordinary temperature of the room. The colour formed at first disappeared in four days without application of heat. I then neutralised with hydrochloric acid, and obtained the same product as above, which was treated in the same manner.

The three substances so obtained appeared quite similar, and turned red when moderately heated in a porcelain dish, melting finally at a higher temperature. They dissolved in sodium hydroxide solution without colour. When heated to 110° C. with hydrochloric acid they formed ammonium chloride and phenolphthalein, as shown by various tests. They all dissolved in strong nitric acid with a marked yellow colour, which disappeared on addition of alkali.

It is apparent, therefore, that the phenol-di-imido-phthalein can be formed at ordinary temperature as well as in a sealed tube at 160°, although the preparation of a large amount at the lower temperature would require a much longer time.

The combination between the free alkali and the trace used as indicator in a practical titration would naturally require but a very short time at the ordinary temperature.

The rapidity of liberation of ammonia from an ammonium salt by fixed alkali depends on the temperature, and hence the very slight disturbance of the reaction with the mixed solutions in the above experiments carried out at a low temperature. Addition of sodium hydroxide seems to aid the reaction with ammonia solution, as shown by experiments in which I added the phenolphthalein to ammonia solution and then the sodium hydroxide from a burette. With half-normal solutions the colour was lost in half an hour by mixing 25 c.c. sodium hydroxide, 20 c.c. ammonia, and 0·2 c.c. of the indicator. Similar results were obtained with other solutions.

The above experiments show that the phenolphthalein can be used with ammonia by taking certain precautions, and they also suggest why the behaviour of this alkali was not sooner recognised. By working at a low temperature with a sufficiently large amount of the indicator, it was shown that fairly sharp results can be obtained. However, as we have other good indicators, it may never seem necessary to take these precautions.

After the introduction of the phenolphthalein as an indicator, some time elapsed before its extreme sensitiveness was realised, and undoubtedly more was then added to a solution than is now considered necessary. Under these circumstances the difference in behaviour between soda and ammonia would scarcely be noticed, and it remained for later observers, working with less of the reagent, to detect the discrepancy.

I am greatly indebted to my assistant, Mr. Mark Powers, for help in the details of the above experiments.—*American Chemical Journal*, vol. xi., No. 2.

ON THE
CONVERSION OF SOME OF THE HOMOLOGUES OF BENZOL-PHENOL INTO PRIMARY AND SECONDARY AMINES.*

By RACHEL LLOYD.

(Concluded from p. 196).

CARVACROL.

FROM the results obtained with thymol it was natural to suppose that its isomer, carvacrol, would yield similar products.

The carvacrol used was obtained from Schuchardt, and boiled constantly at 236°. The same proportions of zinc-ammonium bromide and ammonium bromide were used as in the foregoing investigations, and the mixture was heated for the same number of hours at 350°—360°.

The reaction-mass consisted of a light golden-brown under-layer, and a darker overlying layer of a granular consistence, intermixed with a considerable quantity of a light yellow oil. The sides of the tubes were covered with drops of water. Pressure, almost none.

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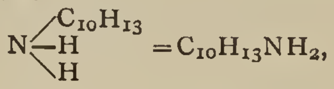
* *Ber. d. chem. Gesell.*, xi., 1297.

* "University Studies, Published by the University of Nebraska," October, 1888.

In the corresponding experiments with carvacrol, zinc-ammonium chloride, and ammonium chloride, the pressure in tubes was considerable; the escaping gas possessed an agreeable aromatic odour and burned with a feeble flame. In these experiments more carbonised substance was formed than when the bromine compounds were employed. The products were isolated by previously described methods.

Carvacrylamine:—



$$N\begin{cases}C_{10}H_{13}\\H\\H\end{cases}=C_{10}H_{13}NH_2,$$

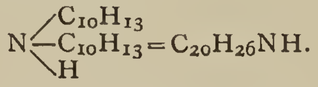
a yellowish brown oil distilled by the first distillation at 240°—245°, leaving a small quantity of carbonised substance in the bulb; by the second, almost entirely between 241°—242°. The freshly distilled amine was nearly colourless, and upon exposure to the air turned yellow, then brown. It solidified and crystallised indistinctly at −16° C.

The analysis gave the following result:—

0·1497 grm. substance gave 0·4448 grm. carbon dioxide and 0·1351 grm. water, corresponding to 0·1213 grm. C. and 0·1501 grm. H.

Calculated for $C_{20}H_{27}N$.				Found.
C_{10}	120	80·54 per cent	..	81·03 per cent
H_{15}	15	10·06 ,,	..	10·02 ,,
N	14	9·40 ,,	..	— ,,
	163	100·00 per cent		

Dicarvacrylamine:—



$$N\begin{cases}C_{10}H_{13}\\C_{10}H_{13}\\H\end{cases}=C_{20}H_{26}NH.$$

The raw, dark coloured, oily, secondary amine was distilled with super-heated steam; the oil which came over in light golden drops and floated on the surface of the milky distillate was extracted with ether, dried over caustic potash, and finally re-distilled in vacuum. The greater portion distilled at 344°—348°; above this temperature decomposition took place. The fraction so distilling was almost colourless, had a most pleasant odour, dissolved readily in alcohol, ether, and benzol. At −18° C. the body retained the consistence of an oil. With concentrated sulphuric acid, a golden tint was produced, which changed by the addition of a nitrate or nitrite first to green-blue, then to blue.

The analysis gave the following result:—

I. 0·1856 grm. substance gave 0·5814 grm. carbon dioxide and 0·1619 grm. water, corresponding to 0·15856 grm. C. and 0·01798 grm. H.

II. 0·2322 grm. substance gave 10·5 c.c. of moist nitrogen (thermometer 22° C., barometer 720 m.m.), equal to 0·011396 grm. N.

Calculated for $C_{20}H_{27}N$.				Found.
C_{20}	240	85·41 per cent	..	85·45 per cent
H_{27}	27	9·61 ,,	..	9·68 ,,
N	14	4·98 ,,	..	4·90 ,,
	281	100·00 per cent.		

The percentages of carbonised substance, unchanged phenol as well as the bases obtained by corresponding experiments with the bromides and chlorides of zinc and ammonium, are here tabulated.

	Zinc-ammonium bromide.			Zinc-ammonium chloride.			
Carvacrol.	I.	II.	III.	I.	II.	III.	
Carvacrylamine ..	30	35	36	28	27	25·6	p.c.
Dicarvacrylamine ..	40	38	39	32·1	29·6	27·4	,,
Unchanged phenol ..	24·2	20	20·3	32	34·3	40·2	,,
Carbonised substance	0·5	0·9	1	3	4·1	4·5	,,

Derivatives of Carvacrylamine.

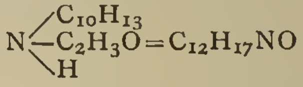
The platinum double salt—$(C_{10}H_{13}NH_2.HCl)_2PtCl_4$—was made by precipitating a hydrochloric acid solution of the amine with platinum chloride. A yellow precipitate in the form of needles shot out at once from the golden-coloured solution. These needles were re-crystallised from alcohol in beautiful prisms grouped in clusters. The crystals were dissolved with difficulty in hot water, but readily in hot alcohol and benzol.

An analysis of the salt dried at 100°—110° gave the following result:—

0·5024 grm. substance gave 0·1384 grm. platinum.

Calculated for $(C_{10}H_{13}NH_2.HCl)_2PtCl_4$.		Found
27·48 per cent Pt.	..	27·55 per cent Pt.

Acetylcarvacrylamine:—

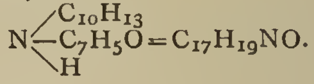


$$N\begin{cases}C_{10}H_{13}\\C_2H_3O\\H\end{cases}=C_{12}H_{17}NO$$

was formed readily by the action of acetic anhydride upon a calculated amount of the base. Action began at once, the solution became quite brown in colour. To insure complete reaction, the substances were warmed for an hour at 130°.

The white mass which separated was crystallised from a mixture of alcohol and water in glistening white plates, melting at 115°. The crystals dissolved in an abundance of hot water, more readily in benzol than in ether, with readiness in hot alcohol.

Benzoylcarvacrylamine:—



$$N\begin{cases}C_{10}H_{13}\\C_7H_5O\\H\end{cases}=C_{17}H_{19}NO.$$

To form this compound a grm. of the base was treated with an excess of benzoyl chloride. Action took place immediately with evolution of hydrochloric acid. Upon warming, a further evolution of gas took place, and a crystalline mass of a yellowish tint was formed. Upon treating the mass with sodium carbonate it became white and was crystallised from hot benzol in shining crystals.

The crystals had the appearance of flat rhombs and feathery aggregates, were insoluble in hot water, with difficulty soluble in cold, easily in hot alcohol, but readily soluble in ether or benzol; melting-point 102°.

The analysis gave the following result:—

0·2184 grm. substance gave 0·6455 grm. carbon dioxide and 0·1500 grm. water, equal to 0·1760 grm. C. and 0·1666 grm. H.

Calculated for $C_{17}H_{19}NO$.				Found.
C_{17}	204	80·63 per cent	..	80·58 per cent
H_{19}	19	7·51 ,,	..	7·63 ,,
N	14	5·53 ,,	..	— ,,
O	16	6·33 ,,	..	— ,,
	253	100·00 per cent		

Derivatives of Dicarvacrylamine.

The platinum double salt—$(C_{20}H_{26}NH.HCl)_2PtCl_4$—was prepared after the method used with the double salt of dithymylamine. The product so obtained was more crystalline than the isomeric salt, and after thorough washing and drying over sulphuric acid in vacuum, granular feathery aggregates of a beautiful golden colour were formed.

The analysis of the salt dried at 100° gave the following result:—

0·2039 grm. substance gave 0·0464 grm. platinum.

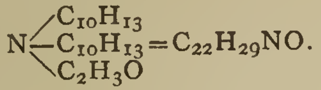
Calculated for $(C_{20}H_{26}NH.HCl)_2PtCl_4$.		Found.
20·01 per cent Pt.	..	19·93 per cent Pt.

The *hydrochloric acid salt*—$C_{20}H_{26}NH.HCl$—formed most readily by conducting dry hydrochloric acid gas into a solution of the base in benzol. The salt was precipitated as a white granular crystalline mass, which was easily decomposed by water with separation of the base. The mass was filtered off, washed with benzol, and dried over sulphuric acid in vacuum. An analysis of the salt dried at 100° gave the following result:—

0·2464 grm. substance gave 0·1110 grm. silver chloride.

Calculated for $C_{20}H_{26}NH.HCl$.		Found.
11·18 per cent Cl	.. ..	11·15 per cent Cl.

Acetyldicarvacrylamine:—



$$N\begin{cases}C_{10}H_{13}\\C_{10}H_{13}\\C_2H_3O\end{cases}=C_{22}H_{29}NO.$$

The method used in the preparation of this body was the same as that used with the isomeric phenols. The glistening white scales obtained by crystallising the product of the reaction in hot benzol were easily soluble in hot alcohol and in hot ligroin; melting-point, 78°.

The combustion gave the following result:—

0·2171 grm. substance gave 0·6480 grm. carbon dioxide and 0·1787 grm. water, corresponding to 0·1767 grm. C. and 0·0198 grm. H.

Calculated for $C_{22}H_{29}NO$.				Found.
C_{22}	264	81·73 per cent	..	81·38 per cent
H_{29}	29	8·98 ,,	..	9·12 ,,
N	14	4·34 ,,	..	— ,,
O	16	4·95 ,,	..	— ,,
	323	100·00 per cent		

Summary of Results.

The above experiments have shown that primary and secondary amine, together with carbonised substance, are produced when isobutylphenol, isoamylphenol, thymol, and carvacrol are heated to 320°—360° with an excess of zinc-ammonium bromide and ammonium bromide, or with the chlorides of zinc and ammonium.

Better results were obtained by using the bromine compounds.

The percentage of amines reached its maximum—seventy per cent—with carvacrol; the three other phenols yielding only forty-five to sixty per cent of the original substance.

In a manner similar to that used with the cresols and xylenols, these more complicated homologues of benzolphenol have been converted into amines; but the bases so obtained have not formed chemical combinations so readily as the bases obtained from the phenols of simpler form.

So far as I know, the primary base—carvacrylamine—has not been previously described.* When freshly distilled, it is an almost colourless oil of a disagreeable odour; boiling-point, 241°—242°. In a freezing mixture it became solid with an indistinctly crystalline structure. Its derivatives are beautifully crystalline. For further identification of the amine, its platinochloride and acetyl and benzoyl derivatives were studied.

The secondary bases, namely, diphenisobutylamine, diphenisamylamine, dithymylamine, and dicarvacrylamine, are oily liquids which boil above 300°, are nearly colourless when first distilled, but colour on exposure to the air. The dicarvacryl and dithymyl bases have a most agreeable odour. In order to study more closely the character of these secondary amines, the platinum double salt and the acetyl and benzoyl compounds were prepared. With the exception of the platinochloride of dithymylamine, the products were well crystallised.

A summary of the work would be incomplete without mentioning the fact that efforts to obtain picrates of diphenisamylamine and dithymylamine were unsucccessful. An analysis of the products obtained by the action of an alcoholic solution of picric acid upon an alcoholic solution of the afore-mentioned bases, corresponded quite closely with the theory for picric acid. In crystal form and melting-point the substances exhibited marked differences. The products will be further examined with the hope of determining what molecular arrangement took place.

NOTICES OF BOOKS.

A Treatise on Chemistry. By Sir H. E. Roscoe, F.R.S., and C. Schorlemmer, F.R.S. Vol. III.—*The Chemistry of the Hydrocarbons and their Derivatives, or Organic Chemistry*, Part 5. London: Macmillan and Co.

This work, when complete, will be without doubt the foremost systematic treatise on chemistry which has ever issued from the British press. Other works, such as that of W. A. Miller, however useful, appear in comparison almost as hand-books—using the term in its English sense—and "Watts' Dictionary of Chemistry" from its form does not take up exactly the same ground. Another advantage of the work before us is that it embodies the results of the latest research, a point which in a rapidly-extending science like chemistry is of no small moment. The volume embraces the description of the benzene-hydrocarbons containing eight or more atoms of carbon, and it concludes with the terpenes and the camphors.

The authors discuss the groups styrolene, cumene, carbostyril, phenylpropiolic, cymene, laurene, mellitene; and proceeding to the compounds containing more than twelve atoms of carbon, the terpenes, and camphors, pinene, camphene, limonene, dipentene, sylvestrene, terpinolene, terpinene, and phillandrene groups.

Among the polyterpenes we find mention of caoutchouc, balata, and gutta-percha.

It is almost a superfluous task to say that the account given of all the many substances here described is correct according to the present state of knowledge, and as complete as space will allow.

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. cviii., No. 14, April 8, 1889.

Fixation of Nitrogen by Vegetable Soil, with or without the Co-operation of Leguminous Plants.—M. Berthelot.—The author has succeeded in establishing by certain proofs that a fixation of atmospheric nitrogen really takes place principally in certain vegetable soils, giving rise to the formation of complex organic compounds of the order of the albumenoids, whilst it does not take place in the same soils if sterilised. These phenomena along with others tend to refer the fixation of nitrogen to the microbia contained in the soil. The fixation of nitrogen does not take place exclusively by means of the lower plants properly speaking, moulds, fungi, algæ, &c., which may be developed on the surface of the soil. On the contrary, the surface layer is often less rich in nitrogen than the entire mass. The question whether plants contribute by their aërial portion to the fixation of nitrogen requires a renewed study. It seems to the author difficult to contest in principle that such an immediate fixation takes place to a certain extent under

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* Since these investigations were made, Söderbaum and Widman have obtained cymidin (carvacrylamine) by another method. See *Berichte der Deutschen chem. Gesellschaft*, xxi., 2127.

the continuous action of atmospheric electricity of feeble tension.

Experiments on the Putrefaction and on the Formation of Farmyard Manure.—J. Reiset.—The author commenced his researches in 1854 with the preconceived notion that nitrogen was gradually fixed during the slow combustion of organic matter in presence of alkaline carbonates. In 1856 he came to an opposite conclusion, viz., that in all cases when a nitrogenous organic matter undergoes putrid decomposition a part of its nitrogen escapes in the gaseous condition—a conclusion confirmed by the researches of Messrs. Lawes, Gilbert, and Pugh. The author considers, however, that the discovery of the chemical activity of microbia opens a new phase of this question. He mentions a *Bacillus denitrificans*, observed by MM. Gayon and Dupetit, which even decomposes potassium nitrate with an escape of pure nitrogen. He asks if there is not an abundant source of nitrogen during the decomposition of organic matter under water, and quotes an analysis made by Bunsen of the gases obtained from the mud of a pond in the Botanical Garden of Narburg. This gas, after removal of the carbonic acid, contained 51·5 per cent of free nitrogen.

Speed of Transformation of Metaphosphoric Acid.—Paul Sabatier.—At one and the same temperature the solutions are transformed the more rapidly in proportion as they are more concentrated. It is also accelerated with a rise of temperature.

Separation of Cobalt and Nickel after Oxidation in Ammonical Solutions.—Adolphe Carnot.—(See p. 208).

The Solubility of Salts.—H. W. Bakhurs Roozeboom.—A reply to M. Le Chatelier's memoir, inserted in *Comptes Rendus* for March 18, 1889.

Preparation of the Hydrochloric Ethers by Means of Alcohols saturated with Hydrochloric Acid and Heated in Closed Vessels with a Large Proportion of the Strongest Hydrochloric Acid.—H. Malbot.—The preparation of hydrochloric ethers by previous saturation of the alcohol with hydrochloric acid gas has not been found to give satisfactory results. The absolute quantity of water present is of less importance than the relative proportion of water and acid. A much better result has been obtained by first saturating the acid perfectly with hydrochloric acid gas and then adding a strong dose of the most concentrated hydrochloric acid.

On Methyl-acetanilide.—H. Girard.—The substance described by Dr. Dujardin-Beaumetz in the *Comptes Rendus* for March 18 is prepared by M. Brigonnet under the name exalgine. The substance, it is stated in the memoir, has the scientific name "ortho-methyl-acetanilide," and it is said that "like all the aromatic compounds, it may exist in three modifications, ortho, para, and meta." Now the name ortho-methyl-acetanilide is applicable only to a body described by Beilstein and Kuhlberg under the name *aceto-ortho-toluide*, prepared by means of orthotoluidine and acetic acid. The substance prepared by M. Brigonnet is not novel; it was described by Hofmann in 1874. Its true name is methyl-acetanilide, and it cannot exist in three modifications, since the phenyl radicle contained in its molecule is not substituted.

Analysis of Cinchonas, and the Relative Solubility of their Proximate Principles in Water, Alcohol, and Dilute Hydrochloric Acid.—E. Landrin.—This paper will be inserted in full.

Solubility of Different Minerals in Sea-Water.—J. Thoulet.—The author has examined the solubility in sea-water of obsidian, pumice, amphibole, orthose, marble, shells (*Pectunculus philosus* and *Cardum edule*), and coral of the species *Cladocera*. The minerals were powdered, separated by sifting into uniform granules of the size of a small millet seed, dried in the stove at 125°, and separated into two approximately equal portions, each of which was carefully weighed. One set of the samples were placed in stoppered bottles with known volumes of filtered sea-water, agitating several times daily. After a week the water was drawn off by means of a filter-syphon, so that no solid fragment might be removed, and replaced by a new quantity of sea-water. The experiment lasted for seven weeks. The check portions were treated in a similar manner with distilled water. The solubility in sea-water was found extremely slight and notably inferior to the solubility in fresh water. This fact is explained by the total absence of free carbonic acid in sea-water, which has an alkaline reaction with litmus and coralline. In the cases of marble, orthose, shells, and coral the loss was negative on account of the algæ which germinated in the sea-water. The author therefore proposes to repeat the experiment in the absence of light.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Naphtha.—Will some reader kindly inform me how I can by calculation convert pounds of coal-tar naphtha into gallons? Also how I can by calculation reduce the percentage of coal-tar naphtha? For instance, supposing I have 100 gallons 50/90 benzol, testing 53 per cent 100° C., how can I reduce this to 50 per cent at 100° C. by calculation.—E. J. B.

MEETINGS FOR THE WEEK.

Monday, 6th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Heat Engines other than Steam," by H. Graham Harris.
—— Society of Chemical Industry, 8. "On Explosives," by C. Napier Hake.
—— Royal Institution, 5. General Monthly Meeting.
Tuesday, 7th.—Royal Institution, 3. "The Italian Renaissance Painters; their Education," by Jean Paul Richter.
—— Institute of Civil Engineers, 8.
—— Pathological, 8.30.
Wednesday, 8th.—Geological, 8.
—— Society of Arts, 8. "Origin and Manufacture of Playing Cards," by George Clulow.
—— Microscopical, 8.
Thursday, 9th.—Royal, 4.30.
—— Royal Institution, 3. "The Science of Locomotion in its relation to Design in Art (illustrated by the Zoopraxiscope," by Eadweard Muybridge.
—— Institute of Electrical Engineers, 8.
—— Mathematical, 8.
Friday, 10th.—Royal Institution, 9. "Optical Properties of Ozone and Oxygen," by Prof. Dewar, F.R.S.
—— Astronomical, 8.
—— Quekett Club, 8.
Saturday, 11th.—Royal Institution, 3. "The Origin and Development of Opera in England," by Joseph Bennett.
—— Physical, 3. "On an Electiostatic Field produced by Varying Magnetic Induction," and on the Concentration of Electro-magnetic Waves by Large Cylindrical Lenses," by Prof. O. J. Lodge, F.R.S.

THE CHEMICAL NEWS.

Vol. LIX. No. 1537.

RESEARCHES ON THE CHEMISTRY OF SELENIC ACID AND OTHER SELENIUM COMPOUNDS.*

By Sir CHARLES A. CAMERON, M.D., F.R.C.S.I., V.P.I.C., Professor of Chemistry and Hygiene, R.C.S.I.;

and JOHN MACALLAN, F.I.C., Demonstrator of Chemistry, R.C.S.I.

Although selenic acid was prepared by Mitscherlich so far back as the year 1827, few chemists appear to have studied its properties. This want of interest in selenic acid is rather surprising, seeing that it possesses so close a relationship to sulphuric acid, which is so important a compound. Finding the chemistry of selenic acid so meagre, we resolved to make an investigation of this body, with the view of bringing, so far as we could, its chemistry abreast with that of sulphuric acid, and also in the hope that its study would yield results which might throw additional light on the relations of the latter acid. The following pages contain the results at which we have arrived.

Preparation of Anhydrous Selenic Acid, H_2SeO_4.

Selenic acid has hitherto been known only in a dilute form. When heated to upwards of 260° C. it commences to decompose into selenium dioxide, oxygen, and water, which prevents any further concentration. Berzelius describes it as containing, when of greatest strength, 4 per cent of water; but it has been obtained since his time, in a more concentrated condition, by Fabian, who, by evaporating the acid to a temperature of 265°, found it to have a strength of 94·9 per cent, and by placing this acid, while still hot, under the receiver of an air-pump, increased its strength to 97·4 per cent. Sulphuric acid, as is well known, has not been obtained in a perfectly anhydrous state by ebullition—although in its case decomposition does not occur; for when it reaches a strength of about 98·66 per cent it boils without further change. When, however, an acid of this strength is surrounded with a freezing-mixture, the anhydrous acid, H_2SO_4, crystallises out. An attempt was first made to obtain anhydrous selenic acid by similar means. Great care was taken to obtain an acid of pure quality. An examination was specially made for nitric, sulphuric, hydrochloric, and hydrobromic acids. Selenious acid, when present, was removed by diluting with about 30 parts of water, saturating with hydrogen sulphide in the cold, filtering, and concentrating on the water-bath. The acid thus treated was then examined for sulphuric acid and found to contain none. A portion of the acid, when ignited, left a residue equivalent to 0·07 per cent of the anhydrous acid present in the specimen used in the experiment; this was ascertained to consist of neutral sodium selenate, and was, of course, derived from an acid salt, of which it was necessary to take account in the succeeding experiments.

Some of this acid was gradually heated until the temperature rose to 250°. It was next poured into an open dish, and allowed to cool slowly over sulphuric acid, under an exhausted receiver. The strength was then taken with semi-normal soda solution, which was specially prepared for these experiments by making a solution in water of pure caustic hydrate prepared from sodium, and bringing it carefully to the required strength; 11·81 c.c. of soda solution were required for neutralisation by 0·4371 grm. of acid, equivalent to 97·75 per cent of selenic acid, being thus a little stronger than that obtained by Fabian in a similar way.

The acid thus concentrated was then poured into a stout wide glass tube, having one end closed, and the open end fitted with an indiarubber cork, through which passed a glass rod for the purpose of keeping the viscous liquid stirred, and a capillary tube for admission of air, in order to expose the acid to the full atmospheric pressure. The necessity for these precautions in the case of sulphuric acid has already been fully pointed out by Marignac (*Annales de Chimie et Physique*, xxxix. (1853), 184), the discordant results arrived at by various observers being probably due to the different conditions under which they worked. The latter precaution is particularly necessary, as we have observed that sulphuric acid occupies less volume in the solid than in the liquid state.

The temperature of the acid was then gradually lowered. Its viscosity increased as it became colder, until at a temperature of −51·5° C. it was as thick as soft pitch—the tube might be inverted without the acid flowing, and a glass rod could be moved in it only with great difficulty. Still it did not freeze, until, after vigorous stirring maintained for a couple of minutes, a crystal appeared, and then the entire mass almost instantaneously crystallised, the temperature rapidly rising. When removed to a warm room the crystals were rather permanent, and when nearly melted re-crystallisation could easily be induced by exposure to moderate cold as long as any crystal remained, showing that previous to freezing the acid had been in a more or less superfused condition. It was found to be impossible, however, to separate the crystals by draining the liquid portion, as the latter was so viscous that it carried the crystals with it. Under the microscope they were seen to be long prisms.

An attempt was next made to examine the conditions under which selenic acid becomes strengthened in a vacuum, with the object of obtaining, if possible, a more concentrated acid; and the following arrangement was made for the purpose:—The glass receiver of an air-pump was fitted tightly at its neck with an indiarubber cork, through which passed a bent tube, connected horizontally with another and wider tube containing solid potash. This was connected with a wide U-tube, filled with pieces of potash about half an inch long, and kept cool by immersion in a beaker of water. Connection was then made with a small stout flask containing the selenic acid, and varying in size from 100 to 250 c.c., as required. The potash tube next the receiver was intended for the purpose of preventing acid fumes from injuring the air-pump, and for the same reason a vessel of potash was placed within the receiver. The air-pump employed gave a very good vacuum; when all the connections were made and the pump exhausted there was often scarcely any appreciable difference in the levels of the columns of mercury in the gauge. For temperatures up to 100° the flask containing the acid was heated in a beaker of water; for higher temperatures oil was used. Soon after commencing the experiments it was found necessary to make an arrangement for the purpose of stirring up the viscous acid and exposing fresh surfaces to the vacuum, and the following plan was devised:—A test-tube, which fitted easily the neck of the flask, was shortened by removing evenly a portion of the open end. It was then inverted and pushed down into the flask, so that when the open end was below the surface of the acid the closed end extended sufficiently far into the neck of the flask to prevent the tube from being thrown down by the ebullition of the liquid. The vapour given off from the acid within the tube became gradually expanded as the temperature rose, and passed in a stream of bubbles through the acid, keeping it well agitated. The tube also served the purpose of preventing splashing from the boiling acid up into the neck of the small flask.

Some selenic acid, which had been previously partially concentrated, was kept in an open dish on the water-bath

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* A Paper read before the Royal Society, May 2, 1889.

for four hours and its strength then determined: 0·6364 grm. required for neutralisation 14·72 c.c. of seminormal soda solution, equivalent to 83·68 per cent of selenic acid —a strength intermediate between a monohydrate and a dihydrate. The acid thus obtained at 100° under the ordinary pressure of the atmosphere, was stronger than that obtained by Graham from dilute sulphuric acid by heating it to the same temperature in a vacuum until it ceased to lose weight—the dihydrate $H_2SO_4,2H_2O$ remaining, showing the greater affinity for water possessed by the latter acid.

Selenic acid, concentrated as above described, was poured into the flask previously referred to, and gradually heated. Weak selenic acid commenced to pass over at 55°, evidenced by the potash liquefying and effervescing, owing to the presence of potassium carbonate which it contained, being the ordinary commercial potash. It was then heated slowly up to 100°, kept at that temperature so long as any acid distilled over, and the strength of the residue taken; 0·9432 grm. required for neutralisation 24·10 c.c. of seminormal soda solution, equivalent to 92·44 per cent of selenic acid. Subsequent to this experiment, acids heated on various occasions to 100° were found to have the following percentages of anhydrous selenic acid:—92·03, 92·08, 93·28, and 93·70; the different results being found due to the varying conditions of the experiments, such as the length of time of heating, the quantity of potash and its proximity to the acid, the amount of the latter and the size of the flask containing it.

The acid which had been heated to 100° was next heated to 150°. At the latter temperature the more or less dilute acid distilling over appeared in the form of dense white fumes resembling those of sulphuric acid. 0·6898 grm. of the residue left neutralised 18·42 c.c. of semi-normal soda solution, equivalent to 96·58 per cent of selenic acid. It was again heated to 150°, and kept at that temperature so long as any acid distilled over: 0·417 grm. of the residue left neutralised 11·21 c.c. of semi-normal soda, equivalent to 97·25 per cent of selenic acid.

A fresh portion of acid was heated to 155° and kept for some time at that temperature: 0·8045 grm. of the residue neutralised 21·72 c.c. of semi-normal soda, showing 97·67 per cent of selenic acid. It was next heated to 162°, and the strength of the residue taken: 0·7291 grm. neutralised 19·72 c.c. of semi-normal soda, equivalent to 97·85 per cent of selenic acid.

The same acid was then heated to 216°, and the residue obtained was allowed to remain in the flask during the night. In the morning it was found to be frozen into a crystalline mass so hard that it was necessary to use a steel chisel in order to remove portions for examination. When dissolved in water and tested it was found to contain some selenium dioxide. Trials were then made to ascertain if a lower temperature would produce a similar result without decomposition of the acid; 180° was found to be sufficient for the purpose, and the following course was finally adopted:—The acid which had been concentrated on the water-bath, as far as possible, was heated gradually in the flask to 100°, and kept at that temperature so long as any acid distilled over, the greater part of the water being thus removed. The U-tube was then disconnected, emptied, and re-filled with stick potash. The flask was next heated gradually to 180°, kept at that temperature until no more acid distilled over, and then immediately cooled. A still better arrangement was to use so little acid that it was unnecessary to change the potash. The acid was heated gradually and continuously up to 180°, allowing bubbles to pass slowly through it, as before described. When 180° was reached the potash was watched, and as soon as it ceased to be acted upon, the flask was immediately cooled. An hour or less was generally found sufficient time for a small quantity of acid.

A specimen obtained in this way was found, when examined, to be very free from selenium dioxide, a little of it diluted with water and saturated with hydrogen sulphide merely giving a faint colouration without any precipitate. Another portion was acidified with hydrochloric acid and barium chloride added; on boiling the filtrate with stannous chloride it only became darkened in colour without any precipitation of selenium. 0·6725 grm. was taken to estimate the strength. 18·54 c.c. of semi-normal soda were required for neutralisation, equivalent to 99·73 per cent of selenic acid; 0·724 grm. of another acid prepared in a similar way, but which contained rather more selenium dioxide than the last, required for neutralisation 19·94 c.c. of semi-normal soda, equivalent to 99·64 per cent of selenic acid. A portion of a third acid weighing 0·329 grm., was dissolved in water, barium chloride added, and also hydrochloric acid in order to prevent any selenious acid from precipitating. The resulting barium selenate weighed 0·6337 grm., equivalent to 99·75 per cent of selenic acid. As has been already mentioned, the acid employed contained an acid potassium selenate equivalent to 0·07 per cent of neutral sodium selenate found. Taking this into account, and calculating on the acid with the sodium selenate deducted, the three results become respectively—

I.	II.	III.
99·80	99·71	99·77

The difference between the above results and 100 per cent must be ascribed partly to the very hygroscopic character of the acid in the anhydrous condition, and consequent slight absorption of moisture during the process of weighing. It is necessary to observe, however, that in making the above calculations, and all through in this paper, 78·87 has been adopted as the atomic weight of selenium, the number given by Meyer and Seubert in their "Recalculations of the Atomic Weights." If 78·80, the number given in Clarke's "Recalculations," be taken, the three results become—

I.	II.	III.
99·75	99·66	99·72

Petersson and Ekman state that the results of a great many analyses show that the most probable atomic weight of selenium is 79·08 (*Berichte der Deutschen Chemischen Gesellschaft*, ix., 1210). If this number be taken, the above percentages become respectively—

I.	II.	III.
99·94	99·85	99·91

The results arrived at from the foregoing experiments lead to the conclusion that *at 180° in a vacuum, selenic acid parts with all combined water, and remains as the anhydrous acid*, H_2SeO_4.

It may be well here to summarise the precautions necessary to be taken in preparing the anhydrous acid, so far as we have ascertained them. They are briefly as follows:—To use for the purpose an acid as pure as possible, to have a thoroughly good vacuum, to avoid too high or prolonged heating, and to keep a sufficient quantity of solid potash in close proximity to the acid all through—which may be arranged by using a small flask, and having the tube leading from it short and wide.

(To be continued).

Enamelled Steel Dishes.—Messrs. Jones Brothers and Co., of Wolverhampton, have lately introduced dishes made of very thin sheet-steel, smoothly coated with highly glazed white enamel. The one before us is rectangular in shape, and has ridges along the bottom so as to fit it for photographic requirements, but the same kind of enamelled steel dish could easily be made of shapes and sizes to suit the chemical laboratory; and although we have not tested the glaze we should say that a glaze which is sufficiently resisting to stand the chemical agent used in photography would be of considerable use in many branches of chemistry.

NOTE ON A SEDIMENT DEPOSITED FROM A MIXTURE USED IN CALICO PRINTING.

By J. A. WILSON.

In the production of the Turkey-red discharge style a mixture is made for producing the yellow pattern, consisting of tartaric acid, lemon juice, and lead nitrate. On standing this liquor deposits the above sediment, consisting of lead and tartaric, citric, and other organic acids, probably from the lemon juice, since lemon juice contains 4 or 5 ounces of organic acids, not citric or tartaric, to the gallon.

An analysis of the sediment gave—

	Per cent.
Moisture	9·48
Tartaric acid	34·87
Citric acid	0·04
Other organic acids	6·01
Lead	46·66
Other matters and loss	2·94
	100·00

The Laboratory, Tottington,
April 16 1889.

SOME OBSERVATIONS OF THE INFLUENCE OF ADHESION AND SOLUTION ON AFFINITY.

By H. N. WARREN, Research Analyst.

The important influence of cohesion in preventing chemical action, and the manner in which the force of adhesion, as displayed in the production of solution, may act in favouring chemical action, are well known to those employed in analytical pursuits, frequently observed by the incautious addition of too strong an acid when employing barium nitrate as a precipitant for the sulphates. Since barium nitrate is soluble in dilute acid and water, but insoluble in a concentrated acid, when concentrated nitric acid is added to barium carbonate it occasions but a slight effervescence, which speedily terminates, although the acid may be in large excess. This may even be preserved for an indefinite time provided it be hermetically sealed in a glass tube; if the liquid, however, be diluted with a small quantity of water a brisk action is temporarily renewed, but again soon terminates. On a further addition it recurs, and eventually, on the addition of a sufficiency of water, the whole of the barium carbonate is decomposed and dissolved. For a somewhat similar reason several alcoholic solutions of acids are without action on the carbonates, unless the resulting salt be soluble in alcohol. Thus, an alcoholic solution of tartaric acid will not decompose the carbonate of potassium.

An alcoholic solution of HCl is without action on potassium carbonate, but will decompose calcium carbonate. An alcoholic solution of nitric acid decomposes calcium carbonate but not potassium carbonate. The above-mentioned tartrates are insoluble in alcohol, so are potassium chloride and nitrate, but calcium chloride and calcium nitrate are freely soluble in that menstruum. Again, metallic magnesium will not decompose water at all ordinary temperatures, but if previously amalgamated with mercury, and the amalgam thus obtained be thrown into water, decomposition at once takes place. On the addition of ammonium sulphide to an alkaline solution containing a salt of nickel a dense black somewhat flocculent precipitate of nickel sulphide is produced, but on maintaining a slow current of sulphuretted hydrogen through a hot solution of nickel picrate, the sulphide is gradually precipitated upon the sides of the vessel containing the same in the form of a brilliant mirror, surpassing in appearance the finest quality of plumbago.

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A NEW AND EASY METHOD FOR THE RAPID AND SURE DETECTION OF MERCURY IN MINERALS.

By ALEXANDER JOHNSTONE, F.G.S. (London and Paris),
Assistant to the Professor of Geology and Mineralogy in the University of Edinburgh.

A student of modern mineralogy has neither the time nor the inclination to determine qualitatively the metallic and non-metallic elements of the minerals which are continually being brought under his notice by the tedious, if accurate, ordinary wet way analytical methods of the chemist. And yet it is of the utmost importance that he should be able to identify with perfect accuracy the elementary or simple substances of the naturally occurring raw materials of his science—but in the very shortest possible space of time. Accordingly, the most advanced mineralogists of to-day, in determining the composition of their ores and veinstones, very properly make use, as much as possible, of the rapid blowpipe methods of testing, such as heating, with and without fluxes and other chemicals, in partially closed tubes, in open tubes, on charcoal, platinum, aluminium, in borax, boracic acid, &c., &c. The whole department of blowpipe analysis, however, has been for the last score of years so sadly neglected, not only in this country and America, but also in Germany and Scandinavia, where its foundation was laid at the end of the last and the beginning of the present century, that the mineralogist is not unfrequently, against his will and the best interests of his science, forced to fall back, for confirmations at least, on the slow processes of present day analytical chemistry.

With the object in view of completing a working system of quick and certain determinations of elements, on the basis of Berzelius's and Plattner's blowpipe operations, the author has spent much time in carefully investigating the nature and reactions of the known tests, and where these have failed to give under all circumstances rapid and satisfactory results, in seeking for new ones to supply their places. As a result of this search for other and better means of identification two new tests have been discovered, one for antimony and the other for mercury.

An account of the former test has already been published in the Chemical News, vol. lviii., p. 296, and vol. lix., p. 15; to give a description of the latter is the object of the present communication.

This new method for the detection of mercury, which has been in operation in the author's laboratories for the last six months, depends on the fact that when a small quantity of iodine in the form of vapour, *newly liberated* from a compound, is allowed to impinge on metallic mercury, it instantly converts it into the characteristic scarlet mercuric iodide. The method of applying the test and the various preliminaries necessary in every case of blowpipe analysis are briefly detailed below.

The author may here mention that he has very carefully examined all known mercury minerals, and other minerals containing only the slightest trace of that metal, by his process, which in every case has rapidly yielded very satisfactory results.

The first operation in blowpipe analysis consists in heating in a narrow glass tube, closed at one end, first the powdered body *alone*, and afterwards, if the previous heating affords certain results, the same with the *addition of a flux*. A substance containing mercury yields, when heated by itself in the closed tube, a sublimate which is either metallic or non-metallic in character. Most compounds of mercury are decomposed by heat alone, and so furnish, when subjected to a certain temperature, the former sublimate; but mercur*ous* chloride, and bromide, and mercur*ic* chloride and iodide, and to a certain extent the sulphide also, are volatile without decomposition, and accordingly produce sublimates of non-metallic lustre. All compounds of mercury, however, when dry and intimately mixed with three times their bulk of ordinary anhydrous fusion mixture ($K_2CO_3+Na_2CO_3$), yield, under the influence of heat, metallic mercury, which condenses on the cooler portions of the tube above the assay. This metallic sublimate, when unmixed with other matters (metallic or otherwise), and in large quantity, usually shows distinctly enough its characteristic globules; but when impure or small in amount the globular character is not at all evident, and it may then be quite easily mistaken for arsenic alone, and sometimes, though rarely, for antimony. In the latter case this new process will afford quick and certain means of determination, while in the former it should also prove useful, as trustworthy confirmation. If the substance, then, which is undergoing examination gives with, if not without the aid of flux, a metallic sublimate, pour into the tube two drops of concentrated nitric acid, and immediately afterwards a single drop of a fairly strong solution of potassium iodide in water. The nitric acid *at once* splits up the iodide of potassium, and the iodine is liberated in fumes which act on any mercury in the sublimate or in the assay, and *instantly* produce the unique scarlet iodide of mercury, which is largely thrown up against the sides of the tube. The antimony tri-iodide produced in like manner is brownish in colour, and becomes yellowish after exposure to the air for some little time. The arsenic tri-iodide is yellow, and this, as in the case of mercury, forms at once; but if the bottom of the tube containing the excess of nitric acid be heated slightly the fumes from that body quickly decompose the iodide, and a spongy dark grey mass of arsenic is driven all around the upper part, at least, of the tube. In the same way the nitric acid quickly decomposes the antimony iodide, while it does not act at all *nearly so rapidly* on the mercuric iodide. The table below shows perhaps more clearly how this test would be applied in the ordinary course of blowpipe analysis.

Table for the Detection of Mercury in Minerals.

a. Heat the powdered substance in a small piece of hard glass tubing (say with a ¼-inch bore) closed at one end.

1. A *metallic* sublimate is produced. Proceed further by *b.*

2. A non-metallic sublimate is formed. Heat a fresh portion of the substance *mixed* with about three times its bulk of fusion mixture. A metallic sublimate forms. Proceed further by *b.*

3. There is no evidence of the slightest volatilisation other than water. *No* mercury is present in the mineral.

b. Pour into the tube containing the metallic sublimate and assay *two* drops of strong nitric acid, then at once *one* drop of potassium iodide solution, and heat the bottom of the tube *a little.* A scarlet mass forms and remains on the sides of the tube. Mercury is present in the body tested.

Detection of VERY MINUTE *Quantities of Mercury.*

When the mercury occurs in very minute quantities the metallic sublimate described above may not be perceptible on the sides of the glass tube. In this case, when only the *merest traces* of mercury are looked for in the substance, proceed as follows:—Place in the closed tube, as already detailed, the mixture of powdered substance and flux, and introduce on the end of a stout wire a small piece of gold leaf, which should be held just over the surface of the mixture. Now apply heat for a minute or so. *Any* mercury present will be volatilised, and the vapour will combine with the gold to form a whitish amalgam. Take out the wire with the gold leaf on its end after sufficient heat has been applied to the mixture in the tube. Touch the surface of the leaf which faced the assay with a single drop of concentrated nitric acid, and on the top of this add immediately a drop of potassium iodide solution; the fine scarlet iodide will at once very distinctly appear on the amalgamated surface of the gold leaf if any mercury whatever was present in the body subjected to examination.

SEPARATION OF COPPER FROM LEAD, CADMIUM, MAGNESIUM, MANGANESE, MERCURY, ZINC, &c.

By G. VON KNORRE.

The metals must be present as sulphates or chlorides. The solution, which, if necessary, is reduced to a small volume by evaporation, is neutralised with ammonia if free mineral acids are present, and acidified with a few drops of hydrochloric acid. It is then heated almost to a boil, and there is added an excess (five parts to about one of the copper present) of nitroso-β-naphthol, previously dissolved in boiling acetic acid at 50 per cent. It is convenient to filter the hot solution of nitroso-β-naphthol through a moistened filter and let the filtrate flow into the hot solution containing the metals, stirring meanwhile. After the liquid had stood for some hours in the cold the copper nitroso-naphthol is filtered off and washed with cold water until a drop of the filtrate, if evaporated on platinum foil, leaves no solid residue. The washings, even then, have a yellow colour which does not affect the results. When dry, the filter and precipitate are placed in a capacious tared porcelain crucible, the filter is closed, the crucible is loosely covered, placed upon a sheet-iron plate, and cautiously heated with a small flame until vapours no longer escape. The temperature is then gradually raised, and the crucible is finally ignited with access of air until the carbon is burnt off, when the copper oxide can be weighed. If the quantity of copper nitroso-naphthol is considerable, pure oxalic acid or ammonium oxalate should be added to the precipitate on incineration in order to secure quiet decomposition. In presence of silver the copper precipitate is argentiferous.—*Zeitschrift für Analytische Chemie.*

ON THE FORMATION OF MARINE BOILER INCRUSTATIONS.*

By Professor V. B. LEWES, F.C.S., F.I.C.,
Royal Naval College Associate.

In the older forms of marine boilers, working at comparatively low pressures, sea water was almost universally employed; but with the introduction of high pressure tubular boilers the amount of deposit formed was so serious, and the difficulty of cleaning out the incrustation from between the tubes so great, that it became almost imperative to discontinue the use of the sea water, and to rather accept the expense of supplying the boilers with distilled water, than risk the burning and destruction of the tubes and plates in inaccessible portions, where the deposit had to be allowed to collect until the time could be spared for a complete clean out and refit. But, after several years' experience of this system, it is found that the trouble has only been transferred from the steam boilers to the distilling apparatus, and that the enormous deposits formed in the latter cause them frequently to

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* Read at the Thirtieth Session of the Institution of Naval Architects, April 11th, 1889. Admiral Sir John Hay, President, in the Chair.

break down or become in some way or another unfit for use, so necessitating the introduction of sea water into the boiler to eke out the supply of distilled water from the condensers.

Under these circumstances, I have thought that it might be acceptable to bring before the members of this Institution the results of a series of experiments recently made in the laboratories at Greenwich, together with some suggestions founded upon them, which might be of value in attempting a solution of this very serious evil.

I propose in this paper to show the nature and cause of the deposits formed from each class of water used in marine boilers, and then, by a study of the characteristic properties of each constituent of the incrustation, to arrive, if possible, at a method for its prevention.

The waters at present in use in marine boilers may be classified as—

1. Sea water.
2. Distilled water.
3. Mixtures of (*a*) sea water and distilled water; (*b*) sea water and fresh water.

By fresh water is here meant the water, either from spring, well, or river, which is taken on board when in port, and which, under certain circumstances, is used mixed with condensed water or sea water, in the boiler.

Such water is very variable in composition, but, as a rule, contains as its chief saline constituents the carbonates of lime and magnesia, held in solution by carbonic acid present in the water, and also small quantities of the sulphates of these metals, and traces of common salt.

Sea water contains a far higher proportion of saline matters in solution than fresh water, and also in totally different proportions, as although sea water is only river water concentrated by the evaporative power of the sun's rays during long ages, yet, owing to deposition during the flow of the water down rivers, and also to its being used by certain forms of marine life, calcic carbonate (carbonate of lime), which is the chief saline constituent of fresh water, is reduced to a mere trace in salt water, whilst the salt has become the all important constituent, and the sulphates of lime and magnesia, together with chloride of magnesium, are also present.

The wide difference in composition of fresh and salt water may be seen from the following analyses:—

Salts in Solution in River and Sea Water.
Grains per Gallon.

	River water. Thames.	Sea water. Lowestoft.
Calcic carbonate (chalk)	10·80	3·9
Calcic sulphate (gypsum)	3·00	93·1
Magnesic sulphate	0·25	124·8
Magnesic chloride		220·5
Magnesic carbonate	1·25	trace
Sodic chloride (salt)	1·80	1850·1
Silica (sandy matter)	0·56	8·4
Oxides of iron and alumina	0·27	trace
Organic matter	2·36	trace

Distilled water is presumably free from all dissolved solids, but the condenser water always contains some of the lubricants from the cylinder; and in the days of animal and vegetable lubricators, like fat and oils other than mineral, this water, on account of the super-heated steam breaking the oils up and liberating fatty acids, caused a large amount of damage to the plates of the boiler; but with the use of mineral oil lubricators of the right kind this trouble is done away with, and a slight coating of organic matter is, as a rule, the only incrustation found in a boiler using distilled and condenser water only.

The great difference existing between sea and fresh water would lead one to expect a wide difference also in the kind of deposit formed from them, and this is found to be the case, as the following analyses of incrustations formed in the boilers of steamers using fresh river water, the brackish water at the mouth of a river, and sea water respectively, show:—

	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

These may be taken as typical deposits, and show that with fresh water the incrustation may be looked upon as consisting of calcic carbonate, with small quantities of other compounds; that with a mixture of fresh and salt water the deposit consists of nearly equal parts of the calcic carbonate and sulphate; whilst the sea water gives practically calcic sulphate.

The presence of calcic sulphate exercises a very marked influence upon the condition and physical properties of the incrustation, as, under the conditions in which it is formed in a boiler, it separates in a crystalline form, and binds the deposit into a hard mass, an action which is also aided by the presence of magnesic hydrate.

A deposit consisting of calcic carbonate only, or of calcic carbonate and traces of the oxides of iron and alumina, sodic chloride, &c., is separated as a soft powder, which remains suspended in the water for some time, and which can fairly easily be removed from the boiler on cleaning; whilst, if calcic sulphate is present, the scale is extremely hard, and generally requires the use of hammer and chisel to detach it from the plates and tubes, an operation which is extremely injurious, and tends to shorten the life of the boiler.

The three principal constituents of boiler incrustations may therefore be looked upon as calcic carbonate, calcic sulphate, and magnesic hydrate, and the causes which lead to their deposition must now be considered.

Calcic carbonate is practically insoluble in pure water, that is to say, it requires more than 10,000 parts of pure water to dissolve one part of the carbonate;[*] but carbonic acid, which is present in all natural waters, when in contact with calcic carbonate converts it into bicarbonate, which is soluble, and this forms the so-called "temporary hardness" in fresh waters. On heating such a water the bicarbonate is decomposed, carbonic acid gas escapes, and the calcic carbonate being insoluble, is deposited. Calcic carbonate is slightly more soluble in saline solutions, such as sea water, than in pure water, but the difference is so small that the above may be looked upon as applying equally to fresh and salt water.

Calcic sulphate is to the marine engineer the most important constituent of boiler incrustation, and its separation as a deposit from water is dependent upon a totally different class of phenomena to those which bring about the precipitation of the calcic carbonate. Calcic sulphate is dissolved in water by the solvent power of the water itself, and not through the agency of carbon dioxide, and therefore merely boiling water at ordinary pressures does not suffice to cause its deposition, and for this reason, it forms, together with soluble magnesium salts, the "permanent hardness" of fresh water.

The solubility of calcic sulphate in pure water varies very considerably with the temperature.

So that calcic sulphate is most soluble in water at 95° F. or 35° C.[†] roughly, one part of calcic sulphate being dissolved in 400 parts of water; and, inasmuch as the solubility of the salt is considerably decreased at 212° F.

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[*] Soluble in 16,000 parts of pure water according to Brande; 12,858 according to Kremers; 16,000 to 24,000 according to Buchholz.

[†] Poggiale, *Ann. Ch. et Phys.*

100 parts of water, at a temperature of		Dissolve calcic sulphate.
32° F. or	0° C.	0·205
41° ,,	5°	0·219
53·6° ,,	12°	0·233
68° ,,	20°	0·241
86° ,,	30°	0·249
95° ,,	35°	0·254
104° ,,	40°	0·252
122° ,,	50°	0·251
140° ,,	60°	0·248
158° ,,	70°	0·244
176° ,,	80°	0·239
194° ,,	90°	0·231
212° ,,	100°	0·217

or 100° C., if a saturated solution be taken at 95° F. or 35° C., and is then heated to 212° F. or 100° C. a precipitation of a portion of the calcic sulphate will take place.

Calcic sulphate is much more soluble in a saline solution, such as sea water, than it is in fresh water, but its solubility rapidly decreases, (1) on concentration of the saline solution, and (2) on increase of temperature and pressure.

To trace the effect of concentration on the calcic sulphate a considerable volume of sea water was taken and slowly evaporated at ordinary atmospheric pressure, the composition of the water being ascertained by analysis, and the density of the water being taken at successive stages of the concentration.

Sea water having a density of 1·027 ($\frac{1}{32}$ salinometer) was allowed to concentrate by exposure to air until it had a density of 1·029, and it was then evaporated, and analyses made at the following densities :—

Saline Constituents per Cent.

Density	1·029	1·05	1·09	1·225
Sodic chloride	2·6521	4·4201	7·9563	23·8689
Calcic sulphate	0·1305	0·2175	0·3915	none
Calcic carbonate . ..	0·0103	0·0171	none	none
Magnesic carbonate ..	0·0065	0·0032	none	none
Magnesic chloride ..	0·2320	0·3865	0·6960	2·0880
Magnesic sulphate ..	0·1890	0·3150	0·5670	1·7010

The deposits formed during concentration were carefully collected and analysed, and it was found that the deposit formed up to the density 1·05 consisted of basic magnesic carbonate only. The deposit taking place between densities 1·05 and 1·09 consisted of—

Basic magnesic carbonate and hydrate	17·6
Calcic carbonate	82·4
	100·0

no trace of calcic sulphate having yet come down, whilst between the densities 1·09 and 1·225 the deposit consisted of pure calcic sulphate only, so that on the concentration of the sea water three distinct stages of deposition may be traced :—

1. Deposition of basic magnesic carbonate.
2. Deposition of calcic carbonate with remaining traces of the basic magnesic carbonate and hydrate, and, finally,
3. Deposition of the calcic sulphate.

If the sea water be heated and concentrated above a density of 1·225, the salt commences to crystallise out.

The deposition of the calcic sulphate during the concentration of the sea water is due to two causes ; in the first place, although it is more soluble in a dilute solution of salt than in fresh water, yet it reaches its maximum solubility at a density of 1·033, and after this point concentration of the saline solution diminishes the amount which can be held in solution, and the calcic sulphate is perfectly insoluble in a saturated brine. The second cause for its deposition is the rise in boiling-point which accompanies the increase in density, the higher the temperature the less the solubility of the calcic sulphate, so that when a temperature of 284° to 302° F., or 140° to 150° C. is reached it becomes perfectly insoluble, both in sea and fresh water.

These experiments show that, if sea water be boiled merely under atmospheric conditions, it would be quite possible, by taking care that its density does not rise above a certain point (1·09), to prevent the deposition of the calcic sulphate ; but any such regulation of the density is rendered abortive by the fact that pressure and consequent raising of the boiling-point acts upon the calcic sulphate in solution in exactly the same way as concentration and increased temperature, so that in the older forms of boiler, working even at a comparatively low pressure, most of the sulphate was deposited, whilst in the high pressure boilers now in use, if the water contains the smallest trace of calcic sulphate, it will be deposited ; and, as any deposit formed amongst the tubes in such a boiler would be almost impossible to get at to clean away, it is practically impossible to use sea water in them, and they are supplied with the water from the condenser augmented by distilled water made in special distilling plant. The question has been raised as to whether, if sea water were mixed with distilled water so as to reduce its density very low, it would deposit the calcic sulphate ; but experiment shows that, even if sea water is mixed with many hundred times its bulk of distilled water, the minute trace present is deposited under pressure when the temperature approaches 284° F. or 140° C. So that when, through a breakdown in the distilling apparatus, sea water has to be used with the condenser water in even very small quantities, slight scale is sure to be formed. When a saline solution containing calcic sulphate is heated under pressure or concentrated until calcic sulphate begins to separate, the sulphate will continue to precipitate even after the liquid has cooled down or the pressure has been removed ; and, finally, when calcic sulphate has separated at a high temperature or pressure from sea water, even though the water has only the ordinary density (1·027), the rate at which the sulphate will re-dissolve is so extremely slow that the re-solution is practically nil.

These two last properties are due to the form in which the calcic sulphate separates from sea water under pressure. Calcic sulphate occurs in nature as gypsum in which each molecule of calcic sulphate is combined with two molecules of water of crystallisation : when calcic sulphate is deposited from sea water in a boiler it comes down in small crystals containing two molecules of calcic sulphate to one of water ; whilst, after deposition in the boiler and in contact with the heated plates and tubes, it undergoes a further change of crystalline form, loses all water, and becomes "anhydrite," which is pure calcic sulphate free from water of crystallisation, and it is this change in crystalline form which binds deposits containing it into such a hard mass.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 18th, 1889.

Mr. William Crookes, F.R.S., Vice-President, in the Chair.

Messrs. J. L. Hoskyns-Abrahall, D. Carmody, C. J. McNally, M.D., C. Proctor, and W. J. Waterhouse were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Evans, care of Messrs. Savory and Moore, 86, King's Road, Brighton ; William Taylor Gibbs, Richmond House, Plaistow, Essex; Byron B. Goldsmith, 19, East 74th Street, New York City, U.S.A.; Charles James Grist, West View, Grange Road, Egham; Alfred Edward Tibson, 79, South Hill Park, Hampstead Heath, N.W.; Ignatius Singer, Nailsworth, South Australia.

The following papers were read:—

36. "*Sawarri Fat.*" By. J. Lewkowitsch, Ph.D.

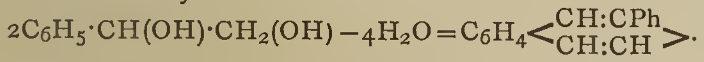
Sawarri nuts contain 63 per cent of a white solid fat, of which the author has determined the physical constants. The density is 0·8981 at 40° C. relatively to that of water at 15° C.; the melting-point lies between 29·5° C. and 35·5° C.; the solidifying-point at from 23·3° to 29° C. The acids from the fat melt at 48·3° C. to 50° C., and solidify at 47 to 46° C.

Saponification value (Köttsdorffer)	199·51	
Insoluble acids (Hehner's value)	96·91	p. c.
Glycerol determined by the acetin method .	9·14	,,
Free acids	2·4	,,
Mean molecular weight of the acids	272·8	,,
Soluble acids (Reichert's value)	0·65	,,
Iodine value of the fat (v. Hübl)	49·5	,,
Iodine value of the acids	51·5	,,
Acetyl value (Benedikt)..	77·5	,,
Iodine value of the acetylised fatty acids ..	51·8	,,

The author intends to examine the acids in the manner indicated by Hazura.

37. "*Note on β-Phenylnaphthalene.*" By Watson Smith.

Zincke and Breuer (*Annalen*, ccxxvi., 23—60) and Zincke (*Annalen*, ccxl., 137—146) succeeded in synthesising β-phenylnaphthalene by the dehydration and condensation of styrolene alcohol—



$$2C_6H_5\cdot CH(OH)\cdot CH_2(OH) - 4H_2O = C_6H_4<\begin{matrix}CH:CPh\\CH:CH\end{matrix}>.$$

β-Phenylnaphthalene melts at 101°, and is easily soluble in alcohol, ether, benzene, and chloroform; on oxidation with chromic anhydride in glacial acetic acid solution it yields a quinone which crystallises in fine bright yellow needles, melting at 110°; this quinone possesses the characteristic property of rapidly polymerising on exposure of its solution to light, an insoluble polymeride being precipitated. In 1879 the author obtained a phenylnaphthalene by passing a mixture of bromobenzene and naphthalene through a red-hot tube (*Chem. Soc. Trans.*, 1881, 546), and for reasons then fully stated, he considered it to be β-phenylnaphthalene. Zincke attempted to obtain the hydrocarbon by the author's method, but seems to have failed, as he gives it as his opinion that it cannot be prepared in this way, or, that if a hydrocarbon is formed, it must be α-phenylnaphthalene. The author's attention was recently called to these facts, and especially to the latter statement by Professor Schorlemmer, and he was thus led to attempt the preparation of Zincke's quinone from some of a fairly abundant stock of phenylnaphthalene still remaining. The result was that the conversion into the quinone by Zincke's method proceeded with the utmost ease, a product answering in every respect to the quinone described by that chemist being obtained, amply confirming the author's earlier conclusion that the phenylnaphthalene obtained by him was the β-isomeride.

The author cannot understand that any such difficulty as Zincke describes should arise in preparing phenylnaphthalene by the pyrogentic method. Three products are principally obtained after removing excess of bromobenzene, viz., naphthalene, dinaphthyl, and phenylnaphthalene; there may also be a minute quantity of diphenyl. Fractional distillation easily removes naphthalene and diphenyl, leaving phenylnaphthalene boiling at 345°, and dinaphthyl boiling above 440°. Boiling with somewhat dilute alcohol now extracts phenylnaphthalene, and leaves behind dinaphthyl, which is insoluble in this liquid. Usually a second sublimation is necessary to obtain a product melting at 101°, that first obtained melting at about 96° C.

Discussion.

Dr. Armstrong remarked that it was most probable that the original product was the α-derivative; the proof now advanced that the hydrocarbon obtained by Mr. Watson Smith's method was the β-compound was of interest, as affording an indication that isomeric change of the α- into the β-derivative took place at high temperatures.

38. "*Nitro-β-Chloronaphthalene.*" By Henry E. Armstrong and W. P. Wynne.

β-Chloronaphthalene is readily nitrated by dissolving it in its own weight of glacial acetic acid, and adding about 2½ molecular proportions of nitric acid ($d = 1·42$); the mixture is allowed to stand for two or three days. β-Bromonaphthalene behaves similarly. Nitro-β-chloronaphthalene crystallises from spirit in sulphur-yellow needles melting at 116°; on distillation with PCl_5 it yields the dichloronaphthalene melting at 63·5°, and is therefore the heteronucleal 1 : 2′ α-nitro-β-chloronaphthalene. On reduction it yields the corresponding amidochloronaphthalene. The authors are studying the sulphonic acids derived from this amine.

39. "*The Action of Halogens on Betanaphthol.*" By Henry E. Armstrong and E. C. Rossiter.

If betanaphthol be treated with a single molecular proportion of bromine it is converted, as shown by Smith, into a homonucleal-monobromo derivative, which presumably corresponds in constitution with 1 : 2 chlorobetanaphthol; if an excess of bromine be used, a tetrabromonaphthol is produced, and as this yields bromophthalic acid it contains one of its four bromine atoms in the second nucleus. The authors have sought to determine at what stage the bromine atom becomes introduced into the second nucleus.

By treating betanaphthol with two molecular proportions of bromine it is almost entirely converted into dibromobetanaphthol; this crystallises from acetic acid with one molecular proportion of the acid in prisms melting at 84°; the acid of crystallisation is spontaneously given off on exposure of the crystals. The pure substance crystallises from petroleum spirit in woolly needles melting at 106°. On oxidation with alkaline permanganate it yields bromophthalic acid; whence it follows that on introducing a second atom of bromine into betanaphthol it enters the non-hydroxylised nucleus.

The preparation of a tribromonaphthol appears to present difficulties, a mixture of di- and tetra-derivatives being usually obtained. Together with the bromonaphthols, relatively small amounts of yellow products are always formed, which probably correspond to the chlorinated keto-compounds described by Zincke.

When betanaphthol is submitted to the action of a single molecular proportion of chlorine, it yields but a relatively small amount of chlorobetanaphthol, the chief product being a resinous substance (Cleve); this result has found an explanation in Zincke's experiments, which show that chlorine tends to convert betanaphthol into additive keto-compounds. The authors find that a theoretical yield of chlorobetanaphthol (m.p. 69°) is obtainable by gently warming betanaphthol suspended in thrice its weight of carbon bisulphide with a molecular proportion of sulphuryl chloride, SO_2Cl_2. On attempting to prepare dichlorobetanaphthol by further treatment with SO_2Cl_2, little besides resinous matter was obtained; alphanaphthol, in like manner, when submitted to the action of two molecular proportions of the chloride, afforded a large amount of resinous matter. Chlorobetanaphthol is almost entirely converted by a single molecular proportion of bromine into a bromochlorobetanaphthol, corresponding to the dibromobetanaphthol previously described. It also crystallises with one molecular proportion of acetic acid in long prismatic needles melting at 92°; the pure substance sublimes in fine needles melting at 101°, but does not crystallise satisfactorily from any solvent.

Schaeffer's betanaphtholsulphonic acid is converted by bromine into a monobromo derivative, which may also be obtained by sulphonating Smith's bromobetanaphthol (Armstrong and Graham); the corresponding chloro-acid is readily formed on sulphonating chlorobetanaphthol, together with a small quantity of an isomeric acid yielding more soluble salts. The brom- and chlor-acids behave alike on treatment with excess of bromine, being converted into the bromhydroxynaphthaquinonesulphonate, $C_{10}H_3BrO_2(OH)\cdot SO_3H$, first described by Armstrong and Graham; a relatively very small proportion of dibromhydroxynaphthaquinone being also produced. Armstrong and Graham came to the conclusion that the bromhydroxysulphonate — which contains the bromine in the quinonic nucleus—was the final product of the action of bromine, but later experiments have shown that this is only the case when the experiment is made by treating Schaeffer's salt with bromine; if the pure bromhydroxyquinonesulphonate be used instead, the quinonic nucleus becomes destroyed and a sulphophthalic derivative is obtained. The hydrogen bromide produced in the formation of the quinone sulphonate from Schaeffer's salt, in fact, protects the former from oxidation.

Armstrong and Graham succeeded in obtaining only a small quantity of a dibromo-derivative from Schaeffer's acid, the tendency being for the action to extend at once to the formation of the quinonesulphonate; by brominating a solution of the potassium salt of Schaeffer's acid in muriatic acid, Armstrong and Streatfeild succeeded, however, in preparing a tribromo-derivative. Both the di- and the tri-bromo acid gave easily soluble salts, and, as on treatment with bromine, they were converted into quinone sulphonate, the bromine atoms are contained in the hydroxylised nuclueus. By sulphonating the above-described bromochloro- and dibromobetanaphthols, the authors have obtained sulphonic acids, the salts of which are difficultly soluble, and which, on treatment with bromine, yield a large proportion of the dibromhydroxynaphthaquinone already mentioned; the production of this compound is confirmatory of the heteronucleal constitution of the two di-derivatives of betanaphthol. Bromochlorobetanaphthol yields two isomeric acids on sulphonation; it is noteworthy that neither these nor the acid from the dibromo compound yield Schaeffer's acid on reduction; as this acid is obtained on reducing the acids produced on sulphonating chloro- and bromobetanaphthol, it follows that the sulphonation of the mono- and di-derivatives of betanaphthol takes place in a different manner—it may be that, as in the case of betanaphthol, a sulphate is first produced, and that the subsequent isomeric change takes a different course; or perhaps a sulphate is formed in the case of the mono-derivative, while direct sulphonation is affected in that of the di-derivative. The authors are engaged in further investigating the sulphonic acids of the chloro- and bromonaphthols generally.

40. "*β-Methoxynaphthalenesulphonic Acids.*" By J. Percival, B.A.

It has been shown by Armstrong and Amphlett that if β-ethoxynaphthalene be sulphonated by means of chlorosulphonic acid without application of heat, a mixture of two sulphonic acids is obtained, one of which corresponds to Schaeffer's betanaphtholsulphonic acid; and that if the product be heated on the water-bath for a short time this latter acid is alone obtained, an isomeric change taking place. The author has undertaken a series of experiments with the object of determining whether any effect is produced by varying the radicle introduced in place of the hydroxylic hydrogen of betanaphthol; in the first instance he has studied the behaviour of β-methoxynaphthalene prepared from betanaphthol, and finds that there are very marked differences to be observed in the behaviour of the methoxy- and ethoxy-compounds.

The product obtained without application of heat chiefly consists of an unstable acid together with a relatively small proportion of a stable acid corresponding to Schaeffer's betanaphtholsulphonic acid; but after heating during a couple of hours on the water-bath the unstable acid is no longer present, having undergone isomeric change into the stable acid. If the aqueous solution of the unstable acid be heated nearly to boiling, the acid is decomposed, β-methoxynaphthalene separating; in this way it is easy to ascertain the amount of unstable acid in the original product of sulphonation. Even a solution of the barium salt of the unstable acid gradually undergoes decomposition when evaporated, β-methoxynaphthalene and barium sulphate becoming separated. No such behaviour was noticed in the case of the barium salt of the unstable ethoxy acid, although this salt was observed to decompose at about the temperature at which the water of crystallisation was expelled, 130—140°. On adding bromine to a solution of the unstable methoxy acid, a precipitate is at once formed consisting of tribromo-β-methoxynaphthalene; this crystallises from benzene, in which it is very soluble, in long slender white needles melting at 105°; no such precipitate is obtained from the unstable ethoxy acid.

The salts of the unstable acid are very soluble, the potassium salt crystallising in plates, which aggregate into nodular masses, containing half a molecular proportion of water. The salts of the stable acid are difficultly soluble; like the corresponding ethoxy acid, it is readily converted by bromine into a bromo-β-methoxysulphonate, and ultimately into bromhydroxyquinonesulphonate, identical with that obtained from Schaeffer's acid.

41. "*The Acids Formed by Displacing NH_2 in Brönner's Betanaphthylaminesulphonic Acid by Halogens.*" By W. Houlding, B.Sc.

Arnell has shown that two isomeric acids are formed on sulphonating β-chloronaphthalene, and subsequent experiments by Forsling and others have proved that these acids correspond to the Badische and Brönner modifications of betanaphthylaminesulphonic acid; the 1 : 2′ acid is the chief product, and the 2 : 3′ acid the minor product, especially if chlorosulphonic acid be employed as sulphonating agent. Armstrong and Wynne have shown that although the minor product when heat is not applied, the 2 : 3′ acid becomes the major product if after sulphonation the crude acid be heated during several hours at 150—160°; and they have consequently suggested that the 2 : 3′ acid is not a direct product of sulphonation, but results entirely from the occurrence of isomeric change. β-Bromo- and β-iodonaphthalene were each found in like manner to afford two isomeric acids, which it was to be presumed corresponded to those obtained from β-chloronaphthalene; but Armstrong and Wynne have pointed out as noteworthy that the melting-point of the sulphochloride of the iodo acid obtained as minor product was abnormally low, thus—

	Chlorosulphochloride.	Bromosulphochloride.	Iodosulphochloride.
Major product ..	130°	147°	174°
Minor ,, ..	109	125	92·5

The author has therefore carefully compared the acids prepared from Brönner's 2 : 3′ betanaphthylaminesulphonic acid with those obtained by sulphonating β-chloro-, β-bromo-, and β-iodonaphthalene. As was to be expected, his results entirely confirm those of Forsling with reference to the identity of the chloro acid from Brönner's acid with the minor product of sulphonation of β-chloronaphthalene—that which affords a sulphochloride melting at 109°. It is noteworthy that both the chlorosulphochloride and chlorosulphobromide, m. p. 124°, yield the same sulphonamide melting at 183°, which is a proof of the non-occurrence of an isomeric change such as was observed by Gessner in the case of α-bromonaphthalenesulphonic acid. In like manner, the author finds that the bromo acid from Brönner's acid is identical with the minor product of sulphonation of β-bromonaphthalene: the salts of the acids are similar in appearance to those of the corresponding chlor acid, and are also all anhydrous; the sulphochloride melts at 124°; the sulphobromide at 118°: both sulphochloride and bromide yield the same sulphonamide, melting at about 204°. By distilling the bromosulphochloride with PCl_5 it is converted into a chlorobromonaphthalene, which crystallises in thin plates, melting at 137°; the corresponding dibromonaphthalene was obtained in small needles melting at 149°, but owing to the small amount at disposal this melting-point cannot be regarded as sufficiently determined. The iodo acid obtained from Brönner's acid was found to differ considerably from that obtained as minor product on sulphonating β-iodonaphthalene, the sulphochloride melting at 140° instead of 92·5°, and the sulphonamide at about 223° instead of 211°; the salts of the two acids also differ, the barium and sodium salts of that from Brönner's acid crystallising both in anhydrous plates and in monohydrated needles.

It appears therefore that on sulphonating β-iodonaphthalene either the initial change is the same as that which occurs on sulphonating the chloro and bromo compounds, and the consequent isomeric change follows a different course; or sulphonation is perhaps simultaneously effected in two different ways, neither iodo acid being the product of isomeric change.

With the object of determining the nature of the change experiments have been instituted with the iodo acids, corresponding to the three amido acids isomeric with Brönner's; the results will form the subject of a subsequent communication.

ROYAL INSTITUTION OF GREAT BRITAIN.

Annual Meeting, Wednesday, May 1, 1889.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Vice-President, in the Chair.

The Annual Report of the Committee of Visitors for the year 1888, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Real and Funded Property now amounts to above £81,000, entirely derived from the Contributions and Donations of the Members.

Forty-five new Members were elected in 1888.

Sixty-four Lectures and nineteen Evening Discourses were delivered in 1888.

The Books and Pamphlets presented in 1888 amounted to about 296 volumes, making, with 570 volumes (including Periodicals bound) purchased by the Managers, a total of 866 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuble services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President.—The Duke of Northumberland, K.G., D.C.L., LL.D.

Treasurer.—Henry Pollock.

Secretary.—Sir Frederick Bramwell, Bart., D.C.L., F.R.S., M.Inst.C.E.

Managers.—Sir Frederick Abel, C.B., D.C.L., F.R.S.; Sir James Crichton Browne, M.D., LL.D., F.R.S.; William Crookes, F.R.S.; Francis Galton, M.A., F.R.S.; Colonel James A. Grant, C.B., C.S.I., F.R.S.; The Rt. Hon. Sir Wm. R. Grove, M.A., D.C.L., F.R.S.; William Huggins, D.C.L,, LL.D., F.R.S.; David Edward Hughes, F.R.S.; Rev. John Macnaught, M.A.; William Henry Preece, F.R.S., M.Inst.C.E.; William O. Priestley, M.D., LL.D., F.L.S.; John Rae, M.D., LL.D., F.R.S.; William Chandler Roberts-Austen, F.R.S.; Lord Arthur Russell; Basil Woodd Smith, F.R.A.S.

Visitors.—William Anderson, M.Inst.C.E.; John Birkett, F.R.C.S.; Alfred Carpmael; Ernest H. Goold, F.Z.S.; Charles Hawksley, M.Inst.C.E.; John Hopkinson, M.A., F.R.S., M.Inst.C.E.; Victor Horsley, F.R.S., F.R.C.S.; Ludwig Mond, F.C.S.; Edward Pollock; Lachlan Mackintosh Rate, M.A.; Arthur William Rücker, M.A., F.R.S.; John Bell Sedgwick, J.P., F.R.G.S.; Thomas Edward Thorpe, Ph.D., F.R.S.; Thomas Tyrer, F.C.S.; James Wimshurst.

NOTICES OF BOOKS.

Thirteenth Annual Report of Her Majesty's Inspectors of Explosives: being their Annual Report for the Year 1888. London: Her Majesty's Stationery Office.

The first point to which the Inspectors draw attention, and with only too good reason, is "the unsatisfactory character of much of the work done by the Local Authorities and their officers, and the still more unsatisfactory and, in some instances, wholesale neglect of their duties by many of these authorities." The general condition of the factories and magazines inspected is by no means unsatisfactory. Some private establishments of this kind, it is said, may challenge comparison with any factories or magazines in other countries, whether public or private.

The total number of manufactories (under continuing certificate and license) is now 112, exclusive of "toy firework" factories. During the four years before the Act came into operation, 1871—74, the average fatality was 37.

Several new explosives have been added to the licensed list, namely, Fortis explosive, carbo-dynamite, carbonite, di-flamyr, securite, bellite, miner's safety explosive, E.C. Company's sporting powder, the same Company's rifle powder, socket (? rocket) light signals, Pain's instantaneous pyrotechnic fuzes, and priming tubes. The authorised definition of roburite has been twice altered.

Several new explosives have been submitted for examination. Of these, flameless securite, smokeless powder, and lithotrite passed. Bronolithe and silatvar are still under examination, and stone carbonate, matagnite, romite, safety gunpowder, Howittite, and nitrolactus were rejected.

In the factory of the New Explosives Company, Limited, at Penrhyndendraeth, in Merionethshire, serious illegalities were detected, *e.g.*, packing gun-cotton for conveyance in a Gladstone bag! Convictions were obtained in five of the six cases, but the penalties inflicted were utterly inadequate. Illegalities in small firework factories seem to be habitually committed, as the local officials do not take the trouble to study the provisions of the Order in Council. The manufacture of fireworks in private houses has been considerably diminished, and might, it is thought, have been entirely extinguished had the local authorities done their duty.

No case of the unlawful entry of a magazine has come to light during the year. Two stores, however, have been unlawfully broken open and portions of blasting-gelatin and of dynamite have been stolen. The Inspectors believe that explosives are very frequently conveyed by road without the precautions which the law demands. Such irregularities can only be detected by the local authorities. In one case a cart conveying a ton of gunpowder was sent through the Borough of Dudley in charge of a boy fifteen years of age. A box containing 2000 detonators was on one occasion sent by railway with a false label so as to mislead the railway company as to the contents of the box.

In the special report of Dr. Dupré, chemical adviser to the Inspectors, it is mentioned that "Obertier's copper," an ingredient used in fireworks, is dangerous, as liable to spontaneous decomposition, in which chlorine compounds are given off. The paper tubes for the so-called pill-box stars contain free sulphuric acid, due to the alum employed in the preparation of the paste. Of course, as Dr. Dupré does not fail to point out, the presence of free sulphuric acid along with chlorates is utterly inadmissible.

A fatal dynamite accident has some curious features. A miner had kept a cartridge of gelatin dynamite in his trousers pocket and omitted to remove it before his trousers were hung up to dry on the oven door of his cottage. The heat caused the cartridge to explode with fatal results to a lodger who was standing in front of the fire at the time! This is only one of the many instances of mischief from miners and quarrymen being allowed to carry explosives about with them, and take them to their dwellings. Common prudence demands that such perilous matter should remain in the custody of trustworthy officials and be served out to the workmen only when and as wanted for immediate use.

No serious instances of outrages with explosives, actual or intended, are recorded in the realm. A small charge of gunpowder was exploded, without doing any harm, close to a new small-pox hospital at Trooper's Hill, St. George, Gloucestershire. It was probably due to public indignation at the erection of a source of infection on what had been a public pleasure-ground. Several outrages are reported from the Continent. Four attempts have been made in Paris to blow up registration offices for café waiters, and the Police Station in the Rue de la Peile was similarly attacked. In the United States a plot was discovered to assassinate the judges, police, and witnesses who had been concerned in the prosecution of the Chicago anarchists, and a dynamitard was charged with attempting to throw a bomb at President Cleveland. Two explosions of blasting-gelatin took place in Fort Morbut and Fort Tarshyne, at Aden. A sentry was killed, some guns were dismounted, and their carriages were damaged. The Inspectors, from a consideration of the evidence, conclude that both these calamities were due to spontaneous decomposition in consequence of the high temperature. Mention is made of the fact that "high" explosives, commonly supposed incapable of exploding by mere ignition without a detonator, have sometimes been known to explode. Thus in an experiment at Lydd a ton of gun-cotton (in tins containing 2½ lbs. each) was set on fire; it exploded with startling abruptness and injured Sir F. Abel, who was only about 30—40 yards distant.

Into petroleum explosions, great and small, the Report does not enter fully; but it is mentioned that further legislation in connection with the storage and sale of petroleum is pending.

The impression left upon our minds by the examination of this Report is that the Inspectors are doing a very useful work, but that they are insufficiently backed up by the local authorities, and that the penalties inflicted for contravention of the Explosives Act are ridiculously trifling in view of the risk to life and property involved by such neglect.

The Art of the Assayer ("l'Art de l'Essayeur"). By A. Riche, Director of Assays at the Mint; Professor of Inorganic Chemistry at the Paris School of Pharmacy; Member of the Academy of Medicine. With the Co-operation of Edmond Gelis. Paris: J. B. Baillière et Fils.

The author defines the art of the assayer as "that portion of analytical chemistry which has for its object the qualitative and quantitative determination of the precious metals." As such, he enumerates gold, silver, and also platinum, which he states enters into the composition of a great number of trinkets. He includes also the determination of the metals which often accompany gold and silver and nickel, which have now become an article of commerce.

It must here be remarked that some authorities include under assaying all analytical operations performed in the dry way, whilst other writers speak of the assay of cinchona-bark, of opium, of guano, and of other organic compounds and mixtures.

The preliminary sections on apparatus and operations need not detain us. We remark merely that certain very convenient appliances for the production of heat by means of coal-gas do not appear to be mentioned.

The hydrometer recommended for determining the specific gravity of liquids is, of course, Beaumé, and the comparative table here given differs seriously from those commonly met with in standard works. Thus we generally find 76° B = sp. gr. 2·000, but here, 76° B = 2·116.

The processes given for the assay of the precious metals and their chief alloys are clearly described, illustrated where necessary, and are fully in accordance with the present state of chemical science. The author does not express any opinion on the possibility of a spectroscopic assay of the precious metals.

New Commercial Plants and Drugs. No. 11. By T. Christy, F.L.S., &c. London: Christy and Co.

The substances here described are exclusively for medical purposes; hence, we cannot venture to pronounce any opinion as to their value; but certain statements made in the preface demand very serious consideration, and, we fear, contain too much truth. Mr. Christy, after complaining of the paucity of chemical and pharmaceutical research, says that "we have in Britain several institutions expressly and expensively fitted for the purpose? But what is the use of them if students are not taught to understand the value of original research? . . . The fault certainly lies at the door of those entrusted with the teaching of our students, and who, instead of encouraging them to take up original research, which is practically the best teacher of all, keep them bound down to the old fossilised lines, and render them practically useless as thoughtful workers."

Mr. Christy should throw in his influence with those who are combatting the examination system of education with all its corollaries. This is the real cause why we are not doing in every science what we otherwise could, and what we ought.

But we think he is mistaken when he intimates that researches carried out in Britain have to be published on the Continent before the English press will notice them. We think that both in pure and technical chemistry the amount of original work done in Britain and published in British journals and transactions is certainly not smaller than that which France has to show.

CORRESPONDENCE.

HYDROCYANIC ACID.

To the Editor of the Chemical News.

Sir,—I have found out that pure anhydrous hydrocyanic acid is obtained by passing dry arseniuretted hydrogen gas over dry potassium cyanide, gently heated,—

$$AsH_3 + 3KCN = 3HCN + K_3As.$$

This is a much more economical way than using sulphuretted hydrogen and mercuric cyanide.

I have also discovered that arsenide of potassium or sodium is formed by passing dry arseniuretted hydrogen gas over dry, heated sulphide of potassium or of sodium—

$$2AsH_3 + 3K_2S = 2K_3As + 3H_2S,$$

or—

$$2AsH_3 + 3Na_2S = 2Na_3As + 3H_2S.$$

The previous book methods used the metals potassium or sodium; but it is easy to see that my way is much more economical. It is necessary in all these three operations that the gas and solids be perfectly dry or the reaction does not take place.

I generally make my arsenious hydride by acting upon 1 part of zinc and 2 parts of white arsenic with hydrochloric or dilute sulphonic acid.—I am, &c.,

G. W. Blythe.

5, Alderley Road, Hovlake,
Cheshire, May 1, 1889.

ACTION OF FERROUS SULPHATE ON SOILS.

To the Editor of the Chemical News.

Sir,—It would occupy too much of your valuable space to follow "X" in all his claims for Dr. Griffiths's experiments, but I think the following remarks show that Dr. Griffiths has *not* added *much*, if anything, to our previous knowledge.

In the oldest edition of "Johnston and Cameron" at hand just now (10th Edition, 1877, p. 394) they say:—"Ferrous sulphate applied in the form of a weak solution to sickly bleached plants has been observed to *change their colour to green and to improve their appearance generally. It has been applied to diseased trees.* Used in *large* quantities it is *poisonous* to vegetation." Dr. Griffiths's experiments commenced *after* 1880.

Every agricultural chemist knew, before Dr. Griffiths was born that all the copperases were germicidal, and that agricultural bluestone was, in great measure, green copperas.

Dr. Griffiths started with Amies' chemical manure, which, according to his own showing, consisted largely of copperas. Long before Dr. Griffiths worked upon it Amies, Co., said:—"As an insecticide (*sic*) it has great power in affording protection against the various parasitic destroyers of vegetable life. It has been found to overcome the potato, vine, and cucumber diseases."

"X" and I are at variance in regard to the meaning attachable to a direct plant-food. A substance is not (in my opinion) a *direct plant-food* unless it is absorbed as such, and without decomposition by the plant, and afterwards elaborated in its tissues. Now, all properly conducted chemico-agricultural experiments go to prove that, wherever the conditions are such that green vitriol can be absorbed unchanged (through absence of aëration and cognate physical and chemical influences in the soil) by the plant, then such green vitriol is *plant poison*. But, on the other hand, where there the conditions are such that green vitriol, when applied to the land, may be oxidised and decomposed, then copperas can be profitably and safely used, just in proportion to the ability of the soil to decompose and alter it into harmless substances. Then green vitriol is an *indirect* plant-food.

Dr. Voelcker assigned the post of honour amongst the questions answered by soil analyses to whether or not the soil contained green vitriol, which, he said, occasionally occurs naturally in peaty and clayey soils—the very ones which want aëration, &c., thus supporting the view I have indicated.

When I do publish my agricultural experiments I shall invite criticism on the deductions I draw. I am sorry "X" is indignant at my having the audacity to criticise those of Dr. Griffiths.

"X" advises me, let me return the compliment. Cast French authorities aside and study the writers upon chemistry as applied to agriculture of your own country, from Lord Dundonald downwards.—I am, &c.,

John Geddes McIntosh.

Sulphuric Acid in the Air.—A medical contemporary alleges that 350 tons of sulphur are thrown into the air every winter day in London. This quantity represents upwards of 1000 tons of monohydrated sulphuric acid daily, not merely wasted, but employed in mischief.

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. cviii., No. 15, April 15, 1889.

The Late Prof. Chevreul.—In conformity with the very unusual wish of the family no *éloge* was pronounced at the funeral of the late illustrious *savant*, and the learned world is thus deprived of the appreciative surveys of his achievements, which some of his colleagues would have felt it an honour to deliver.

Researches on the Thionic Series.—M. Berthelot.—A thermo-chemical paper which does not admit of useful abstraction.

Experiments on Putrefaction and on the Formation of Farmyard Manure.—J. Reiset.—The author gives the details of his experiments mentioned in the last number of the *Comptes Rendus*. He believes that he has been the first to point out the abundant production of hydrogen carbide during the fermentation. During this anaerobic fermentation the loss of nitrogen may become even more abundant than in slow combustion in the presence of oxygen.

On the Solubility of Salts. A Reply to M. Roozeboom.—H. Le Chatelier.—The author considers that the difference of opinion between M. Roozeboom and himself is much smaller than the former seems to suppose. M. Roozeboom has completely accepted the opinion that with every sudden change in the state of a solid salt which is dissolving there necessarily corresponds a sudden change in the track of its curve of solubility.

Speed of Transformation of Metaphosphoric Acid in Presence of Acids and Alkalies.—Paul Sabatier.—The author finds that the transformation is more rapid in presence of the strong mineral acids, such as the sulphuric and hydrochloric, whilst organic acids, such as the acetic, retard the phenomenon. With very small doses of sulphuric acid the accelerating influence is apparently null, or even negative at low temperatures. The more rapid destruction of the metaphosphoric acid is doubtless due to the temporary formation of dissociable hydrates, produced by the acids at the expense of the metaphosphoric acid. If saturated with an alkali the transformation of the metaphosphate into acid phosphate is imperceptible at 0°, very slow at 43·5°; prolonged boiling effects a complete transformation. In a liquid partially saturated we find the transformation slower than in the free acid, but more rapid than in an acid completely saturated. These results confirm the hypothesis formed as to the constitution of vitreous metaphosphoric acid. The chief reaction is a splitting up, which is effected less easily when the acid is saturated with a strong base.

Researches on Certain New Metallic Sulphides.—Arm. Gautier and L. Hallopeau.—The authors, on treating iron at a red heat with carbon disulphide, have obtained a sulphide, Fe_4S_3, a substance of a crystalline fracture and of a yellowish grey colour with bronze reflections. It can be filed and polished like soft iron. Its sp. gr. is 6·975. It is rather more magnetic than iron monosulphide. It undergoes no change on exposure to the air, and is not readily oxidised, even at a red heat. Weak acids dissolve it with an escape of hydrogen sulphide and hydrogen. If metallic manganese is heated to 1400° in the dry vapour of carbon disulphide it becomes covered with a black layer of MnS, a compound which has been obtained before in the crystalline state by another method. No subsulphide is formed. If manganese silicate (rhodonite) is treated at white-redness with the vapour of carbon disulphide a new compound is obtained, Mn_3S_4. It decomposes water, evolving H_2S, and leaving a hydrated manganese oxide.

A Contribution to the Study of the Ptomaines.—Oechsner de Coninck.—The ptomaine $C_8H_{11}N$, if oxidised with potassium permanganate, yields the same pyridin-carbonic acid as does nicotin.

The Combustion-heat of Some Organic Bodies.—M. Ossipoff.—The author has made a thermo-chemical study of the cinnamic, atropic, and terebic acids.

On Calcium and Strontium Malonates.—M. Massol.—A thermo-chemical memoir not adapted for useful abstraction.

New Synthesis Effected by Means of Cyano-succinic Ether.—L. Barthe.—The author has obtained benzyl-cyanosuccinic ether.

The Determination of Organic Nitrogen by the Volumetric Method by Soda-Lime, and by Kjeldahl's Process.—L. L'Hote.—In the author's opinion the method of Kjeldahl does not afford the simplicity, the dispatch, and the accuracy of the soda-lime method. It gives figures comparable to those of the latter method when the acid liquid to be distilled is colourless. This transformation of the organic nitrogen into ammoniacal nitrogen is easy for crystalline substances, such as oxamide, cafeine, and urea, but it is not always possible, even after a considerable time, for many agricultural products. The methods of Dumas and of Will-Varrentrapp give approximately the same results.

No. 16, April 23.

The Nitroso-Compounds of Ruthenium.—A. Joly.—The author shows the existence of a very extended series of nitroso-ruthenium derivatives. He describes a nitroso-sesquichloride to which he assigns the formula $RuCl_3(NO)+H_2O$, and a nitroso-sesquioxide.

The Transformation of Nitro-Camphor into Nitroso-Camphor.—P. Cazeneuve.—The author has succeeded in transforming nitro-camphor into nitroso-camphor under a direct reductive action, heating chloro-nitro-camphor in aqueous alcohol with copper precipitated by zinc.

The Proportion of Gluten in Wheat.—E. Gatelier and L. L'Hote.—The authors' results seem to prove that the propertion of gluten in wheat may be increased by cultivation, and that it depends on the proportion of nitrogen to phosphoric acid used in the manure.

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

Colorimetric Determination of Manganese: Assay of the Lead Peroxide used.—Prof. L. L. de Koninck.—The lead peroxide of commerce is prepared by treating an alkaline plumbic solution with a current of chlorine. This gas carries with it manganese chloride derived from its preparation, which, in contact with the alkali and the excess of chlorine, is converted into peroxide. Hence lead peroxide commonly contains manganese peroxide, and must of course be absolutely rejected in the colorimetric determination of manganese in steels. To detect manganese in lead peroxide in the moist way, a quantity of the product must be heated with an excess of undiluted sulphuric acid until the metals are converted into sulphates. On adding then with great caution a volume of water double or triple that of the acid used, then a fresh quantity of peroxide, and on heating for a few moments, if manganese is present the well-known colour of permanganic acid will appear.

Preparation of Chlorine Gas for Analysis.—Prof. L. L. de Koninck.—The author produces chlorine gas in the cold by the action of gaseous hydrochloric acid upon granulated pyrolusite. The gas is led up through a column of pyrolusite and the chlorine is dried by a passage over calcium chloride or pumice soaked in sulphuric acid.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. iv., No. 38.

Report Presented by M. Le Chatelier on Behalf of the Committee of Chemical Arts on the Alloy known as Delta Metal.—Delta metal, which is an alloy of 57 parts of copper with 43 parts of zinc and a few hundredths of foreign metals, is interesting on account of the ease with which it is forged and stamped at a dull red heat (500°), on account of its resistance, in which it approximates to steel, its immunity from atmospheric action, and its low price. The sole drawback which it presents is the difficulty of melting it without volatilising a part of the zinc.

Report Presented by M. de Luynes on Behalf of the Committee of Chemical Arts on M. Hélouis' Process for Colouring Metals for Embroidery.—No definite account is given of the process which M. Hélouis adopts for depositing thin films of metal upon textile fibres. He does not make use of electric action, but of heat.

Report Presented by M. Müntz on Behalf of the Committee of Agriculture on M. Milliau's Process for Detecting the Falsification of Olive Oil with Seed Oils.—In examining a suspected oil or fat, M. Milliau first liberates the fatty acids, and applies to them the special reagents required.

No. 39.

Report Presented by M. Bérard on Behalf of the Committee of Chemical Arts, on the Safety Papers and Inks presented by M. Schlumberger.—The author incorporates certain reagents with the stuff of the paper. No particulars of the safety inks are given.

MEETINGS FOR THE WEEK.

Monday, 13th.—Society of Arts, 8. (Cantor Lectures). "Heat Engines other than Steam," by H. Graham Harris.

Tuesday 14th.—Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Societyof Arts, 8. (Applied Art Section). "Venetian Glass," by Dr. Salviati.
— Royal Institution, 3. "The Italian Renaissance Painters; their Employments," by Jean Paul Ricbter.

Wednesday, 15th.—Meteorological, 7.
— Pharmaceutical, 11. (Anniversary).
— Society of Arts, 8. (Ordinary Meeting). "The Use of Spirit as an Agent in Prime Movers," by A. F. Yarrow.

Thursday, 16th.—Royal, 4.30.
— Institute of Electrical Engineers, 8.
— Chemical, 8.
— Royal Institution, 3. "Chemical Affinity," by Professor Dewar.
— Sanitary Institute, 5. "Fires and Fire-escapes, and the Prevention and Arrest of Fires," by H. E. Davis.

Friday, 17th.—Royal Institution, 9. "Optical Torque," by Professor Silvanus P. Thompson.

Saturday, 18th.—Royal Institution, 3. "The Origin and Development of Opera in England," by Joseph Bennett.

THE CHEMICAL NEWS.
Vol. LIX. No. 1538.

A NEW, EASY, AND RAPID METHOD OF DETECTING MINUTE QUANTITIES OF IRON IN MINERALS.

By ALEXANDER JOHNSTONE, F.G.S. (London and Paris).
Assistant to the Professor of Geology and Mineralogy in the University of Edinburgh.

By means of a good strong flame, produced in the ordinary way by the mouth blowpipe, heat for a minute or two a small portion of the mineral, preferably in a powdered condition, on *clean* platinum foil, with about four times its bulk of potassium nitrate or chlorate. The platinum should be heated from below, as it is not desirable that the flame should touch the assay. After the mass has been ignited as stated, add to it, *before it has cooled down*, by means of a piece of glass tubing, *pure* concentrated nitric acid drop by drop, until a single drop remains not dried up. Next pour on to the top of the unevaporated nitric acid, also by means of a narrow glass tube, two or three drops of an aqueous solution of potassium sulphocyanide. A *distinct* red colouration will immediately arise and remain if any iron was present in the mineral examined. As this test is extremely delicate, nitric acid quite free from iron must be obtained; and it is essential that the potassium nitrate or chlorate should also be pure. The platinum foil must be perfectly clean, and the dropping tubes must be rinsed with water before and immediately after the application of each test.

AN APPARATUS SUITABLE FOR LECTURE PURPOSES, TO ILLUSTRATE THE INFLUENCE OF PRESSURE ON THE VOLATILISING POINT OF ICE, AND OTHER PHENOMENA.

By Professor SYDNEY YOUNG, D.Sc.

It was first observed by Carnelley that when a block of ice with a free surface for evaporation is exposed to pressures lower than 4·6 m.m. it cannot be melted, no matter at how great a rate heat is supplied to it by radiation.

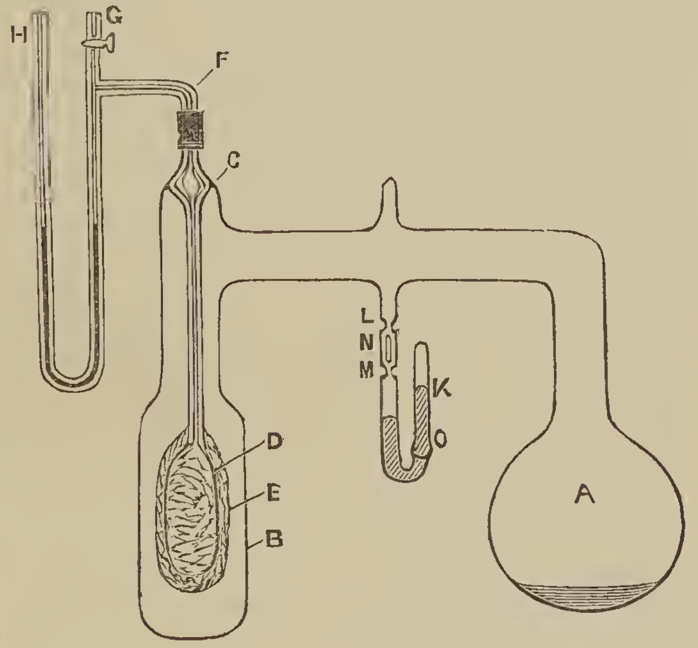
At a meeting of the Owens College Chemical Society eight years ago I suggested that the maximum temperature to which ice can be heated under any given pressure lower than 4·6 m.m. could be ascertained from the curve representing the vapour-pressures of ice at different temperatures, just as the boiling-point of water under any pressure is given by the curve of vapour-pressures of water (*Nature*, 1881, p. 239).

In 1883 Dr. Ramsay and I proved experimentally that this is the case, and we determined the temperatures of volatilisation of ice and other solids, obtaining in the following year an experimental proof of the fact previously predicted from thermodynamical considerations by Prof. Kirchhoff and Prof. James Thomson, that the vapour-pressure of a substance in the solid state at a temperature below its melting-point is lower than that of the substance in the liquid state at the same temperature.

Inasmuch, however, as a good pump is required to reduce the pressure sufficiently, and as the experiment by which these facts are proved is in other respects rather troublesome, it has not, I believe, been usually admitted in an ordinary course of lectures.

It seems possible, therefore, that an apparatus which I have constructed to illustrate the effect of pressure on the volatilising-point of ice may prove useful to other lecturers, more especially as it serves to illustrate some other interesting points. The apparatus is a modification of Wollaston's cryophorus and of that employed by Dr. Ramsay and myself in our investigations. The bulb, A, is similar to that in the cryophorus, but in place of the second bulb there is a wide cylindrical tube, B. At C is fused a tube of narrow bore (say 1 m.m.), to which is sealed a wider tube, D, closed at the end. This tube contains air, and acts as an air thermometer; it is covered with cotton-wool, which is to be saturated with water before beginning the experiment. The narrow tube is open at the upper end, and is connected by an indiarubber tube with the gauge, F G H, which contains sulphuric acid coloured with indigo as an indicator. The gauge is open at both ends, but is provided with a stopcock at G.

As in the cryophorus, the apparatus must be absolutely free from air, and the cotton-wool should be well washed with alcohol and ether to remove all grease, otherwise it may be difficult to saturate it with water. The pressure in the apparatus may be indicated by a mercury gauge, K, but obviously both the construction and the manipulation of the apparatus are rendered somewhat less easy by the addition. The gauge, if added, should have a circular construction at L and a flattened construction at M, a narrow tube, N, closed at both ends, being placed in the tube between the constrictions. When the apparatus is in its usual vertical position the little tube, N, rests on the flattened constriction, and there is free communication between the gauge and the rest of the apparatus; but when, in the transference of water from one bulb to the other, the apparatus is inverted, the tube, N, falling against the circular constriction, closes the tube and prevents the escape of mercury from the gauge. For further security an air or vapour trap may be placed at O.



Description of Experiment.—The cotton-wool is thoroughly saturated and the rest of the water is then transferred to the bulb, A. The gauge is connected with the air thermometer and the stopcock closed. The bulb, A, is then immersed in a beaker of water cooled by a little ice; the diminution of pressure in the apparatus, consequent on the lowering of temperature, is at once indicated by the mercury gauge, and as the boiling-point of water is lowered by reduction of pressure, the temperature of the air thermometer is at once seen to fall. (The bulb, B, may be heated by boiling water or to any desired temperature during the whole experiment). When, by further addition of ice, the temperature of the bulb, A, sinks to 0° the pressure in the apparatus—if air has been completely expelled—falls to 4·6 m.m., and the temperature of the air thermometer becomes constant. The stopcock is then opened so that the sulphuric acid may be at the same level in both limbs at this temperature, which is afterwards shown to be 0° C.

If we now replace the beaker of ice and water by a freezing-mixture at −5° the pressure in the apparatus will be still further reduced, and the temperature of the air thermometer will again fall, but the water will not freeze. We can therefore show—I find with perfect certainty—the cooling of water below 0° without freezing, and also the reduction of the boiling-point of water below 0°.

When the temperature is still further reduced by substitution of a colder freezing-mixture the water in A solidifies, and it will be seen that after the temperature of the air thermometer has fallen a little lower for a moment or two it suddenly rises to the zero-point already determined. After remaining constant for some time, until the whole of the water on the cotton-wool is frozen, the temperature falls rapidly, and it is now found to depend solely on that of the bulb, A, even though the bulb, B, be strongly heated.

A third determination of the zero-point may lastly be made, if sufficient ice remain on the cotton-wool, by removing the freezing-mixture. The temperature of the air thermometer slowly rises to 0°, and remains again at that temperature until the ice is melted.

The following facts are therefore clearly demonstrated by means of this appparatus:—(1) That the vapour-pressure of water (and of ice) depends on the temperature, and that the boiling-point (or the maximum temperature to which water with a free surface for evaporation can be heated) depends on the pressure; (2) that the vapour pressure of water at 0° is 4·6 m.m., and that under a pressure of 4·6 m.m. water boils at 0°; (3) that the boiling-point may be reduced below 0°, the water remaining liquid, but that when solidification begins the temperature suddenly rises and remains constant for a considerable time (it is assumed that this temperature is 0°); (4) that the volatilising-point of ice, like the boiling-point of water, depends on the pressure, and that if the ice has a free surface for evaporation the walls of the vessel surrounding it may be strongly heated without affecting its temperature.

Many of these points may be proved, though not in all cases so directly, without the mercury gauge. The apparatus is a little troublesome to construct, but, once made, the experiments may be conducted with almost as much ease, and with quite as much certainty, as that with Wollaston's cryophorus.

University College, Bristol.

SEPARATION OF IRON FROM CHROMIUM, MANGANESE, NICKEL, ZINC, &c.

By G. VON KNORRE.

In neutral and faintly acid solutions of ferric salts iron is precipitated by nitrosonaphthol quantitatively as ferrinitrosonaphthol, $(C_{10}H_6O.NO)_3Fe$. In this manner iron can be separated from the above metals as well as from aluminium. The precipitation of the iron, which must be present as ferric sulphate or chloride, is effected in the same manner as the separation of copper. Small quantities of ferrous oxide do not prevent the quantitative separation of iron. To about 0·1 grm. of iron present at least 1 grm. of nitrosonaphthol should be used. If considerable quantities of free acid are present ammonia is added until a precipitate begins to appear, which is then re-dissolved in a few drops of hydrochloric acid. The washing and incineration are conducted in the manner described for copper, but the filter must not be too small, as the iron precipitate is very voluminous. The weight taken for analysis must be so small that not more than 0·3 grm. iron is present, as otherwise the bulk of the ferrinitrosonaphthol is too considerable.

The separation of iron and manganese gives very good results. In order to determine the manganese in the filtrate the liquid is concentrated by evaporation, rinsed into a capacious Erlenmeyer flask, and mixed with ammonium chloride and ammonia in large excess. The manganese is then precipitated by Nic. Wolff's method by means of a current of air charged with bromine. It falls as hydrated peroxide. The washings retain to the end a slight yellowish colour, but the results are not affected.

The separation of iron from zinc and from nickel presents no difficulty. In the filtrates zinc is precipitated with sodium carbonate and nickel with bromine-water and pure potassa-lye as nickel sesquihydroxide.

If a solution of chromium oxide containing acetic acid is mixed with a solution of nitrosonaphthol in acetic acid the liquid remains clear at first, but on heating to a boil there appears a red precipitate of chromonitrosonaphthol insoluble in water. Hence, if iron is precipitated by nitrosonaphthol in presence of chrome the results are too high.

Iron and chrome may be separated by acidulating the liquid with hydrochloric acid, as small quantities of this acid do not prevent the quantitative precipitation of iron. To 103 c.c. of the solution containing iron and chrome 5 c.c. of hydrochloric acid are sufficient, and the precipitation is conducted exactly as already described. The chrome in the filtrate cannot be perfectly precipitated by ammonia. The original liquid must therefore be diluted in a measuring-flask to a known volume. The iron is determined in an aliquot portion by means of nitrosonaphthol, and in a second chrome and iron are jointly precipitated by ammonia, when the proportion of chrome is found as difference.

In precipitating iron by means of nitrosonaphthol it is accompanied, not only by copper and cobalt, if present, but also by phosphoric acid.—*Zeitschrift für Analytische Chemie.*

RESEARCHES ON THE CHEMISTRY OF SELENIC ACID AND OTHER SELENIUM COMPOUNDS.*

By Sir CHARLES A. CAMERON, M.D., F.R.C.S.I., V.P.I.C.,
Professor of Chemistry and Hygiene, R.C.S.I.;
and JOHN MACALLAN, F.I.C.,
Demonstrator of Chemistry, R.C.S.I.

(Continued from p. 220).

Properties of Anhydrous Selenic Acid.

Anhydrous selenic acid is a white crystalline solid melting at 58° to a colourless oily-looking liquid. When thoroughly melted it remains in a super-fused state, and usually requires to be cooled to about 5° with constant stirring before it again freezes. The temperature then rises rapidly to 58°, and remains then stationary until complete solidification of the acid has taken place. When at rest it can be cooled lower than 5° without freezing, and it will remain in a stoppered bottle for months, and during frosty weather, in a liquid condition. It instantly solidifies at any temperature below 58° if a crystal of the solid acid be dropped into it, and it freezes sometimes at ordinary temperatures when rubbed with a sharp piece of glass or with the point of a pipette. It thus exhibits the property of super-fusion in a remarkable degree, and to a greater extent than anhydrous sulphuric acid, which, according to Marignac, possesses eminently the property of super-fusion (*Annales de Chimie et Physique* (1853), 39, 184). Its melting-point, 58°, is higher than that of anhydrous

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* A Paper read before the Royal Society, May 2, 1889.

sulphuric acid, 10·5°, but lower than that of telluric acid, which may be heated nearly to redness without melting.

Anhydrous selenic acid crystallises in long interlacing hexagonal prisms. In an impure condition from the presence of selenium dioxide and other substances, its melting-point is lowered; and under those circumstances it is sometimes deposited slowly and spontaneously in the form of double pyramids, many of them intersecting in pairs.

Although much has been written upon the freezing-point of sulphuric acid, but little information appears to be published regarding its crystalline form. It is stated, however, in "Graham's Chemistry," vol. i., that the most concentrated acid when frozen often yields regular six-sided prisms of a tabular form. Chaptal describes the crystals as being six-sided prisms, terminating in pyramids with six faces. Both accounts agree in placing them in the hexagonal system. In order to see if the appearance of the crystals agreed with either of the above descriptions, some sulphuric acid was strengthened by boiling for some time, and then cooled down until it froze. The crystals obtained were found to be long six-sided prisms ending in pyramids, as described by Chaptal, and no prisms of a tabular form were observed. It is thus interesting to find that both anhydrous sulphuric and selenic acid crystallise in prisms in the hexagonal system, but it remains doubtful whether or not they are strictly isomorphous.

Selenic acid in the anhydrous condition possesses a powerful affinity for water, absorbing it quickly from the atmosphere. Their combination is attended with contraction and considerable evolution of heat, but less so than in the case of water and sulphuric acid. Like the latter, it disintegrates and blackens many organic substances, such as cork, indiarubber, &c. From others it withdraws the elements of water; thus, alcohol heated with it yields ethylene, and glycerin, acrolein. On cellulose it has an action similar to that of strong sulphuric acid, paper being converted by it into a tough parchment-like substance. For this reason it should not be filtered through filtering paper, except when cold and very dilute. Iodine dissolves in the super-fused acid when heated, forming a brown-coloured solution. It is acted on violently by pentachloride of phosphorus in the cold—a reaction which we are at present examining. Oxychloride of phosphorus also acts strongly upon it when warmed slightly, the reaction being attended with copious evolution of gas and reduction, apparently, to lower compounds. Selenium dioxide dissolves in it when heated, but the greater part crystallises out again in the cold. There is no evidence of formation in this way of an acid analogous to hyposulphuric acid, $H_2S_2O_6$. The crystals of the solid acid dissolve in strong sulphuric acid and also in Nordhausen acid.

The specific gravity of the super-fused acid, taken with a Sprengel tube at 15°, was found to be 2·6083. The specific gravity of the solid acid was taken in pure benzene of specific gravity 0·8851, which is not acted upon by it in the cold, and in which it is insoluble. As might be expected, it at once blackens commercial benzene. Its specific gravity, taken in this way, proved to be 2·9508 at 15°. It thus resembles anhydrous sulphuric acid in being denser in the solid than in the liquid state. The specific gravity of the liquid acid is much greater than that of anhydrous sulphuric acid, 1·8384; and on the other hand, the specific gravity of the solid acid is less than that of anhydrous telluric acid, which is stated by F. W. Clark to be 3·425 at 18·8° (*Silliman's American Journal* (3), 14, 281; 16, 401).

Monohydrated Selenic Acid: its Preparation and Properties.

Some selenic acid, which had been concentrated on the water-bath, was heated for some time in a vacuum at 100°, and its strength determined: 0·7858 grm. neutralised 20·00 c.c. of semi-normal soda solution, equivalent to 92·08 per cent of selenic acid. The acid so prepared was diluted with sufficient water to reduce its strength to 88·96 per cent, corresponding to a monohydrated acid, H_2SeO_4,H_2O. It was then poured into a wide tube, and its temperature gradually lowered, the same precautions being taken as to stirring and admission of air as were adopted previously in freezing out the anhydrous acid. Its viscosity increased with the fall in temperature, until at $-32°$ it froze into a mass of crystals. These were melted and re-crystallised several times, and the resulting product examined.

A few of the crystals obtained were long needles, but most of them were large and broad, having a general aspect to which the term "glacial" might be applied appropriately, but differing in appearance under the microscope from those of glacial sulphuric acid.

Its melting-point was found to be 25°. Like glacial sulphuric acid, and also like anhydrous sulphuric and anhydrous selenic acid, when once melted it exhibits the property of super-fusion, and to as great an extent as the last-mentioned acid, since it may be cooled to more than 50° below its melting-point with constant stirring before it again freezes. When frozen, it remains quite solid at ordinary temperatures; but if the bottle containing it be removed to a warm room, or much handled, it commences to melt. Like the anhydrous acid, it at once freezes at any temperature below its melting-point when a crystal of the same acid is dropped into it. It resembles the anhydrous acid also in having a melting-point much higher than sulphuric acid of the same strength, that of glacial sulphuric acid being given by Pierre and Puchot as 7·5°, by Jacquelin as 8°, and by Marignac as 8·5°. It resembles the latter acid in having a melting-point lower than its anhydrous acid, but while the difference is about 2·5 in the case of sulphuric acid, the melting-points of the two selenic acids differ by 33°. In the following table their melting-points are compared:—

	Anhydrous.	Monohydrated.
Sulphuric acid	10·5°	8°
Selenic acid	58°	25°

It may be well to state here that 0° is given erroneously in several chemical works as the melting-point of anhydrous sulphuric acid. Marignac, the most recent investigator who has studied the subject, assigns the temperature 10·5° as its true melting-point.

The super-fused monohydrated selenic acid has a specific gravity of 2·3557 at 15°. That of the solid acid was taken in pure benzene, in which it is insoluble, and on which it is without action at ordinary temperatures, even after standing all night. A portion of the liquid acid was poured into the specific gravity bottle, a crystal dropped into it, and the acid, having become firm and cold, weighed, and the bottle filled with benzene. The specific gravity was found to be 2·6273 at 15°. It thus resembles the anhydrous acid in being denser in the solid than in the liquid state; while melting, the crystals sink rapidly in the liquid portion.

This acid commences to boil at 205°, the acid vapour given off being at first very weak, but it increases in strength with the rise in temperature. A more dilute acid is stated to behave in a similar manner, giving off nothing but water until the boiling-point reaches 205°—210°, at which temperature it has the strength of the monohydrated acid, H_2SO_4,H_2O.

The ease with which an acid of this strength can be obtained and crystallised supplies a means of separating impurities from selenic acid, all that is necessary to do being to boil a dilute acid until the temperature reaches 205°, cool, and drop in a crystal from an acid already frozen; the resulting crystals can then be melted and re-crystallised.

It may be well here to draw attention to the conflicting statements which are made in various works regarding the crystalline form of glacial sulphuric acid. "Watts's Dictionary," vol. v., and Richter's "Inorganic Chemistry," state that it crystallises in six-sided prisms; but in several chemical works the crystals are described as rhombic prisms, while Pelouze and Fremy mention that it forms large transparent crystals which are rhomboidal prisms. The crystalline form is thus referred to three different systems. The first description is probably copied by mistake from that of the anhydrous acid. The most recent investigators of the point are Jacquelain (*Annales de Chimie et Physique* (1850), 30, 343), and Pierre and Puchot (*Annales de Chimie et Physique*, (1874), 2, 164). The latter say that the crystalline form appeared to them to be the oblique rhomboidal prism, and that they obtained the crystals, some very large, others thin and very long. Jacquelain describes them as being oblique prisms very inclined and very large; and states that he obtained them, by a rather slow crystallisation, distinctly oblique and very short, and by a quick crystallisation, in very long oblique prisms.

The Existence of Higher Hydrates.

A portion of dilute selenic acid was concentrated on the water-bath and its strength taken: 0·8603 grm. neutralised 19·48 c.c. of semi-normal soda solution, equivalent to 81·92 per cent of selenic acid. The acid so prepared was diluted with sufficient water to reduce its strength to 80·11 per cent, corresponding to a dihydrated acid, $H_2SeO_4,2H_2O$, and its temperature then gradually lowered. When kept at −51° for some time it became as viscous as thick syrup, but did not freeze. The last acid was then diluted to a strength of 57·32 per cent of selenic acid, corresponding to a hydrate of the composition $H_2SeO_4,6H_2O$. The acid thus prepared did not freeze when kept at −49°, and was quite liquid at that temperature.

Although no proof of the existence of higher hydrates than the monohydrated acid was obtained in the foregoing experiments, it appears probable that a dihydrated acid, and perhaps other hydrates, are capable of existing. Sulphuric and telluric acid have both been obtained as dihydrates. Considerable heat is evolved when monohydrated selenic acid is mixed with sufficient water to reduce its strength to that of a dihydrated acid. When the latter is further diluted, there is an additional slight evolution of heat. It is probable that as the freezing-point of monohydrated selenic acid is considerably below that of the anhydrous acid, so the freezing-point of a dihydrated acid is still lower. In order to get an approximate idea of the amount of water which anhydrous selenic acid absorbs, a portion weighing 0·9776 grm. was placed on a watch-glass protected from dust, but with free access of air. After 24 hours the acid weighed 2·0284 grms., showing an absorption in that time of between eight and nine molecules of water by one molecule of anhydrous acid. Another portion weighing 0·4416 grm. was exposed until it ceased to absorb water; the acid then weighed 1·8152 grms., indicating absorption of rather more than 25 molecules of water by one molecule of anhydrous acid. Having arrived at this stage, it commenced to give off a little of the water which it had previously taken up, but the weather became warmer just at this period, so that probably the above amount does not represent the total absorption of which the acid is capable. It is less, however, than the amount taken up by the molecule of sulphuric acid, which is variously stated at from 80 to 100 molecules of water.

(To be continued).

New Metals.—According to the *Chemiker Zeitung* (Coethen), at the last sitting of the Russian Mineralogical Society K. D. Chrustschoff demonstrated the existence of a new metal which he has just discovered, and to which he gives the name Russium. It approximates closely to thorium, and is one of the bodies whose existence was foreseen by Prof. Mendeleeff. We learn also that Dr. Krüss has named the metal which he has detected along with nickel and cobalt Gnomium.

NOTE ON THE

SOLUBILITY OF WHITE PRECIPITATE IN SOLUTION OF AMMONIA CONTAINING AMMONIUM CARBONATE.

By G. STILLINGFLEET JOHNSON.

On testing a solution of mercuric chloride with some ammonia-water, which had been kept in the laboratory for many weeks in a loosely-stoppered bottle, a white precipitate was formed which dissolved easily without heat in excess of the reagent. This unusual reaction was traced to the presence of ammonium carbonate, which had been formed in the solution of ammonia by absorption of atmospheric CO_2.

On subsequently examining the influence of solution of ammonium carbonate in modifying the solubility of white precipitate, I found that this salt is far more powerful than ammonium chloride in preventing precipitation of mercuric chloride solution by ammonia. Not only does the addition of ammonium carbonate to ammonia-water cause resolution of white precipitate as fast as it is formed when mercuric chloride is added little by little; but, even after complete precipitation of a solution of mercuric chloride by ammonia-water, the addition of ammonium carbonate causes the precipitate to re-dissolve.

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ON THE FORMATION OF MARINE BOILER INCRUSTATIONS.*

By Professor V. B. LEWES, F.C.S., F.I.C.,
Royal Naval College Associate.
(Concluded from p. 224).

The presence of magnesic hydrate in boiler deposits has given rise to many theories to account for its formation, the most generally accepted one being that it is due to the mutual decomposition of water and magnesic chloride, which gave rise to magnesic hydrate and hydrochloric acid, the action being accelerated by the presence of metallic iron.

When sea water is evaporated with a large surface of metallic iron present in it, no free chloride can be detected in the distillate until four-fifths of the solution has been distilled over, whilst if the sea water be evaporated alone, it can be taken nearly to dryness without any decomposition. There is no doubt, however, that at a high temperature under pressure in marine boilers this decomposition takes place, but only to a very small extent, some of the deposit of the magnesic hydrate formed being due to the decomposition of the trace of magnesic carbonate first deposited from the water, in contact with the heated tubes, whilst the formation of the bulk of the magnesic hydrate present is explained by the following experiments. A sample of freshly precipitated and carefully washed calcic carbonate was boiled for some hours with a dilute solution of magnesic chloride and the steam led through baryta water. After a quarter of an hour carbon dioxide (carbonic acid gas) was freely evolved and gave a dense precipitate, whilst at the end of the operation the solution in the flask contained a large proportion of the calcium as calcic chloride, and the precipitate remaining was mostly magnesic hydrate. The same experiment was repeated, using sea water instead of the made up magnesic chloride solution, with exactly the same result.

In this reaction, taking place in a boiler, the magnesic chloride and calcic carbonate mutually react upon each

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* Read at the Thirtieth Session of the Institution of Naval Architects, April 11th, 1889. Admiral Sir John Hay, President, in the Chair.

other, soluble calcic chloride and magnesic oxide are formed, and the magnesic oxide uniting with water forms magnesic hydrate, which is precipitated, carbon dioxide escaping.

This explains many points which the former theory leaves untouched—for instance, the fact of calcic carbonate being absent from marine boiler deposits, or, if present, in only very small quantities; and also that chloride of iron is not found in the water of the boiler, which would be the case if any corrosion or pitting was due to the action of free hydrochloric acid.

In many analyses of boiler deposits no magnesic hydrate is returned, but considerable proportions of magnesic carbonate, which naturally would be formed by the magnesic hydrate absorbing carbon dioxide on exposure for any length of time to the air.

Sodic chloride, magnesic chloride, and sulphate are not found as usual constituents of boiler scale; but in cases of heavy incrustation, pockets are found in the deposits filled with microscopic crystals of these salts which have slowly filtered in solution into cavities in the incrustation, and have been deposited there on evaporation of the liquid.

In some heavy deposits the method of formation of the incrustation can be clearly traced, and affords an insight into the changes which must take place in it after deposition.

A sample of incrustation attached to a tube cut from the boilers of H.M.S. *White Swan*, and which had, during three years' service on the East Indian station, completely filled up the spaces between the tubes in an inaccessible portion of the boiler, showed, on cutting a section, that two distinct forms of deposit could be traced; on the sides of the tubes a hard crystalline deposit of a fibrous structure had formed, whilst filling in the spaces between these highly crystalline layers was a softer kind of deposit, soft and loose on the exterior, but resembling alabaster in the interior, where not in contact with air.

A portion of the crystalline deposit from the upper surace of the tube was taken, carefully freed from any of the less crystalline part, and was analysed, giving—

Calcic sulphate	93·90
Silica	5·16
Sodic chloride	0·27
Moisture	0·67
	100·00

The silica was evidently fine sand which had settled out from shore water, and the moisture had most probably been absorbed from the air, so that this crystalline layer was practically pure calcic sulphate. The soft, outer portion of the second deposit which had evidently been formed by the action of air, on analysis, gave—

Calcic sulphate	89·33
Silica	0·52
Magnesic carbonate	6·49
Water	3·66
	100·00

and the inner portion on the surface of which the above had formed, selecting a portion free from pockets or cavities, gave—

Calcic sulphate	84·27
Magnesic hydrate	7·04
Silica	1·94
Oxides of iron and alumina	1·10
Water	5·65
	100·00

Whilst a portion containing a cavity in which were microscopic crystals, gave—

Calcic sulphate	46·06
Sodic chloride	38·66
Magnesic hydrate	4·16
Silica	1·09
Oxides of iron and alumina	0·65
Water	9·38
	100·00

The dual nature of the incrustation was even more marked in a specimen of heavy deposit got from the back of the boilers of H.M.S. *Northumberland*, and which could only be got whilst she was undergoing a thorough refit, and had been probably forming from three to six years, during which period she had been mostly in the Channel. The boilers had been worked at a pressure of about 65 lbs., and jet condensers used. The hard crystalline portion gave—

Calcic sulphate	91·31
Magnesic hydrate	1·77
Sodic chloride	1·39
Oxides of iron and alumina	0·12
Moisture	5·41
	100·00

Whilst the increase of magnesic hydrate was very marked in the non-crystalline portion—

Calcic sulphate	79·76
Magnesic hydrate	5·02
Sodic chloride	4·29
Calcic carbonate	0·97
Oxides of iron and alumina	0 52
Silica	1·10
Moisture	8·34
	100·00

The crystalline crusts of calcic sulphate are always thickest and purest, and, for this reason, hardest in contact with the tubes or plates of the boilers where they have been most heated, but one also finds these layers throughout the deposit, in many cases having a nodular form; and I think this goes to prove that after the deposit has come down as a mud, the calcic sulphate being as deposited already in small dense crystals, sinks through the lighter portions, and forms first a thin, and eventually a thick coating, which, by continuous heating under pressure, changes its crystalline form, giving up moisture, and becomes "anhydrite," whilst the deposit above it gradually becomes thicker and thicker, and more crystallisation of the calcic sulphate takes place, pieces of mill scale and other foreign substances present in the mud forming nuclei round which the "anhydrite" crystallises; the lighter portions, consisting of magnesic hydrate and traces of calcic carbonate, settling into any spaces that remain, and completing the deposit.

These deposits may be taken as a fair example of the incrustations formed by sea water in marine boilers, and, as before pointed out, the admixture of fresh river water would only alter its characteristics by increasing the proportion of calcic carbonate and magnesic hydrate present.

When distilled water only is used, a slight coating is formed, practically consisting only of organic matter, whilst if at any time through a break-bown in the distilling apparatus sea water is mixed with the distilled water, a thin and very hard scale of calcic sulphate is formed. An incrustation of this character gave on analysis:—(See Table, next column).

This scale is of great interest from the presence in it of the carbonate of copper. It is well known that distilled water has a far greater solvent effect upon metals than a water containing salts in solution, and it is quite conceivable that the distilled water from the surface con-

Calcic sulphate	90·84
Magnesic hydrate	0·75
Sodic chloride	1·41
Silica	0·85
Copper carbonate	1·11
Oxides of iron and alumina	0·24
Organic matter	2·96
Moisture	1·84
	100·00

densers attacks the brass and copper tubes and fittings, and deposits the copper on the tubes of the boiler, although only in small quantities; and it is interesting to note that the green spots due to the presence of the copper are all on the under side of the scale, that is, in contact with the metal of the boiler tubes, showing that in all probability it had been deposited, as suggested, from the water in the boiler, and in contact with the iron would set up local galvanic action and tend to produce pitting.

A scale of this character is not as rule very thick, in the case quoted being only one-sixteenth of an inch in thickness in the tubes, and three-sixteenths of an inch on the crown of the furnace.

The importance of preventing boiler incrustation, and thereby saving the enormous waste of fuel and injury which it entails, has not been without its effect upon the minds of inventors, and almost every conceivable substance, from potato paring to complex chemical reagents, have from time to time been patented for this purpose, but they have all more or less failed for marine boilers, because either they have had an injurious effect upon the metal of the plates, or else have produced an enormous bulk of loose deposit which, although easily cleaned out if the various parts of the boiler were accessible, and if it were only being used intermittently, yet in a marine boiler continuously working, rapidly chokes the portions between the tubes, and brings about an even worse state of affairs than that originally existing.

For these reasons, no treatment of sea water in the boilers themselves is practically possible, and with high pressure tubular marine boilers the water used must either be condenser water made up to the required bulk with distilled water, as is at present done, or else the condenser water must be augmented by sea water specially prepared for the purpose in a separate apparatus before being supplied to the boilers; and it is to this latter method I wish now to specially call your attention, as the high solvent action of distilled water upon metals and the cost of its production are primary objections to its use, whilst the constant breaking down from choking of the distilled water apparatus generally ends in the admixture of sea water with the condenser water and the formation of scale in the boilers.

From the data I have brought before you, and from the conditions under which the incrustations are formed, it is evident that if water is boiled under a pressure of 70 lbs., all the calcic sulphate and the carbonates of lime and magnesia will separate out, and by heating water to such a pressure for an hour in an auxiliary vessel, I have experimentally proved that water is obtained which will yield no further deposit when used in the marine boiler. The drawbacks to this process, however, would be that a strong boiler would be required to stand the necessary pressure, and that inasmuch as the deposits formed in this auxiliary boiler would be of the same kind as in the old marine boilers, it would necessitate constant stoppages for cleaning out, as from the binding and hardening effect of the calcium sulphate no mere blowing off would get rid of it, and in the method for treatment of sea water which I should suggest to you, we can take advantage of chemical as well as mechanical means for the separation of all salts in solution which are liable to produce deposits.

In all the more successful of the anti-incrustators sodic carbonate plays the most important part; indeed, several well-known and much-used articles of this class for fresh water boilers are only soda disguised by some cheap colouring matter and sold at a high price, and they act by converting calcic sulphate into calcic carbonate; sodic sulphate, a salt nearly as soluble as the sodic chloride itself, being at the same time formed, and the calcic carbonate precipitates as a soft powder, and there being no calcic sulphate to harden it, it can readily be got rid of.

From time to time the use of sodic carbonate in marine boilers has been advocated, but the serious drawback to its use is that it throws down the magnesium salts as carbonates, and so forms a bulky precipitate which, unless got rid of within a few weeks of its deposition, bakes to a hard mass and forms a bad form of deposit.

In order to separate the whole of the calcium and magnesium salts present, it is only necessary to raise the sea water to the boiling-point with the right quantity of soda solutions, and after separation of the precipitate formed the sea water will contain nothing but sodic chloride and sodic sulphate, both of which are so soluble that there is no fear of anything depositing, unless the solution were evaporated to a density of 1·2, a degree of concentration never approached in a marine boiler even when sea water was used without admixture of condenser water, except on the rarest possible occasions.

The sea water treated as proposed would have a density of 1·026, about $\frac{1}{32}$ on the salinometer, and would be mixed with the condenser water, which would in the proportions usually taken further reduce this to 1·002, and inasmuch as several tons of freshly prepared water would be daily inserted into the boiler, it would take very many months before an objectionable degree of concentration was reached, so that an occasional blowing off of the boiler when in port is all that would be necessary to entirely eliminate the question of density.

The mixture of condenser water and treated sea water would be far preferable to use in marine boilers to the mixture of condenser water and distilled water, as the action of the distilled water on the plates is done away with by the presence of the saline matter in solution, whilst the cost would be a quarter of that at present incurred for distilled water.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 2nd, 1889.

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

Messrs. G. C. McMurtry and H. H. Robins were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George William Howard, 3, Monson Terrace, Tunbridge Wells; Edward Wightman Bell, Spalding; Frederick Charles Knight, Trinidad, Colorado, U.S.A.; D. O'Mahoney, Queen's College, Cork; Benjamin Phillips, Oriental Bank Buildings, Bombay; Emanuel Roberts, Moratua, Ceylon; Robert M. W. Swan, 15, Walmer Crescent, Glasgow.

The following papers were read:—

42. "*Thiophosphoryl Fluoride.*" By T. E. Thorpe, F.R.S., and J. W. Rodger, Associate of the Normal School of Science, South Kensington.

This gas, the existence of which was announced by the authors in 1888 (*vide Trans.*, liii., 766), may be made by the action of arsenic trifluoride on thiophosphoryl chloride, or by heating a mixture of bismuth trifluoride, or better, lead fluoride, with phosphorus pentasulphide.

As the gas is readily acted on by the air or by moisture, and is decomposed at a moderately high temperature, it is necessary to take certain precautions in the preparation if it is wished to obtain it pure. The air in the apparatus should be displaced by dry nitrogen, and the mixture should be heated in a leaden vessel to a temperature not exceeding 250°. The gas has no action on dry mercury, and may be stored in a glass gas-holder.

Analyses and determinations of its vapour-density showed that it possesses the formula PSF_3.

It is a transparent colourless gas, which, under a pressure of 10 to 11 atmospheres at ordinary temperatures, condenses to a colourless mobile liquid.

It is spontaneously inflammable in air, burning with a greyish green flame, forming phosphorus pentafluoride, phosphorus pentoxide, and sulphur dioxide, thus:—

$$10PSF_3+15O_2=6PF_5+2P_2O_5+10SO_2,$$

and spontaneously explodes with oxygen.

When heated or subjected to electric sparks it is decomposed with separation of sulphur and phosphorus, and formation of phosphorus trifluoride, and eventually phosphorus pentafluoride. If the heating is effected in a glass tube at a sufficiently high temperature the gas is ultimately converted into silicon tetrafluoride.

It has no action on oil of vitriol, carbon bisulphide, or benzene. It is soluble to some extent in ether; the solution burns with a greenish flame. Water gradually decomposes it, forming sulphuretted hydrogen, phosphoric acid, and hydrogen fluoride,—

$$PSF_3+4H_2O=H_2S+H_3PO_4+3HF.$$

On shaking the gas with a moderately strong solution of alkali it is absorbed with the formation of a thiophosphate and a fluoride. Thus, with caustic soda,—

$$PSF_3+6NaOH=Na_3PSO_3+3NaF+3H_2O.$$

The gas combines with gaseous ammonia to form a solid product, in accordance with the equation—

$$PSF_3+4NH_3=2NH_4F+P(NH_2)_2SF,$$

and the product is acted on by water, thus:—

$$2NH_4F+P(NH_2)_2SF+H_2O= \\ =2(NH_4F)HF+P(NH_2)_2HSO,$$

forming ammonium fluoride, hydrogen fluoride, and thiophosphodiamic acid. On treating the solution with copper sulphate, copper sulphide is ultimately formed, and the filtered liquid gradually deposits a crystalline salt of a bluish green colour, consisting of a double phosphate and silicofluoride of copper, $Cu_3P_2O_8 \cdot CuSiF_6$.

43. “*The Boiling-point of Sodium and Potassium.*” By E. P. Perman.

Sodium and potassium were boiled in a hollow iron ball, which was heated by means of a blowpipe; the temperature was found in each case by means of an air thermometer, consisting of a glass bulb with a capillary stem which was lowered into the vapour, sealed, and broken open under water. The mean result for sodium was 742°, and for potassium 667°.

44. “*Note on the Heat of Neutralisation of Sulphuric Acid.*” By S. U. Pickering.

The heat of neutralisation is affected by the proportion of water present, and this latter should, theoretically, be infinite. By means of Thomsen's determinations of the heat evolved on diluting the solutions concerned, we can calculate approximately the values of the heat of neutralisation in infinity of water. The values for 2HCl and H_2SO_4 thus become 27,416 and 30,477 cal., instead of 27,480 and 31,380 cal., as they are when 200 H_2O is present; but Thomsen's results on the dilution of sulphuric acid were not extended sufficiently to show an abrupt change which occurs at the extreme end of the curve, and, when the correction is deduced from a more extensive series of experiments which the author has performed, the value for sulphuric acid becomes reduced to 28,197 cal., a value within experimental error, the same as that of hydrogen chloride.

45. “*α-ω-Diacetylpentane and α-ω-Dibenzoylpentane.*” By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, Jun., Ph.D.

Acetobutylbromide and ethylic sodacetoacetate interact readily when warmed together in alcoholic solution with formation of ethylic α-ω-diacetylcaproate,—

$$COMe \cdot (CH_2)_4 \cdot CH(COMe) \cdot COOEt.$$

This compound is a colourless oil, boiling at 238—242° (220 m.m.); when treated with an absolute alcoholic solution of ammonia it yields a crystalline compound, $C_{10}H_{15}NO_2$, melting at about 235° with partial decomposition. It is readily hydrolysed by warm alcoholic potash, yielding α-ω-diacetylpentane, together with smaller quantities of ω-acetylcaproic acid and acetic acid.

α-ω-Diacetylpentane, $COMe \cdot (CH_2)_5 \cdot COMe$, crystallises in waxy plates, melts at 48—49°, and boils at about 213° (under 300 m.m. pressure) without decomposition. It combines with hydrogen sodium sulphite, forming a waxy seemingly amorphous compound, which is decomposed when warmed with water.

By treating the diketone in the cold with excess of hydroxylamine hydrochloride and potassium carbonate it is converted into the dihydroxime,—

$$CMe(NOH) \cdot (CH_2)_5 \cdot CMe:NOH;$$

this separates from a mixture of benzene and light petroleum in the form of a crystalline powder, melting at 84—85°.

ω-Acetylcaproic acid, $COMe \cdot (CH_2)_5 \cdot COOH$, crystallises in colourless plates, melts at 29—30°, and, when pure, distils under reduced pressure with only slight decomposition. The silver salt, $C_8H_{13}O_3Ag$, crystallises from boiling water in colourless plates.

By warming an alcoholic solution of acetobutylbromide with ethylic sodomethylacetoacetate, ethylic α-methyl-α-ω-diacetylcaproate, $COMe \cdot (CH_2)_4 \cdot CMe(COMe) \cdot COOEt$, is obtained as a colourless oil boiling at 255—260°, (200 m.m.). It yields α-methyl-α-ω-diacetylpentane, $COMe \cdot (CH_2)_4 \cdot CMeH \cdot COMe$, when hydrolysed with alcoholic potash.

Ethylic α-ω-dibenzoylcaproate,—

$$COPh \cdot (CH_2)_4 \cdot CH(COPh) \cdot COOEt,$$

is obtained by treating benzoylbutylbromide with ethyl sodobenzoylacetate in alcoholic solution. It is quickly hydrolysed when boiled with alcoholic potash, yielding α-ω-dibenzoylpentane, ω-benzoylcaproic acid, and benzoic acid.

α-ω-Dibenzoylpentane, $COPh \cdot (CH_2)_5 \cdot COPH$, crystallises from dilute methyl alcohol in long needles, melting at 67—68°. The dihydroxime,—

$$CPh(NOH) \cdot (CH_2)_5 \cdot CPh:NOH,$$

prepared by treating an alcoholic solution of the diketone at the ordinary temperature with hydroxylamine hydrochloride and potash, crystallises from methyl alcohol in small glittering needles, and melts at 175—176°.

ω-Benzoylcaproic acid, $COPh \cdot (CH_2)_5 \cdot COOH$, crystallises from light petroleum in long transparent plates, melting at 81—82°. The silver salt, $C_{13}H_{15}O_3Ag$, is a colourless, seemingly amorphous compound, almost insoluble in water.

The authors are at present engaged in investigating the behaviour of diacetyl- and dibenzoyl-pentane towards reducing and dehydrating agents. Very interesting results have been obtained, an account of which they hope to be able to lay before the Society at an early date.

46. “*Acetopropyl- and Acetobutyl-alcohol.*” By Harold G. Colman, M.Sc., Ph.D., and W. H. Perkin, jun.

In a previous communication to the Society (*Trans.*, li., 702) it was shown by one of the authors that acetobutyl-alcohol, obtained by boiling methyldehydrohexonecarboxylic acid with water, differs very widely from the substance of that name previously obtained by Lipp (*Ber.*, 1885, 3280) by boiling ethylic ω-bromopropylacetoacetate with dilute aqueous hydrogen chloride: the boiling-point of the former being 227°, whereas the latter product distilled at 154—155°—a difference of 70°.

In a paper published some time since (*Ber.*, 1888, 2138) "On the Action of Sodium on Ethylic Monochloracetate," Fittig and Erlenbach, in describing a substance boiling at 128°, which they supposed to be acetoisopropylalcohol, took occasion to state that the acetobutyl- and acetopropyl-alcohols previously described by the authors, could not possibly have the constitution assigned to them —owing to their syrupy consistency and high boiling-points—and that the description given by Lipp of his acetobutylalcohol agreed much better with the properties such a substance might be expected to possess. In a later paper (*Ber.*, 1888, 2647) these chemists discovered that their compound was not acetoisopropylalcohol, but was simply acetolethyl ether, $CH_3 \cdot CO \cdot CH_2 \cdot OC_2H_5$. As, however, in spite of this they did not withdraw their previous remarks on the nature of acetobutyl- and acetopropyl-alcohol, and as the authors had extensively used these substances in the synthesis of ring-derivatives, and drawn important theoretical conclusions from the results obtained, they have thought it necessary to again carefully examine these alcohols with a view to further establishing their identity.

In the first place they carefully repeated Lipp's experiment and found that the acetobutylalcohol obtained by him did in reality contain a considerable quantity of this substance, and that the product on distillation apparently boiled at 154—155°. Subsequent experiments showed, however, that this temperature, instead of being the boiling-point, was in reality the decomposing-point of the alcohol; the reason for this being, that the slightest trace of impurity is sufficient to prevent acetobutylalcohol from distilling without the most rapid decomposition into its anhydride (methyldehydrohexone) and water, the thermometer remaining constant at 154—155°. Lipp's acetobutylalcohol, when not too impure, can be distilled with slight decomposition under reduced pressure; the boiling-point noticed in two cases being 157° under 100 m.m. pressure, and 171° under 177 m.m. pressure; on distilling acetobutylalcohol from methyldehydrohexonecarboxylic acid under the same conditions, almost identical boiling-points were noticed.

Pure acetobutylalcohol was obtained from Lipp's crude product by distilling with steam, fractionating the methyldehydrohexone thus obtained, and dissolving it in water. In this way a thick oil was obtained which distilled under ordinary pressure at 225—227°, and was in every respect identical with the acetobutylalcohol from methyldehydrohexonecarboxylic acid.

These and other experiments, an account of which will be given later on, prove conclusively that acetobutylalcohol, when pure, boils at 225—227°, and not at 154—155° as stated by Lipp. Acetopropylalcohol behaves in every respect, physically as well as chemically, as the lower homologue of acetobutylalcohol, and as this substance gives levulinic acid on oxidation, no further experiments in proof of its constitution are necessary.

THE ROYAL SOCIETY.

The following is a list of the principal exhibits at the Conversazione on May 8th, 1889.

The Tintometer.—Invented and exhibited by Mr. J. W. Lovibond, of Salisbury.

An instrument for matching, measuring, and recording the tints and hues of coloured solids and liquids, available for Eggertz's and Nessler's tests, valuation of pigments, standardising coloured solution, &c., &c.

The comparison of the coloured substances under examination with the standard tints and hues is made by means of an extensive series of accurately graded glass slips of different hues and strengths of colour.

Portable Cavendish Apparatus for Demonstrating the Attraction of Gravitation.—Exhibited by Mr. C. V. Boys, A.R.S.M., F.R.S.

This apparatus differs only from the well-known apparatus of Cavendish in matters of detail. First, instead of the beam six feet long carrying heavy weights, used by Cavendish, or half a metre long, used by Cornu, the beam consists of a piece of lead only one centimetre long, and this is enclosed in a round tube of metal, outside which the attracting weights are placed. This reduction of size has been rendered possible by the use of quartz threads, the production of which was shown two years ago. The advantages gained by the reduced dimensions are increased sensibility and almost perfect elimination of temperature disturbances. The particular apparatus exhibited is designed to show the effect, and that it is the same from time to time, rather than to determine the constant of gravitation absolutely. By arranging the two attracting weights and the two ends of the attracted body at different levels, the deflection is nearly double.

Experiment Showing the Insulation of Quartz.—Exhibited by Mr. C. V. Boys, A.R.S.M., F.R.S.

A pair of gold leaves are supported by a short rod of quartz which has been melted and drawn out about three-quarters of an inch. The atmosphere is kept moist by a dish of water. Under these circumstances a glass insulating stem allows all the charge to escape in a second or two. With the quartz, but little change is observed in four or five hours. The quartz may be dipped in water and put back in its place with the water upon it. It insulates apparently as well as before.

Apparatus for Testing the Elasticity of Fibres.—Exhibited by Mr. C. V. Boys, A.R.S.M., F.R.S.

One of these pieces of apparatus consists of a microscope cathetometer arranged vertically, and a gravity bob which is deflected by the vertical pull of the fibre on a side arm. The lower end of the fibre is made fast to a beam carried by the microscope. A scale, to which the upper end of the fibre is fixed, is viewed by the microscope, which thus shows the stretch of the thread; the pulling force is found by subtracting the stretch from the vertical movement of the microscope, and multiplying by a constant previously found. The second piece of apparatus is used to measure the fatigue of fibres after torsion.

Fractures from Casting and Forgings of Manganese Steel, containing from 10 *per cent to* 36 *per cent Mn, Illustrating the Influence of Different Combinations of Iron and Manganese.*—Exhibited by Mr. R. A. Hadfield.

When the manganese exceeds about 12 per cent, notwithstanding the large percentage of iron present, the material is found practically non-magnetic.

Photographic Map of the Normal Solar Spectrum (Second Series) made by Professor Rowland.—Exhibited by Mr. William Crookes, F.R.S., V.P.C.S.

Nine plates of the solar spectrum, wave-length 3270 to 6950. Each plate contains two strips, 3 feet long.

The spectrum has been projected from concave gratings, of six inches diameter and 21½ feet radius, ruled with 10,000 or 20,000 lines to the inch, giving definition hitherto undreamed of. The scale is placed within 1-20th Angström division, or 1-100,000th wave-length of its true position.

There are few instruments which will show more of the spectrum than can be found on this map, even below the line D, for the first line in B is shown widely triple. The original negative shows E, and even finer lines, like that at wave-lengths 5276·1 and 5914·3, plainly double. As to other maps of the spectrum made by measurement and drawing, it may be said that no comparison is possible. The photograph is the work of the sunlight itself, and the user of this map has the solar spectrum itself before him, and not a distorted drawing full of errors of wave-length and of intensity. The superiority is so great that there is no possibility of comparison.

In addition to the nine plates above described, there are exhibited two plates, each 2 ft. 10 ins. long, of the B and D lines. The D lines are 3 inches apart, and the B group has an extent of about 24 inches.

Pitkin and Niblett's Fire-damp Meter.—Exhibited by Mr. James Pitkin.

By means of these instruments it is possible to detect and estimate the percentage of oxygen or hydrogen in mixtures of these gases.

In its simplest form it consists of two ordinary cylindrical bulbed mercurial thermometers. These are mounted on a suitable base, and are then graduated off in the ordinary way to the Fahr. or Cent. scale. One tube registers the temperature of the mixed gases. The other, which is the gas indicator, has its bulb coated with one of those metals which, when in a very finely divided state, have that peculiar property of occluding and facilitating the chemical combination of certain gases. When placed in a gaseous mixture, and during the combination of the gases due to the above property of the metal, a considerable amount of heat is developed. The heat generated thus produces a corresponding rise in the mercurial column. To read the instrument, the difference between the two-scale reading is taken, and then by comparison with a table supplied with each instrument, the percentage of gas may be read off.

In the case of fire-damp and air, or coal-gas and air, the amount of heat developed appears to correspond approximately to the explosive activity of the mixed gases. A sliding scale may be fixed on the instrument, which can be graduated in terms of percentages of any particular gas.

Combustion in Dried Oxygen.—Exhibited by Mr. H. Brereton Baker, M.A., Dulwich College.

(1). Charcoal is heated to redness in dried oxygen without any visible combustion. The oxygen has been in contact with the drying agent for two months.

(2). Sulphur is distilled in oxygen dried by phosphorus pentoxide for five years. No flame is seen. In moist oxygen sulphur burns at a temperature of 320°, its boiling-point is 440°.

(3). Phosphorus is distilled in oxygen dried in the same way. It boils at 290°. In moist oxygen it catches fire at about 60°.

(4). Ordinary phosphorus is not luminous at any pressure in dried oxygen. The tube on the right contains ordinary phosphorus in moist oxygen. If the corresponding mercury reservoir be lowered, the pressure in the tube will diminish, and the phosphorus will become luminous. The tube on the left contains phosphorus which has been carefully purified in oxygen which has been dried by contact with phosphorus pentoxide for four months. By lowering the mercury reservoir on the left, the pressure will be diminished in this tube, but no luminosity will appear. Phosphorus is thus proved not to undergo slow combustion in oxygen at a low pressure, if the oxygen be sufficiently dried. In these experiments the substances must not only be freed from moisture, but also from any traces of hydrogen, which, by its union with oxygen, would produce water. Before they are filled, the glass tubes are heated nearly to their melting-point, to free the glass from adhering moisture.

(5). Amorphous phosphorus is heated in a tube containing pure nitrogen in the vapour of boiling mercury (360°), without undergoing the change to the ordinary modification.

Amorphous phosphorus has been regarded as being incapable of undergoing true combustion. If heated to 260° in air or oxygen it burns, but it is generally supposed that this combustion is preceded by a change to ordinary phosphorus, which burns readily at this temperature. The experiment of heating the amorphous phosphorus in nitrogen proves that it does not change if it is heated in a neutral gas, and therefore that the combustion in oxygen is a true one, and is not necessarily preceded by a transformation to the ordinary modification.

An Experiment Showing an Effect of Light in Magnetising Iron.—Exhibited by Mr. Shelford Bidwell, M.A., F.R.S.

A bar of iron, which has undergone certain preliminary treatment, is placed close to a small reflecting magnetometer. When the iron is illuminated by an oxyhydrogen lamp, it instantly reflects the magnetometer needle, as is evidenced by the movement of the spot of light upon the scale; and when the illumination is cut off the spot of light at once goes back.

The preparation of the iron consists in first magnetising it by a current of electricity passed through a surrounding coil, and then very perfectly demagnetising it by a reversed current of suitable strength. Its magnetic condition is thus rendered unstable, and its susceptibility appears to be greater for a small magnetising force acting in the same direction as that by which the bar was at first magnetised, than for an equal small force in the opposite direction.

For further details see *Roy. Soc. Proc.*, vol xlv., p. 453, 1889.

Preparations of the New Element Gnomium, recently Discovered by Gerhard Krüss and F. W. Schmidt, of Munich.—Exhibited by Dr. Hugo Müller, F.R.S.

Gnomium oxide.

Gnomium chloride (in aqueous solution).

Nickel from which the Gnomium, which up to the present always accompanied it, has been separated.

Nickel oxide free from Gnomium.

Gnomium is a metallic metal which, according to the discovery of Krüss and Schmidt, is always associated with cobalt and nickel, and consequently neither of these metals have up to the present been known in the pure state.

Hollow Cylinder and Sphere, used in the Re-determination of the Weight of a Cubic-inch of Distilled Water, 1889.—Exhibited by Mr. H. J. Chaney.

$t=62^{\circ}$, $B=30$ inches. One cubic inch = 252·286 grains.

Voltaic Balance.—Exhibited by Dr. G. Gore, F.R.S.

Used for measuring voltaic energy in chemical analysis; strength of aqueous solutions; detecting chemical changes in liquids and measuring their rates; detecting chemical compounds and their combining proportions; measuring losses of voltaic energy during chemical combination; measuring chemical energy.

By means of it the influence of 1 part by weight of chlorine in 500,000 million parts by weight of water has been detected.

Films of Metals and Metallic Oxides Deposited by Electric Sparks.—Exhibited by Prof. W. N. Hartley, F.R.S.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, May 6, 1889.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Vice-President, in the Chair.

The following Vice-Presidents for the ensuing year were announced:—

Sir Frederick Abel, C.B., D.C.L., F.R.S.; Sir James Crichton Browne, M.D., LL.D., F.R.S.; William Crookes, F.R.S.; Colonel James A. Grant, C.B., C.S.I., F.R.S.; William Huggins, D.C.L., LL.D., F.R.S.; John Rae, M.D., LL.D., F.R.S.; Henry Pollock, Treasurer; Sir Frederick Bramwell, Bart. D.C.L., F.R.S., Hon. Secretary.

John Tyndall, D.C.L., LL.D., F.R.S., was elected Honorary Professor of Natural Philosophy.

The Right Hon. Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S., was elected Professor of Natural Philosophy.

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

CORRESPONDENCE.

ACETIC SULPHIDE.

To the Editor of the Chemical News.

Sir,—I have just found out that acetic sulphide, which I have never seen mentioned in books before, is obtained by distilling acetic chloride with trisulphide of antimony. Distilled with red oxide of lead, or red oxide of mercury, it yields acetic oxide. I also tried distilling glacial acetic acid saturated with sulphuretted hydrogen gas; but this did not seem to answer.

Acetic oxide is converted by hydrochloric acid into acetylchloride.—I am, &c.,

G. W. Blythe, M.P.S.

5, Alderley Road, Hoylake,
Cheshire, May 2, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Bulletin de la Société Chimique de Paris.
Vol. i., (Ser. 3), No. 7. April 5, 1889.

Notes on the Alkali Industry.—M. Scheurer-Kestner.—The author summarises the attempts which have recently been made at improving the known procedures and at creating novel ones. He notices in the first place Dr. Lunge's researches on the reactions which occur in the alkali manufacture on the Leblanc system, considered from a thermo-chemical point of view. He then examines the recovery of sulphur from tank-waste by the Chance process. Next he turns to consider Mr. W. W. Staveley's process for producing sodium carbonate from phenol and sodium sulphate, a proposal which, according to the calculations of the inventor, has little prospect of proving remunerative. Lastly, M. Scheurer-Kestner considers Messrs. Parnell and Simpson'e process for combining the Leblanc and the ammonia processes.

On a Nitrophenol "Campho-nitrophenol," an Isomer of Nitrocamphor-*α*.—P. Cazeneuve.—The compound obtained has a composition answering to the formula $C_{10}H_{15}(NO_2)O.H_2O$. It is white, more soluble in water than is camphoric acid, soluble in boiling water in all proportions, soluble in alcohol, ether, coloroform, and benzene.

On the Antiseptic Value of Campho-nitrophenol.—P. Cazeneuve.—According to the author's experiments the antiseptic powers of campho-nitrophenol is very feeble. It is poisonous to the higher animals only in very heavy doses.

On the Campho-nitrophenates.—P. Cazeneuve.—Campho-nitrophenol reddens litmus, decomposes carbonates, and forms readily salts, most of which are crystalline. The potassium, sodium, ammonium, copper, lead, zinc, iron, and barium salts are soluble in water. The salts of silver and mercury are sparingly soluble; those of lime, quinine, and cinchonine are insoluble.

Action of Maltose on Diastase during Saccharification.—L. Lindet.—The accumulation of maltose causes the arrest of saccharification; if the maltose disappears in the state of alcohol and carbonic acid, or of an insoluble phenylhydrazine compound, the diastase resumes its saccharifying activity.

Biedermann's Central Blatt fur Agricultur Chemie.
Vol. xviii., Part 3.

Remarks on Hoar-Frost.—John Aitken.—This paper is credited to the "Naturwissenschaftliche Rundschau."

Analysis of Nile Water.—A. Muntz and M. Aubin.—From the *Comptes Rendus.*

The Relations of Atmospheric Nitrogen to Arable Soil.—Th. Schlösing.—From the *Comptes Rendus.*

The Detection of Nitrates in Soils.—M. Frank (*Landwirthschaftliche Jahrbücher*).—A controversy regarding the blue colouration of sand-granules by diphenylamine, which the former author seems to have referred to the presence of traces of nitrates, whilst Kreusler maintains that it is due to the presence of certain oxides of manganese and iron.

On the Humin-Compounds, their Origin and Properties.—F. Hoppe-Seyler (*Zeitschrift Phys. Chemie*).—In this memoir the author examines the formation of humin-substances in plants, the behaviour of cellulose and wood-gum, the composition and properties of tanninreds and phlobaphenes, the preparation and properties of the ulmine and humine compounds from carbohydrates, from phenols, from dead plants, and furfurol from the fusion of azulmic acid with caustic potash. The hymatomelanic acids of peat and lignite do not differ in their behaviour from those of the phlobaphenes.

Analysis of a Soil from the District of Washington.—E. A. Schneider.—From the *American Journal of Science.*

On the Assimilability of the Phosphoric Acid in Basic Slags.—Prof. Petermann (*Bulletin de la Station Agronomic de l'Etat à Gembloux*).—The conclusions arrived at are that finely-ground basic slag is an excellent manure. In experiments made with two kinds of spring-sown grain in a soil containing a sufficiency of the other ingredients of plant-food there was a rapid assimilation of the phosphoric acid present in the slag. The free lime in the slag remained inoperative, though the soils were poor in this constituent, containing only 2·37 and 1·53 parts per 1000. The considerable quantity of ferrous and ferric oxide in the slag was not found disadvantageous either for the prosperity of cereals or for the formation of starch in potatoes.

Experiments with Fish Guano.—Prof. Petermann.—About an equal number of diseased potatoes were found in plots manured with fish guano and in those where it was absent.—This fact is important, as controverting the prevalent opinion that organic manures favour the development of the dangerous *Peronospora.*

Manurial Experiments with Rice.—Prof. C. C. Georgeron.—From the *Bulletin of the Imperial College of Agriculture and Dendrology*, Tokio. A complete manure is recommended.

The Occurrence of Uric Acid in the Urine of Herbivora.—Franz Mittelbach.—The author detected uric acid in the urine of 23 oxen, 7 cows, 7 sheep, and a number of horses. It was not absent in any of the specimens examined. This result, if found general, will throw a new light on the comparative metabolism in the herbivora and in man.—*Zeitschrift Physiol. Chemie.*

Elementary Analysis of the Hæmoglobine of the Blood of Dogs.—Alfred Jacquet (*Zeitschrift Physiolog. Chemie*).—The hæmoglobines of the horse and the dog are not identical. That of the former contains less carbon, more nitrogen, less sulphur and iron, and more oxygen.

The Signification of Potash in the Plant.—R. Lupke (*Landwirthschaftlich. Jahrbucher*).—On experimenting on species of *Phaseolus* the author found that the presence of potash was not indispensable to the growth of the plants, though the plants fell short of their normal condition. What is the exact function of the potash, whether it is required for the chemical existence of the plant or if it subserves certain vital processes, are questions not yet solved.

Researches on the Nitrogenous Nutriment of Cereals and Legumens.—H. Hellriegel and H. Wilfarth (*Zeit. Rüben. Industrie*).

The Formation of Asparagine and the Relations of Non-nitrogenous Compounds to the Conversions of Albumen in the Vegetable Organism.—Prof. E. Schulze (*Landw. Jahrbücher*).

The Signification of Reserve-matter in Trees.—R. Hartig (*Botan. Zeitung*).

The Bacteria of the Tubers of the Papilionaceæ.—W. Beyerinck.—The last four memoirs do not admit of useful abstraction.

The Transformation of Potato Starch in the Human Stomach.—Dr. H. Zechnissen (*Centralblatt fur Medicin*).—In the human stomach, if empty, or with almost neutral or faintly acid contents, the dissolved starch is quickly converted into maltose and dextrine. After the previous ingestion of food the starch is never converted into sugar.

The Alsatian Method of Meadow-Culture.—N. N. (*Zeit. Spiritus Industrie*).—The land intended for irrigation is laid out in terraces.

The Ash of Coke as Manure.—N. Passerini (*Le Statione Speriment. Agrar. Ital.*).—The ash of coke contains 5·7 per cent phosphoric anhydride and 0·53 of potash. A mixture of 700 parts coke-ash with 200 parts ammonium sulphate is recommended as a good manure.

Kainite as a Protection against Frost.—According to Heyking (*Sächsland Zeitung*) a top-dressing of kainite is said to have resisted a temperature of −7·5°.

Poisonous Character of Air Expired.—R. Würtz (*Central-blatt Medicine*).—The air expired was passed through a 1 per cent solution of oxalic acid, which is then neutralised with calcium carbonate and rendered alkaline with lime-water. The filtrate was neutralised with hydrochloric acid and evaporated in a vacuum and yields a mixture of hydrochlorates consisting chiefly of ammonium chloride. There was also present a base precipitable by mercury-potassium iodide, from which soluble salts of gold and platinum were obtained. The aqueous solution of the hydrochlorate has a peculiar aromatic odour.

The Occurrence of Fluorine in the Organism.—G. Tamman (*Zeit. Phys. Chemie*).—All organs rich in phosphorus contain ponderable quantities of fluorine, whence this element seems to play an important physiological part in the system.

MISCELLANEOUS.

Faraday Lecture.—Professor Mendeleeff's lecture will be on the Periodic Law of the Chemical Elements; it will be delivered in the theatre of the Royal Institution, Albemarle Street, W., on Tuesday, June 4th, at 8.30 p.m. Fellows requiring additional tickets for the Faraday Lecture are requested to apply to Mr. Hall. The tickets are available for ladies. The dinner at which the Fellows will entertain Professor Mendeleeff will take place at the Holborn Restaurant on Wednesday, June 5th, at 7 p.m. Tickets may be obtained from Mr. Hall, price half-a-guinea, not including wine.

Royal Institution.—The two following important donations have recently been made:—Mrs. de la Rue has presented to the Royal Institution the philosophical apparatus of the late Dr. Warren de la Rue; which will be preserved there as the historical collection commemorative of the important scientific work of Dr. Warren de la Rue, and of the eminent position he has so long occupied as a promoter of Science and of the special objects of the Institution; and a fine portrait of Sir Humphry Davy has been presented by Mr. James Young, grandson of the late Dr. James Young, F.R.S., of Kelly, the distinguished chemist, and former owner of the portrait, which makes a valuable addition to the collection of historic portraits now in the Royal Institution.

The Parkes Museum.—A General Meeting of this Society was held on Friday last, Dr. G. V. Poore in the chair, for the purpose of completing the arrangements necessary for carrying out the amalgamation of the Parkes Museum with the Sanitary Institute. Although the Parkes Museum will cease to exist as a separate body, it will still be carried on in the same premises as part of the Sanitary Institute, or combined Society, and its scope will be enlarged, and its usefulness greatly increased. In order to conform to legal technicalities it was necessary that it should be wound up, but it is satisfactory to note that the Parkes Museum in closing its works was able to transfer to the new Institute its Museum and Library, which has been a collection of many years, the lease of the premises, and also a cash balance amounting to nearly £900.

A Modification of the Kjeldahl Process.—Prof. J. W. Gunning.—The modification consists in adding to the acid employed a quantity of potassium sulphate. He uses a mixture obtained by melting together one part K_2SO_4 and two parts of ordinary acid. He remarks that there is scarcely any glass in commerce which does not give off noteworthy quantities of alkali if in contact with hot watery vapour in the act of condensation.—*Zeitschrift fur Analytische Chemie*, Vol. xxviii., Part 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 advertising columns.

Toughened Glass for the Laboratory.—Can glass retorts, &c., be purchased, which will only break by violence, but not by heat, or even sudden change of temperatures?—G. W. B.

Pigments.—Will any correspondent inform me which are the standard works in English, French, or German dealing practically with pigments and mixing colours?—B.

Fruit Essences.—I want a work on the best mode of producing artificial fruit essences and flavouring extracts (artificial). By supplying this information you will greatly oblige.—G. Newell, M.D.

MEETINGS FOR THE WEEK.

Monday, 20th.—Society of Arts, 8. (Cantor Lectures). "Heat Engines other than Steam," by H. Graham Harris.

Tuesday, 21st.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Royal Institution, 3. "Some Recent Biological Discoveries," by E. Ray Lankester.

Wednesday, 22nd.—Geological, 8.
—— Society of Arts, 8. (Ordinary Meeting). "The Use of Spirit as an Agent in Prime Movers," by A. F. Yarrow.

Thursday, 23rd.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "Chemical Affinity," by Professor Dewar.

Friday, 24th.—Quekett Club, 8.
—— Royal Institution, 9. "The Solar Surface during the Last Ten Years," by the Rev. S. J. Perry.

Saturday, 25th.—Royal Institution, 3. "The Origin and Development of Opera in England," by Joseph Bennett.
—— Physical, 3. "On a Relation existing between the Density and Refraction of the Gaseous Elements and some of their Compounds," by the Rev. T. Pelham Dale. "On a Waterspray Influence Machine," by Mr. George Fuller. "Notes on Polarised Light—(*a*) On the Transition Tints of Various Orders, (*b*) Lecture Illustrations of the Rotation of the Plane of Polarisation, (*c*) On the Rotation of Circularly Polarised and non-polarised Light," by Prof. S. P. Thompson, D.Sc. "Terrestrial Magnetism as Modified by the Structure of the Earth's Crust," by Dr. Edmund Naumann. "On the Molecular Weight of Caoutchouc and other Colloric Bodies," by Dr. J. H. Gladstone and Mr. W. Hibbert.

Analytical Chemist Wanted.—One preferred who has been accustomed to examine Oil and Grease. State experience and salary expected.—Address No. 444, CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

TO ANALYTICAL CHEMISTS, WORKS MANAGERS, AND OTHERS.

Wanted by Advertiser, aged 22, an Appointment as Chemist. Four years as Apprentice and two years as Assistant in the laboratory of a leading Analytical Chemist in the North of England. Good theoretical training and varied experience in Analysis. First-class references.—Apply, "Analyst," CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

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9 AND 10, SOUTHAMPTON BUILDINGS, W.C

TOTTENHAM LOCAL BOARD OF HEALTH.

PROTO-SULPHATE OF IRON OR GREEN COPPERAS.

The Local Board invite Tenders for the supply and delivery at their Sewage Works, Page Green, Tottenham, of PROTO-SULPHATE OF IRON, in Five-ton Lots, as ordered.

Tenders, stating full particulars, to be delivered to the undersigned before Twelve o'clock on Tuesday, 21st instant.

The Board will not be bound to accept the lowest or any Tender.

Dated this 8th day of May, 1889.

By Order,
EDWARD CROWNE.
Clerk to the Board.

Local Board Office,
Tottenham, N.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that MAURICE BAUER, of 8, Union Court, in the City of London, has applied for leave to amend the Specification of Letters Patent No. 9352 of 1885, for "Improvements in extracting fat and other substances from dissolvable materials and in apparatus therefor."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 8th May, 1889.

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 month from the date of the said Journal.

(Signed)
H. READER LACK,
Comptroller-General.

ABEL AND IMRAY,
Agents for the Applicant,
28, Southampton Buildings, London, W.C.

IMPORTANT TO THE SPIRIT TRADE.—An Austrian, thoroughly efficient chemical man in the Fermentation, with thirteen years' practical experience, wants engagement as Manager in large Molasses, Corn, or Pressed Yeast Spirit Works, or Potash Refinery. First class references.—Address, R. B. 517, Rudolf Mosse, Vienna.

TO STEARIN MANUFACTURERS AND DISTILLERS.

TAR, SEBACIC ACID (Residues of Sebacic Acid Distillery), wanted to any amount.—Please address "Theere 528," care of Rudolf Mosse, Prague.

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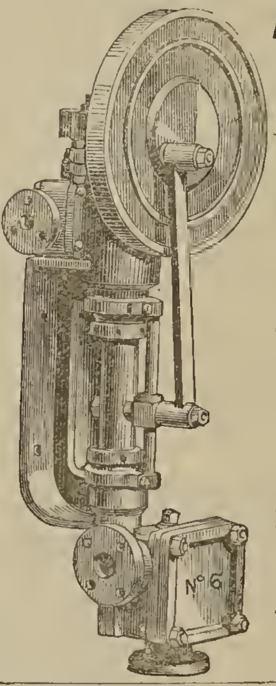

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THE CHEMICAL NEWS.

Vol. LIX. No. 1539.

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLET, F.R.S.,
Professor of Chemistry in the University of Virginia.

After noticing and giving the results of the earlier determinations of the atomic weight of gold, and the recent researches of Krüss and of Thorpe and Laurie, the author reports upon experiments of his own in the same direction, which have occupied much of his time and labour for the last three or four years.

The difficulties connected with the accurate determination of the atomic weight of this metal are remarked upon, and the general principles are reviewed which ought to be observed in all investigations of this kind.

The means and methods of weighing used are stated, and the precautions are described in detail which were resorted to in purifying the metallic gold to be employed in the research, with the history of some samples of "proof" and "trial plate" gold, obtained from the Mint establishments of the United States and England. The general precautions observed in the course of the work are described, particularly the use of an arrangement for evaporating some of the gold solutions with exclusion of the organic matter of atmospheric dust.

A detailed account is given of the methods adopted in seven series of experiments, looking to more or less independent determinations of the atomic weight sought, viz. :—

First Series.—Division of a uniform, neutral solution in water, of auric chloride into two accurately weighed and nearly equal portions; precipitation from the one portion by sulphur dioxide of metallic gold, which was collected and weighed; determination, with special precautions, of the quantity of metallic silver required as nitrate to precipitate the chlorine in the other portion.

Second Series.—Similar treatment of a neutral solution of auric bromide, giving the quantity of gold in one portion and the quantity of silver required to precipitate bromine in the other portion.

Third Series.—Similar treatment of a solution of repeatedly crystallised potassium auri-bromide, again giving the quantity of gold in one portion, and the silver equivalent to the whole of the bromine in the other portion.

Fourth Series.—Determination of the loss by ignition of a weighed quantity of trimethyl-ammonium auri-chloride.

Fifth Series.—Comparison of the weights of gold and silver simultaneously deposited by the same electric current from aqueous solutions of auro-cyanide and argento-cyanide of potassium respectively.

Sixth Series.—Comparison of the weight of gold deposited from a solution of potassium auro-cyanide on electrolysis with the volume of hydrogen liberated by the same current from dilute sulphuric acid, the hydrogen evolved in a voltameter of special construction, and measured of course under well-defined conditions of temperature and pressure.

Seventh Series.—Determination of the volume of hydrogen, under known conditions of temperature and pressure, obtainable by solution in dilute sulphuric acid of a given quantity of specially purified metallic zinc; use of a definite quantity of the same zinc, taken in small excess, to precipitate gold from a neutral solution of auric chloride, and determination of the quantity of metallic gold thrown down; determination of the volume of hydrogen obtainable on solution in dilute sulphuric acid of the *excess* of zinc thus used. Resulting comparison of the quantity of gold in solution as auric chloride with the quantity of hydrogen equivalent to the metal.

The results obtained are thus stated as follows:—

		Atomic weight of gold.		
		Average value from aggregate weights.	Lowest value from a single experiment.	Highest value from a single experiment.
1st series (5 experiments)	..	196·722	196·688	196·770
2nd ,, (6 ,,)	..	196·790	196·731	196·843
3rd ,, (4 ,,)	..	196·775	196·685	196·817
4th ,, (5 ,,)	..	197·225	197·131	197·289
5th ,, (5 ,,)	..	196·823	196·709	196·945
6th ,, (3 ,,)	..	197·137	196·994	197·283
7th ,, (6 ,,)	..	196·897	196·848	196·956

If the general mean be taken of the results of all these series of experiments, using the average value derived from each, and giving all an equal weight, the number 196·910 is obtained for the atomic weight of gold.

But reasons are given for feeling much less confidence in the results of the fifth and sixth series of experiments (made by electrolysis) than in the rest; if these two series be excluded the general mean becomes 196·882.

A certain degree of suspicion as to possible constant error having been shown to perhaps affect the results of the fourth series if this also be left out, and only the firs three and the seventh series be considered, the general mean will be 196·796.

And finally, if, for the sake of comparison with the results of the recent researches of other chemists, only the first three series be included, in which auric chloride and bromide were examined, the general mean will be 196·762—a result rather higher than that of Krüss and lower than that of Thorpe and Laurie, but nearer to the latter than the former.

In conclusion, reference is made to the bearing of the results reached on Mendeleeff's periodic classification of the elements, and on the hypothesis of Prout, and attention is drawn to the desirability of a general re-examination of atomic weights, not by a single method only in each case, or by methods more or less nearly similar or dependent on each other, resting satisfied with a close agreement of results under these conditions, but by as many distinct and independent methods as may be possible for each element examined.

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* Abstract of a Paper read before the Royal Society, May 9, 1889.

DETERMINING THE STRENGTH OF LIQUIDS BY MEANS OF THE VOLTAIC BALANCE.*

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

This method is based upon the circumstance that the greater the degree of concentration of a solution, the larger is the amount of dilution required to reduce its voltaic energy to a given magnitude.

In a research on the "Relative Amounts of Voltaic Energy of Electrolytes (*Roy. Soc. Proc*, vol. xlv., p. 268), I have described the method of measuring the voltaic energy of a substance, and have given the magnitudes of such energy excited in a voltaic couple of unamalgamated zinc and platinum by upwards of one hundred different substances when dissolved in water, in relation to that excited in the same couple by water alone, all the liquids being at the atmospheric temperature.

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* Read before the Royal Society, May 9, 1889.

In the present research, as examples of the applicability of the voltaic balance to determine the degree of concentration of liquids, I have taken aqueous solutions of nitric acid, hydrochloric acid, sulphuric acid, common salt, ammonia, and carbonate of soda, and ascertained the degree of strength of each by chemical analysis, by specific gravity, and by the voltaic balance method. The following numbers represent the proportions of water which were required by one part by weight of each of these substances, in order to reduce its voltaic energy to the same magnitude, viz., to that required to just visibly move the needles of the galvanometer, and they therefore also represent the relative magnitudes of voltaic energy of the substances indicated by the respective formulæ.

	Between—			Temp. ° C.	Average energy.
HCl ..	9,300,000	and	9,388,185	at 16·5 ..	9,344,092
H_2SO_4 .	3,690,476	,,	4,111,446	at 19 ..	3,900,941
HNO_3..	3,039,215	,,	3,369,565	at 19 ..	3,204,395
NaCl ..	190,570	,,	221,428	at 15 ..	207,589
Na_2CO_3	−14,090	,,	−15,550	at 19 ..	−14,795
H_3N ..	−281,818	,,	−313,765	at 15 ..	−297,791

In each example given a known volume of solution was taken, and the proportion of substance in it was found by ordinary chemical analysis. A second portion was taken, its specific gravity ascertained by the method of weighing, and its degree of strength found by aid of the ordinary published tables of specific gravity. A third portion of known volume was then taken, its average amount of voltaic energy measured, and its degree of concentration found by the amount of dilution required to reduce its energy to the same magnitude; the less dilute it was at starting the greater the amount of dilution required. The following are the results:—

By—	HCl.	H_2SO_4.	HNO_3.	NaCl.	Na_2CO_3.	H_3N
Chemical analysis ..	1·85	5·60	2·97	9·13	7·21	1·05
Specific gravity ..	1·70	5·44	2·80	8·74	7·63	1·03
Voltaic balance ..	1·65	5·70	2·90	8·71	7·57	1·06

The variations in the numbers are partly due to inequalities of temperature.

A much less quantity of substance is usually required by the voltaic balance than by either of the other methods, and the operation is quickly and easily performed.

INDIGO STEM ASH.

By JOHN TSAWOO WHITE.

IT may not be uninteresting to record an unpublished complete analysis of the ash of the indigo stem (*Indigofera tinctoria*), an analysis which I finished some three years ago, in the laboratory of the Chemical Examiner to Government, Burma, at a time when I was engaged in some plant-ash determinations.

	I.	II.
Charcoal	4·76	—
Sand	9·99	—
CO_2	8·95	10·56
SiO_2	7·21	8·51
SO_3	5·31	6·27
Fe_2O_3	4·58	5·41
P_2O_5	10·37	12·24
CaO	16·40	19·36
MgO	9·86	11·64
K_2O	16·12	19·03
Na_2O	4·00	4·72
NaCl	1·91	2·26
	99·46	100·00

The sample analysed was grown on the Government Experimental Farm at Alôn, under the charge of Dr. R. Romanis, the Chemical Examiner. Some manuring experiments were tried with nitre and with potassium chloride. The potassium chloride produced no effect, while the nitre is said to make the plants more vigorous.

The ash was prepared by heating the dry stem, after peeling off the bark, on a large sheet of platinum-foil over an argand flame at as low a temperature as possible. The grey ash was weighed, powdered, and put into a stoppered bottle. 1614 grms. of the stem gave 29·4 grms. of ash, equal to 1·8 per cent. The ash determination is given below. The analysis was conducted according to Fresenius.

The numbers in column II. are obtained from those in I. by cancelling charcoal and sand, which are regarded as unessential, and calculating the percentage of the rest. The numbers must be allowed to speak for themselves.

Sand and silica were separated by a strong solution of sodium carbonate in a nickel basin. At first I did not intend to try this separation, but after igniting and weighing the sand and silica together, I thought that I might try its solubility in sodium carbonate. The soluble portion was noted down as silica, and the insoluble matter was called sand. The separation may be imperfect. Will sodium carbonate solution effectually separate silica from sand even after ignition? The potassium oxide was obtained from the weight of its platinichloride.

It was intended to try the composition of the ash of the leaves as well, but the resolution was never carried out.

Rangoon College,
March 28, 1889.

ON THE ATOMIC WEIGHT OF OXYGEN.

By W. A. NOYES.

THE great importance which attaches to the atomic weight of oxygen makes it very desirable that this constant should be determined by several methods and by independent workers.

The method to be described was suggested to the author of this paper when reading Keiser's first paper.* A somewhat similar method has been proposed for a different purpose by Morley.†

The results which I have thus far obtained I consider as only preliminary, and they are presented now because it is necessary to discontinue the work for some time, and because they may be of some interest to others who are working in the same field.

The fundamental idea of the method is that by passing hydrogen into an apparatus containing hot copper oxide, and condensing the water formed within the same apparatus, the weight of the hydrogen can be determined by the gain in weight of the apparatus. The form of apparatus which was found best suited for the purpose is illustrated in the accompanying cut. It was made by Emil Greiner in New York.

C is a bulb with a capacity of 30 to 50 c.c. and will contain 90 to 150 grms. of copper oxide. The tube H was open when the apparatus was received from the maker. A small plug of asbestos was first placed at B, the bulb C was filled with carefully ignited copper oxide (Kahlbaum's best in wire form), and the tube was sealed at H. The volume of the apparatus was then determined by weighing in air and in water, and a counterpoise of nearly the same volume and of somewhat less weight was prepared. The tube F was then connected with a Sprengel pump by means of a bulb containing phosphorus pentoxide, and the air was pumped out. During the exhaustion the bulb was heated in an appropriate air-bath. After exhaustion, the apparatus was allowed to cool and was then weighed,

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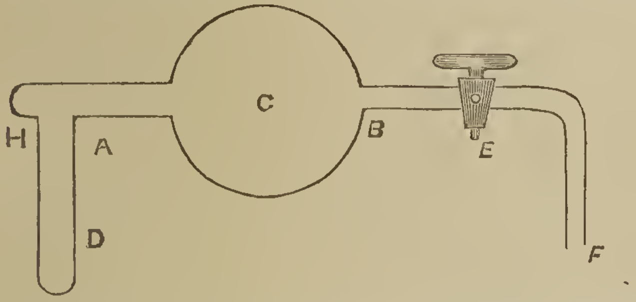
* *Ber. d. chem. Ges.*, xx, 2323.

† *American Chemical Journal*, x., 22.

using the counterpoise before mentioned. The balance used was made by Ruprecht in Vienna, and the weight of the apparatus (150 to 220 grms.) could easily be determined to $\frac{1}{10}$ m.grm. The apparatus was always allowed to stand in the closed balance-case for several hours, and usually over night, before the weight was finally determined. The volume of the counterpoise and weights was the same as that of the apparatus, within 1·5 c.c. in every case, and usually somewhat closer. The greatest difference of temperature between the two weighings which gave the hydrogen was four degrees, and the greatest difference in pressure was seven m.m. Supposing the differences to have occurred at the same time and in the same direction, and the difference in volume to have been 1·5 c.c., the error from this source would have been four one-hundredths of a m.grm.

No correction to vacuum was necessary, as all of the weights for a determination were made with an apparatus of the same volume, and were determined with weights whose relative values had been determined by calibration *in the air*.

After weighing, the apparatus was again placed in the air-bath and heated while it was connected with an apparatus giving carefully purified hydrogen. The connection at F was sometimes made with a short piece of rubber tubing, the two tubes being brought together within it and the whole covered with mercury to prevent possible leakage or diffusion, and sometimes by a ground glass joint lubricated with a little grease. Each method seemed to serve equally well, except in one case, when a little mercury was drawn in through the rubber joint. In that case a low result was obtained, probably because of the vapour of mercury taken up by the hydrogen. When the hydrogen is first admitted to the apparatus through the three-way cock, it rushes over the copper oxide, and only a part of it is converted into water. Very soon a condition is reached when the side-tube D is filled with hydrogen, while the bulb is filled with nearly pure water-vapour. The hydrogen slowly diffuses back to the copper oxide, where it is converted into water-vapour, while the water-vapour diffuses into D and is condensed. The tube A and the opening into D are made about one c.m. in diameter, that the diffusion may be as rapid as possible. D is cooled by immersion into distilled water. From two to four litres of hydrogen can be passed into the apparatus and converted into water in an hour. In a part of the experiments, the results of which are given below, a U-tube was used in place of the bulb to contain the copper oxide, but that form of apparatus was found less suitable.



After passing in a suitable amount of hydrogen, the stop-cock was closed, and by continuing the heating for a short time, all of the *gaseous* hydrogen was converted into water. The apparatus was then cooled and weighed with the same precautions as at first. The apparatus was then connected with a Sprengel pump by means of a bulb surrounded with ice-water. After exhausting the bulb and the tube F, the stop-cock was turned, and the small amount of nitrogen which always remained in the apparatus was pumped out and delivered into a eudiometer, where it was measured and further examined. Meanwhile the tube was heated in the air-bath, and the tube D was surrounded with hot water. As the water in D had been for several hours in an almost perfect vacuum, the water on the outside could be heated to boiling without fear of any ebullition within the tube. The water evaporated quite rapidly from the surface, and 6 or 8 c.c. could be expelled from the apparatus in about an hour. In some of the experiments the apparatus was then connected with a vacuous bulb filled with phosphorus pentoxide, while in others it was cooled and weighed without this step. The vapour remaining in the apparatus in the latter case was very small in amount, and was determined along with the water obtained by re-oxidising the reduced copper. After cooling and weighing, the apparatus was again placed in the air-bath and heated, and oxygen from a gasometer was passed in. The oxygen was passed over heated copper oxide, through a strong solution of caustic potash, and over stick potash and phosphorus pentoxide.

At this point arose one of the most serious questions with regard to the process. It was found that, even after very prolonged heating in pure oxygen, the copper would not take up as much oxygen as had been taken from it by the hydrogen. The explanation seems to be that the hydrogen, as it reduces the copper oxide, leaves the copper in a porous condition, so that the last traces of oxygen can be taken from it by the hydrogen. When the oxygen is passed in, however, the copper on the surface is oxidised first and the copper oxide formed, filling a greater volume than the copper; the pores are almost or quite closed, and the copper within is protected from further oxidation. Whether the copper loses all of the hydrogen which it has absorbed, as Keiser has shown that palladium does, is, perhaps, a question. The only direct evidence which has been thus far obtained on this point was one case in which the copper was heated twice in an atmosphere of oxygen. On the first heating it absorbed two grms. of oxygen and gave 0·0160 grm. water. On the second heating the copper absorbed one-half grm. of oxygen and gave only 0·0013 grm. water. The heating in the second case was continued for two hours. In other cases the heating was continued much longer, and the re-oxidation was still far from complete. Even in some cases when copper reduced in hydrogen and re-oxidised in oxygen was used, the copper could not, after a second reduction, be made to take up the same amount of oxygen again. If the copper remaining unoxidised still retained hydrogen, it would seem that the determinations of Cooke and Keiser must have been subject to an error from the same source. Such an error must have been very small, but it is desirable that some determinations should be made by means of another agent than copper oxide.

After passing in the oxygen, the apparatus was cooled and weighed. It was then heated again, and the gases remaining in it pumped out into a eudiometer, while the water formed was received in a bulb filled with phosphorus pentoxide. On cooling and weighing, the loss of weight, less the weight of the gases pumped out, as determined by analysis, gave the weight of water obtained from the hydrogen which had been absorbed by the copper. Errors in any of these last weights would have only one-ninth as great an effect on the result as errors in the weights by which the amount of the hydrogen was determined. The amount of the water obtained after the oxidation of the copper was quite variable, partly because in some cases the bulb was only connected with the vacuous bulb surrounded with ice-water before re-oxidation and so remained filled with aqueous vapour at a very low tension, and partly because the copper oxide used had been reduced and only partly re-oxidised as stated above, and in such cases the amount of metallic copper was much greater in proportion to the amount of water first formed than in other cases.

The hydrogen was prepared from pure (?) zinc and pure hydrochloric acid. The latter was of specific gravity 1·12, and was boiled carefully and partly cooled in a current of hydrogen before it was introduced into the flask from which it was fed to the generator. Also, pieces of

	Gain.	Loss.	Nitrogen from the hydrogen.	Water by re-oxidation.	Corrected hydrogen.	Corrected oxygen.	Per cent of oxygen re-absorbed.	Atomic Weight.
1.	0·9449	7·4785	0·0006	0·0215	0·9443	7·4976	31	15·880
2.	0·6760	5·3521	0·0016	0·0034	0·6744	5·3551	28	15·881
3.	0·7879	6·2432	0·0013	0·0137	0·7866	6·2554	43	15·905
4.	0·5527	4·3483	0·0006	0·0420	0·5521	4·3856	61	15·887
5.	0·4278	3·3366	0·0004	0·0631	0·4274	3·3927	65	15·876
6.	0·8271	6·5437	0·0006	0·0249	0·8265	6·5658	27	15·888

Mean = 15·886 ± 0·0028

pure zinc were put into it, to more thoroughly wash out dissolved gases and to furnish nascent hydrogen which should remove the last traces of oxygen from the liquid. Contact with the air was carefully avoided, and the acid was fed into the generator from a flask filled above with hydrogen, either by an arrangement similar to that described by Cooke, or with hydrogen from an independent generator. After the introduction of the hydrochloric acid into the feed-flask, a solution of blue chromous chloride was added. This was obtained by the reduction of potassium pyrochromate with zinc and hydrochloric acid. Its purpose was to absorb any traces of oxygen, and to give evidence of any air in the apparatus, by its change in colour. The heavy flask used for a generator had a capacity of one litre, and had but one neck. The rubber stopper, bearing four tubes, was sunk into the neck, and covered with a thin layer of mercury, to prevent possible diffusion. The acid was fed by a syphon, and only its vapour came in contact with the stoppers. When hydrogen from the generator was used in the feed-flask, the stopper of the latter was surrounded with a jacket filled with mercury.

From the generator the hydrogen was passed through a 20-bulb tube filled with a 30 per cent solution of caustic potash, to which some lead chloride was added. The latter revealed the presence of a small amount of hydrogen sulphide. Next was an 8-bulb tube containing a 3 per cent solution of potassium permanganate, then a layer of hot copper. This was omitted in the first determinations, and was introduced from fear of a trace of oxygen from the potassium permanganate. After its introduction, a trace of hydrogen sulphide was found in the strong caustic potash solution which followed. This may have come from the rubber joints at both ends of the tube containing the copper. These joints could not be sealed, as they were between hard and soft glass. The joint at the other end of the potassium permanganate tube was also of rubber, because the solution required frequent renewal. The tubes were brought close together within these joints, and they were covered with jackets filled with water, to prevent diffusion. All other joints were made by fusing the glass together. After the copper, the hydrogen passed a strong caustic potash solution, to which lead sulphate was added in the later experiments, and then over stick potash and over phosphorus pentoxide mixed with asbestos. Glass-wool was avoided, because a specimen examined was found to have so low a specific gravity as to prove that it consisted—in part, at least—of fine glass tubes, and it was feared that the air in these would diffuse out slowly and mix with the hydrogen. After passing the phosphorus pentoxide an overflow tube was provided, dipping under mercury.

In calculating the results, the weight of the hydrogen, determined by the gain in weight of the apparatus, was corrected by subtracting the weight of the gas which was obtained in removing the water formed, as described above. This gas was calculated as nitrogen. In every case but one, however, oxygen was added in excess, then hydrogen, and the mixture was exploded. The results would seem to indicate that the gas contained from six to eleven thousandths of a m.grm. of hydrogen, but it is believed that this apparent result came from the formation of a small amount of oxides of nitrogen by the explosion. The oxygen was determined by the loss in weight of the apparatus after the water was removed. To this was added eight-ninths of the weight of the water obtained by re-oxidising the copper.

Two determinations are omitted in the results given below. In one of these, mercury leaked by the rubber joint, and some of its vapour probably entered with the hydrogen. In the other, a small amount only of the hydrogen was used, and the accidental error was probably large. The other determinations were as in Table above.

It is of especial interest to compare this result with that obtained by Cooke, who prepared his hydrogen from the same materials. His result was 15·869, and the probable error of his first series is one-half greater than that of this series, while that of his second series is but little less than this. *If the correction for nitrogen is omitted, the mean of these determinations becomes 15·867, or almost exactly the same as Cooke's final mean.* It seems to the author that the evidence is almost conclusive that Cooke's hydrogen was contaminated with a trace of nitrogen. While the amount of nitrogen can be rendered very small (in one case less than ½ c.c. in 10½ litres), it would seem to be impossible to entirely exclude it with such generators as Cooke and myself have used.

In this series, the apparatus for purifying the hydrogen and also the condition of the copper oxide was repeatedly varied, in the endeavour to discover sources of constant error. One determination has also been made, using dilute sulphuric acid instead of hydrochloric. The result was 15·874.

The results obtained show that the accidental errors of the determination have been made very small. When the result is compared with that obtained by Keiser, however, I am inclined to believe that there must be in these determinations, as well as in those of Cooke, some source of constant error which has not yet been discovered.—*American Chemical Journal*, Vol., ii., No. 3.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month ending April 30th, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

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

London, May 6th, 1889.

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

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

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

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

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

The quality of the water supply has continued throughout the month to be entirely satisfactory. Its composition has not been found to differ to any noteworthy extent from that observed to prevail during the first three months of the year; but the slight variation that has been recognised is in the direction of an increased degree of freedom from organic matter. Thus, in the case of the Thames-derived samples examined during the month, the mean proportion of organic carbon was found to be 0·154 part in 100,000 parts of the water, as against a mean of 0·164 part furnished by the previous three months' supply. The maximum proportion of organic carbon met with in any single sample of Thames-derived water examined during the month was found to be 0·170 part in 100,000 parts of the water. The difference in mean composition of the Thames-derived water, as supplied by the different companies, was, as usual, wholly insignificant. This, our hundredth monthly report, completes the record of the results of our examination of over 18,000 samples of the water supply of the Metropolis.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 16th, 1889.

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

Messrs. C. Heinrich Trinks and Ernest F. Ehrhardt were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William D. Cargill, B.Sc., Longhaugh, near Dundee; Henry W. Morrow, B.S., Wilmington, Delaware, U.S.A.; and Robert Redwood, 85, Gracechurch Street, E.C.

The following were elected Fellows of the Society:—William Taylor Gibbs, Byron B. Goldsmith, Charles James Grist, John Kitchin, John Edmund Legg, Francis Ransom, Alfred Edward Sibson, Ignatius Singer, Walter J. Sykes, and William Virtue.

The following papers were read:—

47. "*The Magnetic Rotation of Nitrogen Compounds.*" By W. H. Perkin, Ph.D., F.R.S.

In previous communications the author has shown that in the magnetic field the plane of polarisation of light is rotated to a greater extent in unsaturated than in saturated carbon compounds; in the present communication it is shown that in the case of nitrogen compounds the magnetic rotation is in like manner correlated with changes in the valency of the nitrogen.

Nitrates, Nitrites, and Nitro-compounds.—The specific rotation of all these is low, thus—

Nitric acid	1·180
Methylic nitrate	2·057
Ethylic ,,	3·084
Propylic ,,	4·085
Isobutylic ,,	5·180
Ethylenic ,,	3·768
Glyceric ,, (nitro-glycerin	5·405
Isobutylic nitrite	5·510
Nitromethane	1·858
Nitroethane	2·837
Chloropicrin	5·384

The change attending the conversion of nitric acid into an ethereal salt is comparable with that of the acids of the acetic series into ethereal salts, the increase in the value for the nitrate being less than may be expected from the change in composition, thus—

Methylic nitrate	2·057
Nitric acid	1·180
	0·877
Methylic formate	2·495
Formic acid	1·671
	0·824
Usual value of CH_2	1·023

The high rotation of isobutylic nitrite in comparison with that of the corresponding nitrate is an illustration of the influence exercised by unsaturated nitrogen; it is also noteworthy that the rotation of chloropicrin is less than that of chloroform (5·559).

Amines.—Very nearly the same value is obtained for ammonia, whether aqueous or alcoholic solutions be taken, the former giving 1·81, the latter 1·826; the aqueous solution examined contained 31 per cent, the alcoholic 14·48 per cent NH_3: hence it would appear that little, if any, combination takes place between the ammonia and the solvent. Similar observations made with mixtures of equal volumes of isobutylamine and water or alcohol, and with a mixture of piperidine and water in the proportions $C_5H_{11}N : OH_2$, indicate, however, that combination takes place to some extent in these cases, the found and calculated values being as follows:—

	Calculated.	Found.	Difference.
Isobutylamine and water	11·200	11·099	0·101
,, ,, alcohol	10·459	10·361	0·098
Piperidine and water	6·810	6·724	0·086

The effect of hydrocarbon radicles on amines was studied in the following cases:—

Ethylamine	3·609
Diethylamine	5·662
Triethylamine	8·518
Propylamine	4·563
Dipropylamine	7·549
Tripropylamine	11·664
Isobutylamine	5·692
Diisobutylamine	9·936
Allylamine	5·587
Pentamethylenediamine	7·491
Aniline	16·162
Methylaniline	19·629
Dimethylaniline	22·823
Piperidine	5·810
Pyridine	8·761

From these numbers it will be seen that the effect of introducing a single radicle into ammonia is somewhat less than corresponds to a similar change in homologous series, viz., 1·023 per CH_2. The rotation is increased proportionally more by the displacement of a second hydrogen atom, and in the paraffinoid amines a very remarkable increase attends the introduction of the third radicle, indicating a marked difference to exist between secondary and tertiary amines. The effect of methyl in aniline is also very remarkable, the increase in the rotation being more than three times that which usually follows such an alteration in empirical composition in paraffinoid compounds. The value for piperidine is very low, and is in accordance with the conclusion that it is a saturated compound; the value for pyridine is also low in comparison with aniline and benzene (11·297).

The study of the salts of the amines has afforded noteworthy results: instead of the diminution which usually attends the formation of compounds, it is found that the observed rotation is slightly in excess of that calculated by adding the rotations of the constituent compounds in the case of the following ammonium chlorides:—

	Found.	Calc.	Diff.
Ammonium chloride	6·096	6·032	+0·064
Ethylammonium chloride ..	7·997	7·823	+0·174
Diethylammonium chloride	9·896	9·876	+0·020
Piperidinium chloride	10·034	10·024	+0·010

Triethylamine, however, behaves "normally," and a normal result is also obtained in the case of ammonium nitrate and sulphate, thus—

	Found.	Calc.	Diff.
Triethylammonium chloride	11·724	12·732	−1·008
Ammonium nitrate	2·316	2·998	−0·686
,, sulphate	4·963	5·951	−0·988

From the discussion of his results generally, the author arrives at the conclusion that in compounds of unsaturated "triad" nitrogen, the nitrogen has a greater influence than when it is present in the saturated condition, the difference in the values being about 0·5; this is only about half the difference usually observed on comparing the rotations of carbon compounds differing by 2H.

DISCUSSION.

Dr. **GLADSTONE** said that the general result of Dr. Perkin's work, establishing a difference in nitrogen according as it is present in the saturated or unsaturated condition, was in accordance with the conclusion which he had arrived at from the study of refractive power; the peculiarities brought out by the study of the magnetic behaviour, however, were chiefly indicated by peculiarities in dispersive power, being less obvious in the refraction equivalents.

Professor **RAMSAY** said that he should like, on some future occasion, to raise a discussion on the method adopted by Dr. Perkin and Dr. Gladstone in dealing with their results. He thought that the method followed by Schroeder in discussing volume constitution was perhaps applicable, and, at all events, deserving of attention.

48. "*The Nature of Solutions, as Elucidated by a Study of their Densities, Electric Conductivities, Heat Capacity, and Heat of Dissolution.*" By S. U. **PICKERING.**

The solutions which form the subjects of this research are those of calcium chloride, calcium nitrate, and sulphuric acid. The results obtained with the first of these have already been brought before the Society (*Chem. Soc. Proc.*, 1888, 35), and tended to show that the curves representing the densities and heat of dissolution, of solutions of different strengths, though apparently regular on a superficial inspection, are not really so; when they are analysed by differentiation they are resolved into a series of curves or straight lines, showing that breaks occur in the original curves; these breaks, moreover, correspond to hydrates of definite composition. The densities gave a series of straight lines on the first differentiation, bearing out Mendeleeff's statement that such was the nature of the density curves in the case of sulphuric acid and alcohol, whereas the heat of dissolution required two differentiations before it gave straight lines.

With calcium nitrate the determinations which have been made are much more numerous, and the results obtained are of a nature precisely similar to those with calcium chloride. The straight lines formed by the first differential coefficient of the densities are in this case inclined to each other so very slightly, as scarcely to warrant the conclusion that the whole figure is not a continuous curve, were it not that the heat results confirm in every detail the breaks which the rectilineal drawing of the density differential shows. The heat capacities (specific heat) of very weak solutions of this salt have also been determined, and they are found to afford a rectilineal figure, indicating breaks at the same points as those deduced from the density and heat results.

The author has proceeded to an extensive examination of sulphuric acid solutions. On plotting out the first differential of his density results, he was surprised to find that it formed an irregularly curved figure, and not the rectilineal figure given by Mendeleeff, and he was still more surprised to find that on plotting out the values used by Mendeleeff himself, the figure obtained was curvilinear, like his own, and not rectilinear, like Mendeleeff's. This led him to plot out Mendeleeff's values for the first differential of the densities of alcohol, and in this case also he found that they gave an irregular curve, and not the rectilineal figure depicted by Mendeleeff in the *Journal* (*Trans.*, 1887, 780). Mendeleeff's statement, therefore, that he had proved the hydrate theory by showing that the densities differentiated into straight lines meeting at points corresponding to definite hydrates, is erroneous.

On applying a second differentiation to his density results with sulphuric acid the author obtained a series of straight lines, so that the density curve in this case resembles the heat curves in the case of the two calcium salts, and it is probable that the densities of these latter salts give rectilineal figures on the first differentiation only, because the constituent lines are straight within experimental error, and not because they are straight in reality.

The author has made determinations with a series of sulphuric acid solutions at four different temperatures, 8°, 18°, 28°, and 38°. The results obtained and the breaks shown were the same in every case, and the latter were found to become more apparent as the temperature is lower. The same conclusions as to the effect of a lowering of temperature in intensifying the change in general direction of the curve may be drawn from Mendeleeff's determinations with alcohol at different temperatures.

Crompton's interpretation of Kohlrausch's determination of the electric conductivity of sulphuric acid solutions is next discussed. The author agrees with Crompton's conclusion that they give a rectilineal figure after two differentiations, but he differs from him in some of the details as to where the breaks occur, and shows that the most probable position of these breaks agree very closely with those shown by his own density results.

The heat capacity of sulphuric acid solutions up to a strength of 12 per cent was next determined, and the results were found to form a series of very slightly curved lines, indicating breaks very clearly at the same points as did the densities. The original curves probably require two differentiations before they are reduced to straight lines.

The determination of the heat of dissolution of sulphuric acid solutions with the requisite degree of accuracy presented considerable difficulties, owing to the large amount of heat evolved. The results obtained confirmed the author's conclusions as to the nature of the heat curves in the case of the calcium salts. The whole curve was found to be made up of a series of independent curves, each of which gave a straight line on two, or sometimes on one differentiation, and the breaks agree in position with those deduced from the other properties. Although Thomsen's determinations of the heat of dissolution of sulphuric acid are far too few in number to prove the real nature of the curve, the author shows that they are quite sufficient to disprove the perfect regularity which Thomsen and his followers attribute to the interaction. Some marked changes are shown by it, and Thomsen's equation, which is supposed to represent the curve so faithfully, is applicable, in reality, to but 1 per cent of the whole figure.

The various hydrates which are proved by this work to exist in solution are numerous and complex. Those which calcium chloride forms contain 6, 7, 8, 10, 13, 18, 28, 86, and 1500 H_2O; calcium nitrate gives hydrates with 3, 3·5, 4·5, 5, 6, 10, 17, 51, 265, and 1810 H_2O; while with sulphuric acid we find hydrates with $\frac{1}{6}$, $\frac{1}{3}$, $\frac{2}{3}$, 1, $\frac{3}{2}$, 2, 4, 5, 9, 13, 24, 52, 135, 510, 1430, and 4950 H_2O. The existence of these is, naturally, more doubtful in some cases than in others, and it is impossible to determine the exact molecular composition when more than about 10 H_2O is present. In some cases the hydrates of sulphuric acid have been established by six independent sets of results obtained from the study of four distinct properties.

The excessively large amount of water present in the highest hydrate is a matter of especial interest, and the existence of such compounds explains the influence which mere traces of one substance may have on another substance (*e.g.*, impurities in metals). The highest hydrate of sulphuric acid contains only 0·1 per cent H_2SO_4, yet the breaks at the extreme ends of the curve are comparatively more marked and more certain than most of the others. The author has recently given a striking proof of the existence of the break in the heat curve of sulphuric acid at 0·3 to 0·4 per cent, in the fact that the heat of neutralisation of this acid becomes "normal" when this break is recognised.

The progress of differentiation was always applied to the experimental numbers themselves in the first case, but for the second differentiation it was necessary, owing to the magnitude of the experimental error, to take the smoothed first differential curves, and not the experimental numbers. With the heat results, where the error is comparatively large, the first differentiation was performed on the curve representing the results as well as on the experimental numbers.

The author mentions a striking proof that the character of the second differential is not attributable to any peculiarity in the manner in which he drew the first differential figure from which it is deduced. When the contraction produced on mixing sulphuric acid and water in different proportions is plotted out, a figure results utterly unlike that representing the densities, and the first differential figure (obtained from the experimental numbers) which it gives is also quite unlike the first differential from the densities, yet these two dissimilar figures give, on a second differentiation, figures which are identical with each other, both as to the inclination of the straight lines of which they are composed, and as to the points at which these straight lines meet.

It may be noted that the maximum contraction on mixing sulphuric acid and water does not occur at a point corresponding to $H_2SO_4,2H_2O$, as has hitherto been supposed, but at a point some 4 per cent below it, a point coincident with any break.

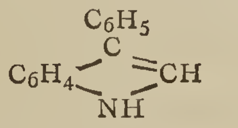
The final conclusion which the author deduces from his work is the absolute rejection of any theory of dissolution other than the hydrate theory.

49. "*The Expansion of Water and other Liquids.*" By S. U. Pickering.

The author gives some determinations of the density of water at different temperatures which indicate sudden changes in the rate of expansion at about 10° and 18°. On examining the results obtained by Pierre, Kopp, Rosetti, Matthiessen, Solly, Despretz, and Hagen, he obtained further evidence of these changes, as well as of another change at 50—60°. Pierre's results also show marked changes at 0° and 2·5°. Pierre's results with eleven organic acids were then examined, and in most of them there appeared to be sudden changes at certain temperatures, which temperatures were different for different liquids. Nearly all of these results show that the densities of liquids, when plotted against temperature, form a series of parabolic curves of the second order, not meeting tangentially, and differentiating, therefore, into a series of straight lines which do not meet at the points where the breaks occur.

50. "*The Formation of Phenylindoles by Isomeric Change.*" By Walter H. Ince, Ph.D.

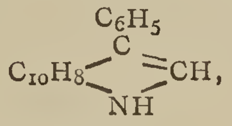
It has been observed by E. Fischer and Th. Schmitt (*Ber.*, 1887, 1071, 1811) that when the phenylindole—



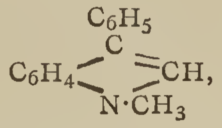
is heated with zinc chloride at 170° it is converted into the isomeride—

$$C_6H_4<\begin{matrix}CH\\NH\end{matrix}\geqq C\cdot C_6H_5.$$

The author finds that the corresponding naphthindole,—



and the methylphenylindole,—



undergo change in a similar manner, although action takes place neither so easily nor so completely as in the simpler case.

51. "*An Improved Soxhlet Extractor and Vacuum Distilling Apparatus.*" By J. Lewkowitsch, Ph.D.

The author attaches a tap at the bottom of the syphon-tube of the Soxhlet extractor, by means of which a few drops of the solvent as it runs from the extracted substance can be withdrawn to ascertain whether the extraction is complete.

For use in distilling small quantities of liquid which froth, and through which it is necessary to pass an air-current while distilling under reduced pressure, he describes a flask made by inserting and sealing in, just above the bulb of a Wurtz flask, a tube which passes down nearly to the bottom of the flask, and there terminates in a fine point.

He also describes a simple adapter for use in fractional distillation under reduced pressure.

At the next meeting, on June 6th, the following papers will be read:—

"Experimental Researches on the Periodic Law." By Dr. B. Brauner.

"The Amylodextrin of W. Naegali." By H. T. Brown and G. H. Morris, Ph.D.

"The Determination of the Molecular Weights of the Carbohydrates." Part 2. By the same.

"Researches on Silicon Compounds." Part 5. By Prof. Emerson Reynolds, F.R.S.

"The Isomerism of the Alkyl Derivatives of Mixed Diazoamido-Compounds." By Prof. Meldola, F.R.S., and F. W. Streatfeild.

"The Atomic Weight of Zinc." By Dr. Gladstone, F.R.S., and W. Hibbert.

"The Amount of Nitric Acid in the Rain-water at Rothamsted, with Notes on the Analysis of Rain-water." By R. Warington, F.R.S.

"The Product of the Action of Sulphur on Resin." By G. H. Morris, Ph.D.

PHYSICAL SOCIETY.

May 11, 1889.

Prof. Reinold, F.R.S., President, in the chair.

Mr. A. Clegg, Prof. V. B. Lewis, and Mr. W. Robinson were elected Members of the Society.

The following communications were read :—

“*On an Electrostatic Field produced by Varying Magnetic Induction.*” By Dr. O. Lodge, F.R.S.

This paper describes a research made with the object of finding some connection between static electricity and magnetism. Several methods of attacking the problem, such as rotating or varying the strength of magnets in the neighbourhood of delicately suspended charged bodies, are indicated, and the one selected was based on an idea of Mr. A. P. Chattock, who conceived that a charged body in the vicinity of a closed magnetic circuit would be affected by varying the magnetic induction. From the theory of the effect it is shown that the magnitude of the quantity sought is exceedingly small, for the expression involves the inverse square of the velocity of light. The E.M.F. induced in any closed curve round the magnetic circuit or solenoid by varying the induction, I, is given by $e = \frac{d\mathrm{I}}{dt}$ (1). If an E.M.F, e, act on a charge, Q, at a distance r from the axis of the solenoid, the work done in one revolution will be $e\mathrm{Q}$ and $e\mathrm{Q} = \mathrm{F}.2\pi r$ (2), where F is the mechanical force. Now, if the E.M.F. in (1) is the same as that in (2) the impulse given to the charged body by destroying the induction will be—

$$\phi = \int_0^\infty \mathrm{F}\,dt = \frac{\mathrm{IQ}}{2\pi r} (3).$$

Since $\mathrm{I} = \frac{4\pi n \mathrm{CA}\mu}{l} = \mu\mathrm{C}$ times a length, and $\mathrm{Q} = s\mathrm{V} = \mathrm{KV}$ times a length, $\therefore \phi = \frac{\mathrm{K}\mu\mathrm{CVA}}{2\pi r}$ (length)^2 and $\mathrm{K}\mu = \frac{1}{\text{“}v\text{”}^2}$

$\therefore \phi \propto \frac{1}{\text{“}v\text{”}^2}$.

The magnetic circuit actually used was a wire gramme ring of trapezoidal section wound with copper over a part of its periphery. The indicating apparatus was a suspended needle consisting of two oppositely changed bodies carried on a small shellac arm to which a mirror or pointer was attached, and was suspended vertically in the plane of the ring. A microscope was used when the needle had a pointer attached. Great difficulty was experienced from Foucault currents when metallic films were used for the needle, and the magnetic properties of other semi-conductors tried further complicated the matter. Eventually the charged bodies were made of paper in the form of cylinders $\frac{1}{8}$ inch diameter and $\frac{3}{8}$ long.

Considerable trouble was caused by the electrostatic action between the needle and exciting coils, and various methods of screening were tried and abandoned, and subsequently the wire was replaced by a single spiral of copper ribbon, the outer turn of which was put to earth. Observation was rendered difficult owing to the wandering of the zero when the needle was charged, but this was minimised by suitably shaping the contour of the needles surroundings. Heat also created considerable disturbance, and the connection currents were cut off by a series of concentric cylinders of tin plate.

The method of observation was to charge the two insulated parts of the needle and then reverse the magnetising current in synchronism with the period of the needle, noting whether the amplitude of any residual swing could be increased or diminished according as the impulse assisted or opposed the motion. In this way slight indications have been observed, and the effects reverse when the charges of the cylinders are reversed.

In explaining the theory of the experiment the author made use of a simple transformer consisting of an ordinary hank of iron wire wound over with insulated copper and provided with several secondary coils, and by it he demonstrated that the primary current increases on closing the secondary, due, as was shown, to the decrease of self induction of the primary caused thereby.

Prof. Fitzgerald, in answer to a question from Dr. Lodge as to the influence of screens, said he had not fully considered the matter in this particular case, and as the general effect of screens depended on the square of “v,” the subject required careful treatment. As a means of checking the results obtained by Dr. Lodge he suggested calculating the impulse and seeing whether its magnitude approximately corresponds with that observed. Commenting on an idea for carrying out a similar experiment attributed to him in the paper, in which a charged gold leaf is placed between the poles of a magnet, Prof. Fitzgerald said he had been misunderstood, for he had conceived a disc parallel to the faces of the magnets, which, when excited, should cause the disc to turn in its own plane.

Referring to the equations for mechanical force given in “Maxwell,” § 619, he pointed out that the coefficient of e in the equation $\mathrm{X} = cv - bw - e\frac{d\Psi}{dx} - m\frac{d\Omega}{dx}$ ought to be P, where $\mathrm{P} = c\dot{y} - b\dot{z} - \frac{d\mathrm{F}}{dt} - \frac{d\Psi}{dx}$, and considered it very important that the existence of the term $e\frac{d\mathrm{F}}{dt}$ should be tested experimentally.

Prof. S. P. Thompson mentioned some experiments on which he was engaged by which he hoped to show electric displacement in continuous dielectric circuits, such as a link of gutta-percha. Up to the present the experiments had not been successful, owing to his inability to place the two gramme ring coils used into such relative positions as to give silence in the telephone connected with the coil used as secondary when currents were sent through the primary.

Prof. Ayrton suggested that Dr. Thompson's difficulty may arise from the fact that such rings do produce considerable external field, even when carefully wound.

Prof. Fitzgerald requested Dr. Thompson to investigate the effects of displacement currents, and of changing vector potential, and pointed out that in a single medium the former can produce no magnetic effect. As regards fields containing different media, he said the calculations would be complicated by the spurious charges on the separating surfaces.

Dr. Lodge, in reply, said he had calculated the momentum to be expected in one arrangement of his experiment, in which a suspended aluminium cylinder surrounds one limit of a rectangular magnetic circuit, which formed the core of an induction coil ; one end of the secondary was put to the core and the other to the cylinder, thus forming a condenser. The result came out about 10^{-6} dyne second, but he could not say whether such a small quantity was observable.

“*On the Concentration of Electric Radiation by Lenses.*” By Prof. O. J. Lodge, D.Sc., F.R.S., and James L. Howard, D.Sc.

The authors' first attempts at concentration were made with mirrors on a comparatively small scale, and owing to the difficulties experienced it was considered advisable to try lenses. Two large cylindrical ones of plano-hyperbolic section were cast of mineral pitch in zinc moulds, the plane faces being nearly a metre square, the thickness at vertex 21 c.m., and each lens weighed about 3 cwt. The eccentricity of the hyperbola was made 1·7, to approximate to the index of refraction of the substance. The lenses were mounted about six feet apart, with their plane faces parallel and towards each other on a table in the college corridor, and an oscillator was placed about the principal facial line of one of them at a distance of 51 c.m. from the vertex. The field was explored by a linear receiver made out of two pieces of copper wire mounted in line on a piece of wood, and the air-gap between their inner ends was adjusted by a screw. When the oscillator worked satisfactorily the receiver would respond at about 120 c.m., and with the lenses the distance was 450. The receiver responded anywhere between the lenses and within the wedge between the second lens and its focal line, the boundaries being clearly defined, but no special concentration was noticed about the focus. Interference experiments were carried out by placing a sheet of metal against the flat face of the second lens, and determining the positions of minimum intensity between the lenses. The distance between these points was 50·5 c.m., corresponding with a wave-length of 101 c.m., whereas the calculated wave-length of the oscillator was 100 c.m.

Prof. Fitzgerald congratulated the authors on their success, and also pointed out that, although large oscillators give good results at distances within a few wave-lengths, yet at greater distances small ones were decidedly superior, owing to the energy of radiation varying as the fourth power of the rapidity. He had recently made experiments on electric radiations analogous to Newton's rings, and had successfully observed the central dark spot and the first dark band. Referring to Dr. Lodge's experiments, he enquired whether any traces of diffraction were observed near the boundary of the bundle of rays between the lenses. Speaking of polarisation experiments Prof. Fitzgerald said waves reflected from films of water exhibited no polarisation, whereas those reflected from non-conductors were completely polarised.

In reply Dr. Lodge said no diffraction effects had been observed, but in the interference experiments to determine wave-length the positions of minimum effect were very decided.

The President, in proposing that the thanks of the meeting be given to the authors of the papers, congratulated the Society on the presence of both Dr. Lodge and Prof. Fitzgerald on the present occasion, when subjects with which they were so well acquainted were brought before the meeting.

OBITUARY.

ROBERT ROMANIS.

The Rangoon College has to record a sad loss, a victim to cholera, in the sudden death on April 13, 1889, of Dr. R. Romanis, D.Sc. (Edin.), F.C.S., F.I.C., &c., the Professor of Physical Science and the Chemical Examiner to Government, Burma.

Dr. Romanis was born in 1853. He joined the Service here in 1878 as Teacher of Science to the then Rangoon High School, now blossomed into a College, and soon it is hoped to ripen into a University. He was appointed Chemical Examiner to Government, Burma, in 1880. In November, 1885, he went up to Upper Burma with the expeditionary force in the last war as a scientific officer attached to the force.

His sudden death must be a startling shock to all, and most of all to his relations in Scotland; for only yesterday evening, being mail day, I saw a letter of his, addressed to a relative, given to his servant to post. He was working in the laborarory yesterday evening till 5.30 p.m., distilling some Arakan petroleum. He went home two or three times during the day. With his usual quiet manner I noticed, later in the evening, nothing but his low and subdued tone of voice. And next morning—he died at 9 a.m.—his servant, who brings his office box, came and told me that his master had died, at the same time bursting into tears. I went over to his house. The corpse was laid out; his features were still sharp and handsome, though his eyes were somewhat sunken in their sockets. The interment in the Cantonment Cemetery took place this evening. As the college is closed, the boys having gone home for the holidays, the funeral procession missed the attendance of the boys in their bright-coloured national costume. Still the funeral did not lack attendance. The Chief Commissioner himself, besides other officials and non-officials, graced the ceremony. It was a fair gathering. As Dr. Romanis was a captain in the Rangoon Volunteer Rifles he had a military funeral, and three volleys were fired into the air after his coffin was lowered.

Three days ago he brought some weeds, dug from some muddy ponds near the Shway Dagon Pagoda. He was looking for diatoms; and he caught, according to some, the cholera germs from those mud pools. If so, he died a martyr to science! Four or five years ago he sent home to Mr. W. Joshua, of Cirencester, some of these low organisms from, I think, these very pools, and Mr. Joshua was fortunate enough to discover about a dozen new species of Desmids.

Though it does not beseem me to speak of myself, I must say that to Dr. Romanis I personally owe a debt of gratitude. He first led me to drink at the fountain of science. To his guidance and care I owe my study of chemistry. He selected me to be his assistant, five years ago, from among his students. I, on my part, did my duty to him ungrudgingly and in love. I can scarce believe that the once familiar face will pace the laboratory no more; that those footsteps will be heard no longer where they had been heard for years! So our college sees extinguished its brightest star in its firmament in a professor gentle, kind, conscientious, and generous—at once loved and respected. His death carries sorrow to many hearts, and he died young—so die those who the gods love.

The last two years he was engaged in examining the products of the distillation of teak. He communicated some of his results to the Chemical Society, but the examination is still unfinished. Besides the records of his annual reports, some of his separately published papers may be noted:—"Coal Outcrops in the Henzada District"; "Oil Wells at Yenangyoung"; "Ash of Wood and other Forest Products"; "Notes on Usar and Reh Soils"; "Experiments in the Cultivation of Sugar-cane in 1882—83." Three weeks ago he applied for three months' privilege leave to go home.

John Tsawoo White.

NOTICES OF BOOKS.

The Patents, Designs, and Trade Marks Acts, 1883—1888 Consolidated, with an Index. By Lewis Edmunds, D.Sc., LL.B., Barrister-at-Law. London: Stevens and Sons, Limited.

The compilation before us will prove of great value to patentees, actual or intending, as well as to patent agents. Not the least of its merits is that it exhibits the manifold defects of existing British patent law in all their deformity. The functions of the examiners here appear very much to resemble those of King Log, whilst those of the patent-examiners in Germany and the United States much more closely resemble those of his successor, King Stork. We have known a German examiner, after having been fairly beaten out of the objections which he had raised to an application for a patent, to bring forward a new one, not mentioned at all in his first report, and to hold to it. We have also known a case where an American examiner could not be got to see the difference between a hydrate and a silicate. One of the most useful duties which, by the Act of 1883, devolved upon the examiners, has been done away with by a later enactment. It was to the effect that if the invention comprised in two applications for patents is found to be the same, the comptroller may, on being duly informed of such similarity or identity, refuse to seal a patent on the application of the second applicant. This salutary provision being repealed there is nothing to prevent two, or possibly even more persons, from obtaining patents for the same invention, and becoming consequently involved in litigation.

The cardinal flaw in our patent system is that an alien not domiciled in the United Kingdom may not only obtain, but continue to uphold, a patent without ever working or allowing it to be worked on British ground. As it is done in other countries, we ought to hold such patent at once invalid and cancelled, unless worked on a commercial scale within a term of, say, three years. This brings us to the point that our patent reciprocity with foreign states is very one-sided. We grant much more to foreigners than they grant to us in return. An alien may obtain a British patent without any scrutiny as to the novelty or the practicability of the process, and may, provided he pays the fees, uphold it for the full term of fourteen years, though he may never work it at all on British soil. On the contrary, a British subject can obtain patents in foreign countries only after an examination more stringent than what a native of such country would have to meet, and when he has actually received a patent he can uphold it only by continuous *bonâ fide* working in the country in question.

One very important industrial country has in its patent system a proviso that if a foreigner applies for a patent and some native thinks proper to come forward and declare upon oath that he has invented the same process, but has been prevented from patenting it by lack of means, by other occupations, absence from home, or sickness, he is pronounced to be the first and true inventor, and the foreigner finds his application dismissed.

We might with advantage borrow and extend one of the features of the German patent law, which refuses protection to proprietary medicines. Did we not only do this, but refuse trade-marks to such concoctions, to alleged medical appliances other than medicines, to "foods" and substitutes for foods, a death blow would be struck at quackery, and many phases of adulteration would cease to exist.

Another shortcoming of our patent system is its limited extent in space, covering merely the United Kingdom and the Isle of Man. Under what is known as the "old law" a patent for a slight additional fee could be obtained covering the whole of "Her Majesty's dominions and plantations abroad." On passing what up to 1883 was called the "new law" this vital clause was quietly struck out. We need an Imperial patent-law, which would give an immense stimulus to invention and industry. A mere stroke of the pen would do this for India and the so-called "Crown colonies." Those colonies which have quasi-independent legislatures could easily be prevailed upon to accept an agreement which would give them, no less than the dwellers in the Home Kingdoms, increased privileges.

Examination of Water for Sanitary and Technical Purposes. By H. Leffmann, M.D., Ph.D., and W. Beam, M.A. Philadelphia: P. Blakiston, Son, and Co.

In their preface the authors remark that "there are several special manuals at hand, but they are limited in scope and contain much matter which does not bear on the problems that confront the sanitary and industrial chemist, devoting much space to the description of processes that are not generally employed, and to the presentation of the details of a local professional quarrel." It would be idle on our part to affect misunderstanding of the last dozen words. But we know of only one special manual in which the details of the "quarrel" in question —which was something very much more than local—have been lately reproduced.

As to the scope of the manual before us, it gives no special directions for the analysis of urines, sewage, sewage-effluents, or industrial waste waters. There are remarks on the detection of a fungus "supposed to be peculiar to sewage." But as the occurrence of this fungus is afterwards pronounced due to the presence of phosphates it cannot be the notorious *Beggiatoa alba*, which grows not merely in sewage but in the waste waters from Leblanc alkali works and from natural sulphuretted springs.

Among the technical applications of water one only—its use for generating steam—receives any special notice.

On the "professional quarrel" above mentioned the author tacitly pronounces his verdict by omitting all mention of the Frankland and Armstrong process for the determination of organic nitrogen.

The well-known Clark process for the determination of the hardness of waters is explicitly rejected in favour of a process devised by Mr. Hehner. A colorimetric process for the determination of nitrates and nitrites is given in preference to the methods hitherto in use.

For the estimation of ammonia, free and "albumenoid," we find here the Wanklyn and Chapman process with unimportant modifications in the apparatus required. For ascertaining the "oxygen-consuming power" the authors describe Dr. Tidy's method, and mention the processes of H. Fleck and A. R. Leeds. They remark, however, that the two latter processes are open to the same objections as is the use of permanganate, and do not seem to possess any decided advantage.

For the determination of free oxygen the authors make no mention of Gerardin's "hydrosulphite" process, but give the method of Mohr as modified by Blarez and a pyrogallol process. It may somewhat surprise the reader to find a method for the detection and estimation of boric acid—a compound, we should think, of exceedingly rare occurrence in drinking-waters, from whatever source. We are glad to see that among the poisonous metals possibly present chromium is not overlooked.

The determination of the specific gravity of waters is pronounced to be, in the majority of cases, not essential. Mr. Wanklyn is of a different opinion, and a medical contemporary, in reviewing the seventh edition of his "Water Analysis," regards the new chapter on this point as embodying "a distinct practical advance."

A method is given for the determination of phosphates, but the authors, in accordance with Mr. Wanklyn, consider that all beyond very minute proportions will be precipitated, though they agree with Mr. Hehner that their presence in noteworthy quantities should be regarded with suspicion. The hardness of a water they consider of little sanitary importance.

Into the question of living organisms in water and their possible effects the authors enter but slightly, rightly judging that bacteriological examination is as yet of uncertain value as regards the potability of water. Upon the purification of water-supplies they express very sound views. They admit, with Dr. Frankland, that carbon filters sometimes seem to act as a hot-bed for the development of microbia. Stone and sand filters they regard as worthless, that is, for the elimination of living organisms. Spongy iron was found to reduce the microbia by about one-half in the best cases, but the unglazed porcelain filters on Pasteur's principle, and also the asbestos filters, give a filtrate practically free from micro-organisms. They quote from Dr. P. Frankland important results as to the removal of organised matter from water both by occlusion (*i.e.*, agitation with finely-divided absorbent solids) and by precipitation. From their own observations they state that a precipitate of aluminium or of ferric hydroxide carries down with it all suspended matters as a large proportion of the dissolved organic matters.

A Table of Specific Gravity for Solids and Liquids. (*Constants of Nature*, Part I.). New Edition, Revised and Enlarged. By Frank Wigglesworth Clarke, Chief Chemist, U.S. Geological Survey. Published by the Smithsonian Institution. London and New York: Macmillan and Co.

The author's "modest work," as he calls it, is a precious and enduring monument of protracted labour and of self-abrogation in the cause of Science. The tables in the present edition have been greatly extended, and now include the specific gravities of 5227 distinct substances and 14,465 separate determinations. In the original edition there were given only 2263 substances. The boiling- and melting-points have been omitted, except where they seemed necessary for the identification of a compound, as that requirement is fully supplied by the tables of Prof. Carnelley.

The Metallurgy of Gold: A Practical Treatise on the Metallurgical Treatment of Gold-bearing Ores, including the Processes of Concentration and Chlorinisation and the Assaying, Melting, and Refining of Gold. By M. Eissler, late Assistant Assayer of the U.S. Mint, San Francisco. Second Edition, enlarged. London: Crosby Lockwood and Son.

In November last we had the pleasure of examining the first edition of this manual, and we felt bound to pronounce it valuable to all persons interested in the metallurgy of the precious element. But the fact of a second edition having been required after the lapse of a few months is a more decisive recommendation than any in our power to offer.

The book in its present form is not a mere reprint, but has been enlarged by about 150 pages. The added matter includes an account of the more recent developments of the chlorination system, and a chapter on smelting gold ores and refining gold bullion.

In view of the not improbable circumstance of a third edition being shortly required, we should suggest that an account of the geological features of the gold-bearing districts of Australia and South Africa might be usefully added.

Stellar Evolution and its Relations to Geological Time. By James Croll, LL.D., F.R.S. Author of "Climate and Time," "Climate and Cosmogony," "Philosophy of Theism," &c. London: Edward Stanford.

The age of the sun is a most important question, since, if established, it yields an outside limit in time for the past duration of our earth, and of course for the evolution of its geological features and its organic inhabitants, probably also of the elements of which it is composed. No little sensation was therefore created some time ago when a most eminent physico-mathematician announced, as the result of his calculations, that the sun could not have been supplying light and heat to the earth for more than twelve million years. Of this term, not much more than the half could be allowed for the age of life upon the earth.

This statement was hailed in certain quarters as fatal to the results of geology no less than to the Lamarck-Darwinian doctrine of organic evolution. The rejoicers, however, had not taken the trouble to ascertain what Sir W. Thomson had really demonstrated. He had shown that the sun cannot have been irradiating our globe for more than twelve million years *if* gravitation be the sole or the main source from which his heat has been derived. But this is not proven. Mr. Croll shows that another theory of the origin of solar heat is possible. Instead of the sun having been constituted by particles of matter, large or small, drawn together by gravitation, he proposes the "impact theory," that our sun was formed from a hot gaseous nebula, produced by the colliding of dark stellar masses. He argues that eternal motion is just as legitimate an assumption as eternal matter. "If the masses were created they may as likely have been created in motion as in rest; and if they were eternal—a view which he subsequently combats—they may as likely have been eternally in motion as eternally at rest." If the sun has thus been formed his original quantum of heat may easily have been so great that the past 100,000,000 years, or even a far longer time, would not suffice for its exhaustion.

Mr. Croll contends that on his theory the absolute motion of stars is due, not to the influence of gravity, but to motions which originally belonged to the two component masses out of which the star arose. "We know that there are stars, *e.g.*, 1830, Groombridge, which have a far greater velocity than can result from gravitation."

The author next marshalls, in support of his impact theory, evidence as to the heat of the sun drawn from geological and biological considerations. This evidence, to persons capable of appreciating the facts, is perfectly overwhelming. We have all along held, with Mr. Croll, that "the grounds upon which the geologists and the biologists found the conclusion that it is more than twenty or thirty millions of years since life began on the earth are far more certain and reliable than the grounds upon which the physicist concludes that the period must be less." He adds, very justly, "the only real ground that the physicist has is that according to the theory which he holds of the origin of the sun's heat a longer period is not possible." The reply of the geologist and the biologist is, "then your theory must go, since it leads to a result not reconcilable with facts."

In the third part the author adduces evidence in support of the theory from the pre-nebular condition of the universe. He sums up the views of Prof. Winchell, of Mr. C. Morris, of Sir W. Grove, of Prof. Clarke, Mr. Norman Lockyer, Dr. T. Sterry Hunt, Graham, Sainte Claire Deville, M. Berthelot, Brodie, Prof. Oliver Lodge, and especially of Mr. Crookes, whose address before the Chemical Section of the British Association in 1886 is largely drawn upon. Dr. G. Johnstone Stoney's inquiries into the pre-nebular condition of matter are also taken into account.

All men of science who pay due heed to the ultimate principles to which they are perforce brought in the course of their researches will find this work deserving a much more thorough scrutiny than space has here allowed us to give it. Mr. Croll has, at all events, swept away a cloud with seemed at one time likely to obscure the general significance of Evolution.

Variations in the Composition of Milk.—Harald Faber (*Tidskrift for Landökonomi*).—From the results of about 50,000 analyses made in the laboratory of the Dairy Supply Company the author concludes that the dry matter less fat is an almost constant value (8·7 to 8·8). The fluctuations in total solids depend almost entirely on variations of the fat. The evening milk contains more fat and more total solids than the morning milk. In October and November the milk is richer in fat and total solids than in other parts of the year.

The Formation of Nitre Earths.—A. Muntz and V. Marcano.—The attention of the authors has been drawn to caves not inhabited by winged animals, and having no superficial deposits of guano, yet containing soil richly charged with nitrates, On boring there have been found the presence of the bones of large mammals abundantly and uniformly distributed through the whole mass of nitre-earth. These bones crumble to powder if touched, and are composed almost exclusively of calcium phosphate; calcium carbonate is totally absent, and there are mere traces of organic matter. The nitre produced at the expense of the nitrogenous organic matter, and secured from the action of rain, has been able to accumulate. The calcium carbonate of the bones has served in nitrification and reappears as calcium nitrate. The brittleness of the bones is due to the action of the nitric ferment. Such caverns abound in Venezuela, not only in the littoral mountains but in the flancs of the Cordillera. The beds reach and even exceed ten metres in thickness, the soil containing calcium nitrate from 4 to 30 per cent and calcium phosphate 5 to 60 per cent.—*Comptes Rendus*, Vol. cviii., No. 17.

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. cviii., No. 17, April 29, 1889.

On Obtaining Photographs in Accurate Values by the Use of Coloured Glasses.—G. Lippmann.—The author mentions the well-known defect in photographs; that, except blues and whites, objects are imperfectly represented, since the plate is much more sensitive for blue rays than for any others, so that an exposure which is sufficient for the blues is quite insufficient for other colours. To obviate this inequality he places a blue glass in front of the lens and exposes long enough for the blue rays to act upon the plate. He then substitutes a green glass for the blue and exposes again, taking care not to touch the camera or displace the object. Finally he uses a red glass. The result of this triple exposure is to give clear photographs, in which green foliage, yellow or red draperies, &c., instead of giving brown tones, are rendered as in a good engraving.

Losses and Gains of Nitrogen in the Experimental Field of Grignon from 1875 to 1889.—P. P. Dehérain.—The results of the observations made at Grignon may be summed up as follows:—All the plots containing notable quantities of combined nitrogen (2 grms. per kilo) and cultivated without manure have lost considerable proportions of nitrogen. These losses greatly exceed the demands of the harvests. They are by no means equal for all crops, being very rapid in soils which have been planted with beets, rather slower for feeding maize, and still slower for soils which have yielded potatoes and wheat. When, after several years of cultivation without manure, the soil has been impoverished down to 1·45 to 1·50 grms. of nitrogen per kilo. the losses ceased and a gain in nitrogen set in. This gain, trifling in soils under varied cultivation, has been considerable for grass-lands.

On the Alloy of the Standard Kilogramme.—J. Violle.—The material adopted is platinum alloyed with 10 per cent of iridium. The alloy has been prepared with the greatest care by Mr. Matthey (Johnson and Matthey), who has succeeded in surpassing decidedly the degree of chemical perfection required by the International Commission, as proved by the analyses of MM. Stas and Debray. The alloy in question behaves like a mixture, both as regards its specific gravity and its specific heat. For this alloy, and probably for every other metal which is physically homogeneous, the sp. gr. is a perfectly defined number, which, when once reached, cannot be modified neither by pressure, nor by tempering, nor by the most violent blows.

Biedermann's Central-Blatt fur Agricultur Chemie. Vol. xviii., Part 4.

Determination of Nitrogen in Arable Soils.—M. Berthelot and G. André.—From the *Comptes Rendus.*

The Loss of Gaseous Nitrogen during the Decomposition of Organic Substances.—Th. Schlœsing.—Also noticed under *Comptes Rendus.*

An Exact Experiment in Manuring Barley.—Dr. J. Hanamann (*Oester-Ungar Zeitschrift Landwirthschaft*).—Ammonia with superphosphate or nitre and superphosphate must be applied for a maximum production.

Manurial Experiments on Oats and Summer-Wheat with Nitre and Superphosphate.—M. Roth (*Sächs. Landwirth. Zeitschrift*).—The use of small quantities of phosphoric acid does not affect the yield of wheat, and in larger doses it occasions a decrease. In case of oats it reduces the financial result in whatever quantity.

Results of Comparative Manurial Experiments with Basic Slag and Superphosphate.—Dr. E. Meissl.—For autumn dressings and where it is desired to give a supply of phosphoric acid for several years, basic slag can mostly be substituted with advantage for superphosphate. For spring dressings and in all cases where phosphoric acid has to be supplied for immediate assimilation slag is never equal to superphosphate.

Increase of Crops by the Use of Ferrous Sulphate in the Years 1887-88.—P. Margueritte-Delacharlonny.—Copperas, if applied to vines, is said to increase the yield and to protect the vineyards aggainst the *Phylloxera* and chlorosis. An application of 800 kilos. copperas per hectare was found to restore meadows attacked by cuscuta. The yield of clover and lucerne was increased, by the application of the same agent in smaller proportions, from 25 to 33 per cent. A satisfactory result was also obtained with potatoes and grain.

The Suppression of the Potato-disease by Means of Iron Sulphate.—P. Margueritte-Delacharlonny.—The results obtained have been very favourable. The sulphate is best applied when the young plants have reached the height of a few centimetres.

An Error in the Determination of Nitrates in Soils.—Michele Giunti.—On extracting nitrates from soils by means of water the results were the lower the longer the water was allowed to act. These losses were entirely avoided if the samples were sterilised by means of chloroform.

Journal de Pharmacie et de Chimie. Vol. xix., No. 8, April 15, 1889.

Researches on the Saccharine Matter of Some Species of Fungi.—Em. Bourquelot.—The sugars detected have been trehalose and mannite. The former is found in mushrooms when in a state of vigorous vegetation, but disappears if they are slowly dried at a low temperature.

On Gold Arseniate.—P. Carles.—A substance lately introduced into medical practice under this name is merely a crude mixture of gold chloride and sodium arseniate.

The Identity of Analgesine and Antipyrine.—A. Petit.—The author demonstrates the identity of these preparations.

On the Dangers which may Arise from Tin Covers containing Lead.—E. Leger.—The covers in question are attached by means of a hinge to stoneware jugs used for containing alimentary or medicinal matter. In such a lid M. Léger finds 76·83 per cent of lead and only 22·41 of tin. Such an alloy is, of course, readily attacked by the organic acids.

MEETINGS FOR THE WEEK.

Monday, 27th.—Society of Arts, 8. (Cantor Lectures). "Heat Engines other than Steam," by H. Graham Harris.
Tuesday, 28th.—Institute of Civil Engineers, 8. (Anniversary).
— Royal Medical and Chirurgical, 8.30.
— Royal Institution, 3. "Some Recent Biological Discoveries," by E. Ray Lankester.
— Society of Arts, 8. "The Westinghouse Alternating System of Central Station Electric Lighting in the United States of America," by James S. Humbird.
Wednesday, 29th.—Society of Arts, 8. "The Science of Ventilation as Applied to the Interior of Buildings," by D. G. Hoey.
Thursday, 30th.—Royal Institution, 3. "Chemical Affinity," by Professor Dewar.
Friday, 31st.—Royal Institution, 9. "An Attempt to Apply to Chemistry one of Newton's Principles," by Professor Mendeleeff.
— Society of Arts, 8. "Indian Wheats," by John McDougall.
Saturday June 1st.—Royal Institution, 3. "The Classification o the Sciences, Historical and Critical," by Prof. W. Knight.

THE CHEMICAL NEWS.

Vol. LIX. No. 1540.

ON THE
PRESENCE OF TIN IN CERTAIN KINDS OF SUGAR, A MEANS OF DETECTING IT, AND THE PROBABLE INFLUENCE OF THIS SUBSTANCE ON THE PUBLIC HEALTH.

By Dr. T. L. PHIPSON, F.C.S. (London),
Formerly of the University of Brussels, and late Assistant Professor in the Laboratoire de Chimie Pratique, Paris;
Member of the Society of Chemical Industry, &c.

A LARGE sample of sugar purchased in London at a well-known Stores as "Demerara" was recently submitted to me for examination. It had a golden yellow colour, was rather moist, and, on dissolving in water, left a considerable amount of residue and formed a solution that was cloudy.

Lady E——, who desired this sugar to be analysed, informed me that her servants objected to use it, but without giving any reason; she herself liked it on account of its intense sweetness, and had used it for about six weeks, but at the end of that time she had suffered from diarrhœa, *accompanied by pain*, which she had not experienced before in similar attacks, and she fancied the sugar may therefore have been the cause of this attack. She left off using this kind of sugar and the ailment ceased in the course of a few days.

Such was the information given to me with the sample in question. The solution of this sugar had a golden colour, a very agreeable aromatic flavour, and a very sweet taste. I made three analyses of the sugar and found that it contained 0·04 per cent of oxide of tin, a considerable amount of glucose, and a large amonnt of ash (2·70 per cent) rich in lime, with some oxide of iron and phosphate of lime. Tin is the principal impurity to which it is necessary to draw attention.

In June, 1881, I was requested to attend a meeting of the West India Committee in London, after having detected a minute quantity of oxide of tin in some samples of sugar sent to me for analysis by some members of the committee. On that occasion I was informed that chloride of tin was used in preparing certain kinds of sugar for the market, in order to give them a golden hue which was much admired; and my opinion was asked as to the influence which the small amount of tin found in the samples analysed might have upon the health of the consumers. I had only two samples to examine, and the quantity of tin in them was so small that I stated my belief that it would exert no noxious influence if it did not go beyond that figure (0·001 per cent), but that great caution would have to be observed. It appears, however, that since then the quantity has increased considerably, and the time has perhaps come when this process of "curing" sugar will have to be very closely looked into.

There are several means by which tin can be detected in sugar and its amount accurately estimated, but certain precautions must be carefully observed, otherwise erroneous results will ensue. The method I follow is this:—Not less than two ounces of the sample are taken, dissolved in a certain quantity of cold water, and, *without separating the residue*, the solution is rendered slightly acid by hydrochloric acid; it is then saturated with sulphuretted hydrogen. For the two ounces of sugar I take about a pint of water and one to two drachms of hydrochloric acid. When the solution is saturated with sulphuretted hydrogen, the bottle is covered with a plate of glass, and the solution *allowed to deposit for at least forty-eight hours*. The clear liquid can be mostly decanted off and the deposit collected upon a filter and washed. It contains the sulphide of tin along with the insoluble impurities. The former is separated by washing with sulphide of ammonium, from which solution the pure sulphide of tin is precipitated by hydrochloric acid, added *just in sufficient quantity only*, and the liquid again allowed to deposit for forty-eight hours. By this means *the whole* of the sulphide of tin is collected. It is dried, and transformed by calcination, with the usual precautions, into stannic oxide, which is weighed.

With regard to the action of tin compounds upon the animal economy, we must remember that by its chemical reactions oxide of tin resembles the oxides of antimony and arsenic very closely, both of which are powerful poisons. Nevertheless Orfila compares the action of tin salts upon the tissues more to that of bichloride of mercury or corrosive sublimate. As tin salts are not used in therapeutics we have little experience of their effects in very small doses; but chloride of tin (stannous chloride) has been long known to be a very dangerous substance. Dr. Christison, in his work on "Poisons," relates a case of voluntary poisoning by it, and Meinel (1851) refers to another case in which chloride of tin had been formed by the action of impure damp salt upon some metallic plates. The poisoning which has occurred of late years by the use of tin vessels has been attributed to lead, the tin being largely adulterated with the cheaper metal.

Wm. Stone, in his "Toxicological Tables" (translated into French from the 11th English Edition by Acar, Pharmacist to the Military Hospital at Antwerp, 1853), says, under the head of "Tin, chloride, hydrochlorate, or oxide," that in poisonous doses these substances produced the following symptoms:—"Nauseous styptic taste, constriction of the throat, vomiting, and *pain all over the abdomen*, abundant stools, pulse small, hard, and frequent, convulsive movement of the face and limbs, sometimes paralysis; death generally occurs when the chloride or hydrochlorate has been taken."

Other remarks on the toxic action of tin salts are to be found in the *Annales d'Hygiene Publique*, by Poumet (1845) and Gobley (1869). In more recent times we have the experiments of Ungar and Bodländer (1887), with several compounds of tin, and, among others, stannous chloride and tartrate of tin and sodium. These experiments were made on frogs, rabbits, and dogs, and in all cases toxic symptoms ending in death ensued with large doses, whilst with very small doses repeated for some time the "results were like those of other metals which gradually undermine the health."

Such being the case, and in view of the enormous consumption of sugar by all classes of people, I am of opinion that the use of tin salt, or any other noxious ingredient, in curing or beautifying sugar, is a practice which should not be tolerated. Taking the above analysis as a fair average result (for the sample weighed about five pounds) it shows that any person who, like myself, consumes about four ounces of sugar per diem, would assimilate nearly 7·10ths of a grain of tin oxide (but probably in the shape of some organic compound or as chloride) every day, if he used this particular kind of sugar. Or, say, that anyone took only a quarter of that amount, one ounce a day, he would absorb nearly 2-10ths of a grain of tin oxide per diem, or close upon 1½ grains a week; and, as metallic poisons have a tendency to accumulate in the liver or other organs, there is no saying how much mischief may be induced by a prolonged consumption of sugar containing such an impurity.

Of late years several noxious substances have been proposed and used in sugar-making; the principal of these are *baryta*, *strontia*, and *oxalic acid*. It will, therefore, become the duty of all chemists who devote themselves to the public health analyses, that is, to the detection of impurities or adulteration in foods and drugs, to search carefully for the substances mentioned, and make the results widely known. A sugar which shows, on analysis, as much as 98 or 99 per cent of cane-sugar may still contain a sufficient amount of some noxious impurity to prove highly injurious to health.

THE CONTAMINATION OF WATER WITH LEAD.

By THOMAS T. P. BRUCE WARREN.

A recent discussion on this subject shows that the contamination of a water supply, when flowing through lead pipes, requires some explanation.

The chemical action of water containing small quantities of CO_2, when passing through an oxidised lead pipe, need only be referred to thus far. The statement that the inner bore of the pipe influenced the amount of lead taken up slightly, deserves more attention. The inner surfaces of pipes vary as the lengths and as the circumferences (D multiplied by 3·1416), so that a pipe double the diameter of another pipe exposes just twice the area to the action of the water. But, supposing that we have the same initial head of water in the two cases, we involve an extra abrading action on the smaller pipe, and consequently, the water-pipes being in other respects alike, we have an increased friction in the smaller pipe, and increased capabilities of being impregnated, which the ratios of D alone will not help us to explain.

The laws affecting friction of water flowing through pipes may be found in any good work on mechanical engineering. When water is exposed to pressure in a lead pipe or tube, so long as the water is quiescent we have no reason to suspect much difference; but when flowing under pressure the conditions are seriously different.

THE ACCURATE DETERMINATION OF CARBONIC ACID AND MOISTURE IN AIR.

By J. S. HALDANE, M.A., M.B.,
and M. S. PEMBREY, Pell Exhibitioner of Christ Church, Oxford.

On an accurate means of determining carbonic acid and moisture in air depends the solution of a number of problems connected with the respiratory exchange of animals. The present research was undertaken chiefly from this point of view, but is probably of equal interest in connection with questions in meteorology and hygiene.

Both carbonic acid and moisture are present in free air in very minute proportions: the former in the proportion by weight of only about 0·045 per cent; the latter in very varying proportions, under 1 per cent as a rule. It is, therefore, hardly a matter of surprise that the accurate estimation of these substances, and especially of the former, should present considerable difficulty.

The first attempt at a quantitative analysis of the carbonic acid in free air seems to have been made by A. von Humboldt.[†] His numerous results were, curiously enough, entirely illusory, since he concluded that about 100 vols. per 10,000 of air were usually present. In 1802 Dalton,[‡] who made the first approximately correct analyses, reduced the amount to 6·8 vols.; and Dr. Saussure[§] had, about 1830, brought it down to a mean of about 4·1 vols. for country air. This result was confirmed by Watson (1834) and Boussingault (1844), who used other methods, and for long was supposed to be nearly correct. Still more recent researches, particularly those of Angus Smith in Scotland,[||] Schuize in Germany, Reiset in France,[¶] and Müntz and Aubin in France[**] and other countries, have gradually reduced it to about 2·9 vols. or less.

There still, however, exists a considerable amount of apparent contradiction on the subject. Even the most recent researches—those made with Pettenkofer's method by Feltz[*] at Dorpat, and Uffelmann[†] at Rostock—do not give results agreeing well with those of other observers. Uffelmann's mean result (3·5 vols.) differs by 20 per cent from that obtained previously at the same place by Schultze (2·9 vols.). Feltz's mean result (2·7) is lower than that obtained by previous observers. Not only are the mean results of different observers different, but there is perhaps still greater want of agreement as regards the limits within which the proportion of CO_2 varies.

The methods at present in use for the determination of carbonic acid in air are, practically speaking, of two kinds: (1) those in which the CO_2 is absorbed by standardised baryta-water, which is afterwards re-titrated; (2) those in which it is absorbed by potash, and afterwards liberated by acid and measured in the form of gas.[‡]

The method best known in this country is that of Pettenkofer,[§] or, more correctly, of Dalton[||] and Pettenkofer. In this method a large bottle is pumped full of the air to be examined. A measured quantity of standardised baryta-water is then added, and the bottle closed and shaken, so as to bring the air in contact with the baryta. After a certain time the baryta solution is again titrated, and the CO_2 estimated from the loss of alkalinity of the baryta-water.

Although this method is simple in principle, it is generally admitted that the results obtained by it for free air may easily be very incorrect. The matter will be more fully discussed in the sequel.

For certain cases where the bottle method is not suitable Pettenkofer[¶] recommends that a measured quantity of air should be allowed to bubble through a long tube placed nearly horizontally, and containing a known quantity of baryta-water. The CO_2 absorbed by the baryta is estimated in the same way as in the first method. Pettenkofer found that about 5 litres per hour is the maximum rate at which the air can be passed. When large volumes of air are taken for each analysis this method is doubtless much more accurate than the bottle method; but for large volumes inconveniently long periods of time are required. With small volumes of air, such as 10 litres, the error of the method may be, as will be shown later, very considerable.

Reiset[**] has recently devised an apparatus which allows large quantities of air to be aspirated through baryta-water. With this apparatus he was able to aspirate as much as 100 litres through 300 c.c. of baryta-water in an hour. The absorption of CO_2 appears to have been complete. Each experiment lasted several hours. He used an enormous aspirator, mounted on a cart, and capable of holding 600 litres of water.

The method in which the CO_2 is absorbed by potash, and afterwards liberated by acid and measured in the form of gas, was, in its first form, used by Mangon and

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[*] Read before the Royal Society, May 2, 1889. (From the Physiological Laboratory, Oxford).

[†] Gilbert's *Annalen*, vol. iii, 1800, p. 79.

[‡] *Manchester Lit. Phil. Soc. Mem.*, 1 82.

[§] *Annales de Chimie*, vol. xliv., p. 5.

[||] "Air and Rain," p. 59.

[¶] *Annales de Chimie*, vol. xxvi., p. 145; vol. xxx., p. 238.

[**] *Comptes Rendus*, vol. lxxxviii., p. 1007.

[*] Feltz, "Kohlensäureghalt der Luft zu Dorpat," Inaug.-Diss. 1887.

[†] *Arch. fur Hygiene*, 1888, p. 262.

[‡] A valuable critical account of the methods hitherto used is given by Blochmann, *Liebig's Annalen*, vol. ccxxxvii. (1887), p. 39

[§] "Abhandl. der techn. Commission der Bayer. Akad.," vol. ii. (1858), p. 3, and *Liebig's Annalen*, Suppl., vol. ii. (1861), p. 23.

[||] The form finally given to Dalton's method is described in a paper by Watson, communicated by Dalton to the British Association (*Brit. Assoc. Report*, 1834, p. 583). Watson used a large bottle, which he filled with air with the help of a pair of bellows. He then added lime-water, and, after shaking, allowed the bottle to stand for several days, at the end of which time he filtered off the carbonate and titrated with dilute sulphuric acid. Pettenkofer independently invented a similar but improved method. He introduced baryta-water as an absorbent and turmeric as an indicator, and avoided the filtration. Watson's mean result for country air (4·1 vols.) was about the same as that obtained by the earlier observers who used Pettenkofer's method.

[¶] *Liebig's Annalen*, Suppl., vol. ii., 1861, p. 23.

[**] *Loc. cit.*, p. 164.

Tissandier* for balloon experiments. A rough form of this method has been for some years in use at the Paris Observatory. The method has been brought to great perfection by Müntz and Aubin,† whose test experiments show that an accuracy to about 2 per cent of the CO_2 estimated may be attained when 200 litres of air are used. For absorbing the CO_2 they use tubes about a metre long, filled with pumice soaked in caustic potash solution free of CO_2. After the experiment the CO_2 is liberated by the addition of acid, and collected over mercury with the help of a mercury pump. The apparatus necessary for these manipulations is complicated, and considerable skill is required in order to avoid sources of error. With this method Müntz and Aubin confirmed and extended Reiset's conclusions, and found that the mean proportion of CO_2 in country air in the northern hemisphere is about 2·85 vols. per 10,000, and that it very seldom rises above 3·1 or falls below 2·6. The results of these three observers are certainly the most reliable of any hitherto published; and in view of the accuracy of their methods there is little ground for doubting the truth of their general conclusion, in spite of the differences between their results and those obtained by some observers with Pettenkofer's method.

The methods for the determination of moisture present in air are of two kinds. Either the percentage is calculated from the readings of some kind of hygrometer, or it is determined geometrically. The methods of the former kind need not be considered here. The latter method consists in aspirating a known volume of air through an absorption apparatus filled with sulphuric acid and pumice. This method is, in its original form, due to Brunner (see below). It was tested and somewhat altered by Regnault in the course of his well-known research on hygrometric methods. A serious objection is that it only gives accurate average results over relatively long periods (an hour or more), while the percentage of moisture present in air rapidly changes.

Some months ago a number of experiments were undertaken by one of us with a view to devising a new form of apparatus for investigating the respiratory exchange of animals. This apparatus implied a very accurate determination on a large scale of CO_2 and moisture in air. The satisfactoriness of the results of the test experiments with the complete apparatus determined us to investigate more thoroughly the methods of determination used, and to endeavour to make them more widely applicable, not only for physiological purposes, but also in all investigations involving very accurate determinations of carbonic acid moisture in air.

The methods are gravimetric and are not new in general principle. We believe, however, that with attention to the details communicated below these methods will be found to be not only exceedingly convenient, but also very much more accurate than the corresponding methods in ordinary use.

Gravimetric methods of dermining CO_2 in air were at one time much employed, although they have been practically disused since the introduction of Pettenkofer's method. In 1832 Brunner‡ described a gravimetric method. He aspirated the air at a rate of about 30 litres an hour through two absorption tubes. The first contained asbestos soaked in sulphuric acid, and the second, which was three feet long, was filled in the first two-thirds with moist slaked lime, and in the last third with sulphuric acid and asbestos. He tested the completeness of the absorption of the CO_2 by allowing the air to bubble afterwards through baryta solution, which remained clear. The increase in weight of the first tube gave the moisture, that of the second tube the CO_2 in the air aspirated. He says he always obtained for free air results lying between De Saussure's maximum and minimum (3·7 and 6·2 vols. per 10,000).

Brunner's method, with various modifications, has been used by a number of subsequent observers. The most reliable results were those of Boussingault, who obtained with large volumes of air a mean of 4·0 vols. per 10,000 for Paris air.* The results of several other observers were certainly quite unreliable.

In 1856 Hlasiwetz† published a paper in which he criticised adversely the gravimetric method. He made a number of analyses by different forms of this method, and found that not only did analyses simultaneously made often entirely disagree, but that in eleven out of fifty-six analyses the absorption apparatus for CO_2 actually lost in weight. These results he set down partly to unavoidable "errors of weighing," and partly to the fact that CO_2 is absorbed by sulphuric acid. Hlasiwetz's criticisms have been generally accepted as conclusive, and since the publication of his paper the gravimetric method seems to have been almost entirely given up.

Later researches on air have certainly confirmed Hlasiwetz's general conclusions as to the unreliability of the gravimetric method. There is no longer any doubt that the apparent variations found by this method in the amount of CO_2 in air were almost entirely due to imperfection in the method. It will be shown below, however, that these imperfections can be completely removed by attention to details.

Soda-lime has for long been in use as an absorbent for CO_2 in combustions. It was first used by Mulder‡ in 1859, and Fresenius§ has shown its superiority to potash solution, &c. Its use in combustions suggested it as a suitable absorbent for CO_2 in the respiration apparatus already alluded to, and we have made use of it in all our experiments. It has the advantage over lime, baryta, potash, &c., that it can be used in an almost dry condition, so that it loses very little moisture when dry air is passed over it.

For absorbing moisture we have used pumice soaked in sulphuric acid; calcium chloride is quite unsuitable for the purpose, as a single experiment showed us. Our first experiments were made with doubly tubulated absorption flasks of about 100 c.c. capacity.‖ These were arranged so that a current of air was passed through a glass tube at the bottom of the flask, then upwards through the absorbent, and out by a second glass tube opening in the neck of the flask. The flasks were connected in series by means of rubber tubing. The first two were filled with pumice soaked in sulphuric acid; the third with coarsely granulated soda-lime; the fourth with pumice and sulphuric acid; the fifth and sixth, when present, were similar to the third and fourth. When a current of air was passed through the increase in weight of the first flask gave the weight of moisture in the air; the second acted as a test of the completeness of the absorption of moisture by the first; the third absorbed CO_2 from the dry air, but also lost moisture, which was recovered in the fourth. Hence the increase in weight of the third and fourth together gave the CO_2 absorbed from the air. The fifth and sixth together acted as an index of the completeness of the absorption of CO_2 by the third.

Experiment A.

22 litres of air were aspirated through the flasks in fifty-five minutes.

Flask	1.	+0·2114 grm.	
,,	2.	+0·0010	
,,	3.	−0·0052	together = +0·0146.
,,	4.	+0·0198	
,,	5.	−0·0190	together = +0·0008.
,,	6.	+0·0198	

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* *Comptes Rendus*, vol. lxxx., 1875, p. 976. Their apparatus was intended for use in the fateful ascent during which Crocé-Spinelli and Sinel lost their lives.

† *Annales de Chimie*, vol. xxvi., 1882, p. 222

‡ *Annalen der Physik*, vol. xxiv., p. 570.

* *Annales de Chimie*, vol. x., 1844, p. 456.

† *Sitzber. der Wein. Acad.* (Math.-nat. Kl.), vol. xx., p. 189.

‡ *Zeitschr. fur Anal. Chem.*, vol. i., p. 3.

§ *Ibid.*, vol. v., p. 87.

‖ Of the pattern used by Voit in his smaller respiration apparatus (*Zeitschrift fur Biologie*, vol. xi., p. 157).

Experiment B.

20 litres of air driven through the flasks in sixty-four minutes.

Flask 1.	+0·2530	
„ 2.	−0·0014	
„ 3.	+0·0012	together= +0·0185.
„ 4.	+0·0173	
„ 5.	−0·0200	together= −0·0028.
„ 6.	+0·0172	

Experiment C.

50 litres of air were driven through in two hours thirty minutes. In this experiment flasks 5 and 6 were replaced by a Pettenkofer absorption tube 100 c.m. long, containing 40 c.c. of dilute baryta-water of known strength, through which the air was made to bubble.

Flask 1.	+0·5660	
„ 2.	+0·0048	
„ 3.	+0·0090	together=0·0468.
„ 4.	+0·0378	

Baryta-water before experiment, 20 c.c. = 20·9 c.c. standard oxalic acid.*

Baryta-water after experiment, 20 c.c. = 20·9 c.c. standard oxalic acid.

Allowance for evaporation, 0·6 c.c.

∴ loss of alkalinity of baryta-water=0·6 c.c.=0·0006 grm. CO_2.

Experiment D.

50 litres of air were driven through in 1 hour 18 minutes. In this experiment the air-current, after passing through flask 4, was divided by means of a T-tube, and passed through two Pettenkofer tubes. The loss of water from these Pettenkofer tubes was determined by means of a sulphuric acid flask placed in the air-current beyond them. The moisture which had collected in the tubing connecting the Pettenkofer tubes and this absorption flask was washed into the flask by means of a current of dry air.

Flask 1.	+0·5205	
„ 2.	+0·0016	
„ 3.	+0·0398	together=0·0754.
„ 4.	+0·0356	

Baryta-water before experiment, 20 c.c.=20·9 c.c. standard oxalic.

Baryta-water after experiment, tube 1, 20 c.c.=20·7 c.c. standard oxalic.

Baryta-water after experiment, tube 2, 20 c.c.=20·9 c.c. standard oxalic.

Loss of water by evaporation, 0·5932.

∴ loss of alkalinity in tube 1=0·4 c.c. standard oxalic, and loss by evaporation in tubes 1 and 2=0·6 standard oxalic.

Together = 1 c.c. = 0·0010 grm. CO_2.

Experiment E.

80 litres driven through in 1 hour 5 minutes. Arrangement as in Experiment D, except that the air-current was divided between six Pettenkofer tubes. The baryta-water from the tubes was mixed in a covered vessel after the experiment and titrated.

Flask 1.	+0·8972	
„ 2.	+0·0204†	
„ 3.	−0·0290	together= +0·0408.
„ 4.	+0·0698	

Baryta-water before experiment ..	(1)	40 c.c.=40·5 c.c. standard oxalic.
	(2)	„ =40·7 „ „
	(3)	„ =40·7 „ „
Mean		40 c.c.=40·63 „ „

Baryta-water after experiment ..	(1)	40 c.c.=40·5 c.c. standard oxalic
	(2)	„ =40·4 „ „
	(3)	„ =40·5 „ „
Mean		40 c.c.=40·47 „ „

Water lost by evaporation=1·165.

∴ loss of alkalinity (=0·16×6) =0·96 c.c. standard oxalic, and loss by evaporation=1·17 c.c. standard oxalic.

Together = 2·13 c.c. = 0·00213 grm. CO_2.

In the majority of these experiments there is an apparent slight escape of moisture and CO_2 through the first sulphuric acid and soda-lime flasks. In experiment B, however, the test flasks, both for moisture and CO_2, show a diminution in weight. This suggested that the apparent escape might be explained by errors of weighing. Such an explanation does not, however, apply to the cases in which there was an apparent escape of CO_2 into the baryta water, and we at first thought that the diminution in alkalinity of the baryta-water was conclusive proof of escape of CO_2. It will, however, be shown later that the errors of experiment connected with Pettenkofer's method fully account for this apparent escape.

The results of these preliminary experiments at any rate showed that the gravimetric method might be used for the animal respiration apparatus. Such an apparatus was accordingly constructed.* The results of a number of test experiments made with it determined us to enter upon the present research, as they showed distinctly that the gravimetric method must be capable of giving much more accurate results than those quoted above.

(To be continued).

RESEARCHES IN THE CHEMISTRY OF SELENIC ACID AND OTHER SELENIUM COMPOUNDS.†

By Sir CHARLES A. CAMERON, M.D., F.R.C.S.I., V.P.I.C.,
Professor of Chemistry and Hygiene, R.C.S.I.;
and JOHN MACALLAN, F.I.C.,
Demonstrator of Chemistry, R.C.S.I.

(Continued from p. 234).

The Conditions which Affect the Freezing-points of Selenic Acid and Sulphuric Acid.

It has long been recognised that in order to determine the melting-point of a chemical compound with accuracy it is necessary, by crystallisation or other means, to obtain it in a pure condition. The necessity for such a precaution is well shown in the case of the oxides and acids of sulphur and selenium. An example taken from the former class of bodies is furnished by sulphuric anhydride. Up to a comparatively recent date great diversity of opinion prevailed regarding the melting-point of this substance until Weber showed that, as hitherto examined, it had usually contained a minute quantity of water, which had the effect of altering its melting-point, crystalline form, and other properties. Sulphuric acid supplies another instance of a similar effect. Its melting-point in the anhydrous condition is 10·5°, while that of the monohydrated acid is 8°; yet commercial sulphuric acid has usually been found to remain liquid above a temperature of −30° or −40°, and it is stated in some chemical works that by addition of a little water to the commercial acid its freezing-point has been lowered to −80°; but it is not mentioned whether this occurred in closed or in open vessels. A still more striking example of the influence of want of purity upon the melting-point is afforded by selenic acid. In the anhydrous state it melts at 58°, but

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* 1 c.c.=0·001000 grm. of CO_2.

† Flask 1 was probably spent.

* A full account of this apparatus will shortly be published. A preliminary paper on the subject was published in the *Proceedings of the Oxford University Junior Scientific Club* for October term, 1888.

† A Paper read before the Royal Society, May 2, 1889.

a slightly dilute acid, as we have found, was frozen only when a temperature of −51·5° was reached, showing a fall of 109·5°; and probably further dilution would be attended by a still greater reduction of the freezing-point. The depression of the freezing-point can be due only partly to superfusion, since the superfused anhydrous acid freezes at about 5°. The monohydrate present in the dilute acid therefore exerts an influence in lowering the freezing point of the anhydrous acid, and also its melting-point. An analogous action probably occurs in the case of some metallic salts, which, although without apparent chemical action upon each other, have a lower fusing-point when mixed than when heated separately. A consideration of the foregoing facts leads to the conclusion that *dilute selenic acid having a strength greater than* 88·96 *per cent contains the anhydrous and also the monohydrated acid existing in a superfused state, and exerting a solvent action upon each other.* In the case of sulphuric acid a similar action evidently occurs. The effects of agitation and of alteration of pressure upon the freezing-points of the above acids have already been referred to.

The Method Used in Freezing Selenic Acid.

Liquefied sulphur dioxide was poured into a thick glass tumbler, holding about half a litre, fitting into a somewhat wider and deeper cylindrical gas jar, which served to retain any of the dioxide splashed from the interior vessel, the whole being imbedded deeply in a considerable quantity of cotton wadding contained in a wooden box. A rapid current of air was driven through the sulphur dioxide, the air being first dried by means of sulphuric acid and then cooled by passing through a leaden worm surrounded by a mixture of salt and pounded ice, or, less effectively, sodium sulphate and hydrochloric acid. Any desired degree of cold within limits could easily be maintained by regulating the current. When the outside air was at 0° about half a kilogramme of sulphur dioxide was found sufficient for more than two hours' use, evaporation taking place but slowly at the low temperature reached, the latter, measured with an alcohol thermometer, falling below −50° C. In warmer weather nearly as low a temperature was obtainable, but consumption of the sulphur dioxide was much more rapid. No arrangement of freezing mixtures produced nearly so low degrees of cold as were attained in the above manner. Doubtless when a supply of dry snow is available, and the weather is very cold, so that the apparatus and materials used can be well cooled down previous to mixing, a very low temperature is obtainable by ordinary freezing mixtures, but those conditions are not often to be met with in these climates. On the other hand, sulphur dioxide is cheap and easily procurable and convenient when used in the manner described.

The Specific Gravities of the Higher Strengths of Selenic Acid.

The specific gravities of selenic acid for the higher strengths, taken in the liquid state at 15°, are given in the following table. The most concentrated acid, of 99·73* per cent strength, has been referred to when describing the preparation of the anhydrous acid; its specific gravity, 2·6083, was taken while in the superfused condition. The next acids down to 94·74 per cent were obtained by diluting that of 99·73 per cent. The acid having a strength of 93·70 per cent was obtained by heating dilute acid in a vacuum at 100°, and it supplied the following strengths down to 82·52 per cent by progressive dilution. That of 81·73 per cent was prepared by concentration on the water-bath, and the remaining four by dilution of the latter. Neither the acid heated in a vacuum, nor that which was kept on the water-bath, contained any trace of selenious acid.

TABLE I.

Percentage of anhydrous selenic acid.	Specific gravity.
99·73	2·6083
99·08	2·5993
98·68	2·5901
98·16	2·5790
97·37	2·5676
96·97	2·5595
96·16	2·5424
94·74	2·5105
93·70	2·4852
92·83	2·4534
91·59	2·4218
90·06	2·3863
89·20	2·3642
88·55	2·3402
87·34	2·3158
86·60	2·2946
85·67	2·2712
84·59	2·2463
83·82	2·2196
82·52	2·1878
81·73	2·1694
80·86	2·1438
79·99	2·1213
79·06	2·0940
73·43	1·9659

Table II. is calculated from Table I., and gives specific gravities interpolated for equal increments of strength. It will perhaps be found most convenient for purposes of calculation, and for showing the relation of the rate of increase of specific gravity to that of the strength.

TABLE II.

Percentage of anhydrous selenic acid.	Specific gravity.
99·73	2·6083
99·50	2·6051
99·00	2·5975
98·50	2·5863
98·00	2·5767
97·50	2·5695
97·00	2·5601
96·00	2·5388
95·00	2·5163
94·00	2·4925
93·00	2·4596
92·00	2·4322
91·00	2·4081
90·00	2·3848
89·00	2·3568
88·00	2·3291
87·00	2·3061
86·00	2·2795
85·00	2·2558
84·00	2·2258
83·00	2·1946
82·00	2·1757
81·00	2·1479
80·00	2·1216
79·00	2·0922
73·50	1·9675

The rate of increase of specific gravity is not uniform for equal increments of strength. It diminishes as the strength increases, as in the case of sulphuric acid, but not regularly. The diminution is very marked at the highest strengths. When sulphuric acid has arrived at the greatest strength attainable by ebullition—98·66 per cent—its specific gravity is stated to decrease until the anhydrous acid, H_2SO_4, is reached. Selenic acid behaves dissimilarly in this respect; the increase of its specific gravity, although not uniform, is maintained throughout.

Berzelius (*Traité de Chimie*, 1830) mentions that selenic acid of 95·9 per cent strength has a specific gravity of 2·6.

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* 99·73 per cent of selenic acid, acid sodium selenate, equivalent to 0·07 per cent of neutral sodium selenate, and 0·20 per cent of water (Se being=78·87).

Fabian gives 2·609 as the specific gravity of an acid of 94·9 per cent strength, and 2·627 for an acid of 97·4 per cent. It will be seen that these results do not agree, nor are they consistent with those we have obtained. If values for the strengths mentioned be calculated from the foregoing tables, an acid of 95·9 per cent will be found to have a specific gravity of 2·5366, while the specific gravities of 94·9 per cent and 97·4 per cent acids will be respectively 2·5141 and 2·5680, being less than those assigned above. Furthermore, the difference between the two specfiic gravities given by Fabian is much less than we find between two acids differing by 2·5 per cent. The most probable explanation of the discrepancy is that the acids which gave the above results contained sufficient selenium dioxide to raise their specific gravities appreciably. It may be shown that the effect of the development of selenium dioxide in selenic acid is to increase the specific gravity relatively to the acidity. In the acids above mentioned, selenium dioxide would exist as such, and not as selenious acid, owing to dissociation of the latter at a temperature below those at which the acids were formed, and the weak affinity for water possessed by the resulting dioxide. Clausnizer (Liebig's *Annalen der Chemie* (1879), 196, 265) gives the specific gravity of selenium dioxide at 15·3° as 3·9538. We have also recently taken its specific gravity, and are in a position to confirm his result. It is thus more than one and a half times as dense as the strongest selenic acid. C. Blarez (*Comptes Rendus* (1886), 103, 804—806) has examined the saturating power of selenious acid. He finds that it is monobasic with cochineal or methyl-orange. With litmus, it is monobasic to ammonia, lime, strontia, and baryta, but with soda or potash the litmus only becomes blue-violet when about 1·5 equivalents of alkali are added. We have obtained a like result with soda or potash and litmus. When one equivalent of the acid is saturated, there is a distinct change in the colour of the litmus, so that in the absence of other acids it might be used as an indicator for selenious acid. Taking 1·5 equivalent of alkali as the limit, the molecule of selenium dioxide in solution will have a less saturating power than that of selenic acid in the ratio of 2 : 1·5. This will be partly counterbalanced by the higher molecular weight of the latter, but the final effect of the substitution of selenium dioxide for selenic acid will be to reduce the acidity. A gravimetric method by which selenium dioxide would be oxidised and estimated as selenic acid, would also show a less acidity compared with the specific gravity than if the pure acid were used, but not to the same extent as when a volumetric process is employed for estimating the strength.

Erratum.—At p. 233, col. 2, paragraph 7 should read as follows, the words enclosed in brackets being inserted:—

"This acid commences to boil at 205°, the acid vapour given off being at first very weak, but it increases in strength with the rise in temperature. A more dilute acid [gives off water only until the temperature reaches 205°. Dilute sulphuric acid] is stated to behave in a similar manner, giving off nothing but water until the boiling-point reaches 205°—210°, at which temperature it has the strength of the monohydrated acid, H_2SO_4,H_2O."

(To be continued).

FATAL POISONING BY CARBON MONOXIDE.

By Prof. W. P. MASON.

In Troy, N.Y., on January 6, 1887, owing to a break in the street mains, a quantity of "Fuel Gas" (see analysis below) passed beneath the frozen crust of earth, and found its way into the adjoining houses. Three deaths, and many more or less serious illnesses, resulted.

The following points, from the testimony of the physicians who made the autopsis, are to be noted:—

The expressions of the deceased were placid. One victim, an old woman, was found seated in a chair holding her false teeth in her hand. The second, also a woman, lay upon the floor. The third, a man, sat upright on a lounge, his head reclining on his shoulder. The fire was burning in the stove, and the lamps were still burning on the table. When found, death had not been very recent, as "*rigor mortis*" was fully developed.

Very searching autopsis were made, with the result of finding nothing whatever abnormal, with the exception of the bright cherry-red colour of the tissues, and the vivid redness and lack of coagula in the blood.

Upon opening the chest cavity the physician bent forward and took one or two long whiffs for the purpose of determining the presence of any odour. Almost immediately he was seized with giddiness and great oppression in the epigastrium, so much so that he had to discontinue his work for half an hour. The effects did not finally wear off until after an interval of about twelve hours.

The painful oppression in the chest, the giddiness, and the subsequent headache experienced by this physician, call most forcibly to mind the symptoms described by Sir Humphry Davy, when he so rashly experimented upon himself with carbon monoxide.

A lawsuit naturally growing out of these cases of poisoning, I was called upon to give the chemical constituents found in the said "Fuel Gas," and the results are appended. I also experimented upon animal life with carbon monoxide mixed with air, obtaining results confirmatory of observations already made, that death usually takes place very quietly, although occasionally with convulsive movements. Chickens and rats were the two forms of life employed.

Blood, treated with carbon monoxide, I found to assume a bright red, almost carmine, colour, which did not alter on exposure to air for a number of days.

Finally, in February, 1888, a bottle of blood taken from the heart of one of the victims at the time of the autopsy, was submitted to me for examination. The bottle was closed with a tight cork. Although over a year old, and possessing strong odour of decomposition, the colour still remained of the brilliant, vivid red noted at the time of taking the specimen. Under the microscope but very few corpuscles remained to be seen, their structure having almost completely broken down.

Examination by the spectroscope revealed the two absorption bands near the line, characteristic of the presence of carbon monoxide in combination. These bands, although very like those indicative of oxyhæmoglobin, may yet be readily distinguished by their location only, particularly if a sample of blood artificially treated with carbon monoxide be at hand for purposes of comparison.

The space between the bands is, moreover, much less clearly lighted than in the case of oxygenated blood. As a confirmatory test, the blood under examination was treated with solid potassium sulphide, and the absorption bands found unchanged thereby—the bands of oxyhæmoglobin, as is well known, change under such treatment to the single dark band midway between the positions of the former ones.

What is of special interest in this case is the ready detection of carbon monoxide in the blood after so long an interval of time.

Ar the present moment, nearly two years from the date of the accident, the blood still retains the characteristics noticed when first examined.

The analysis of the Fuel Gas by volume is:—

CO_2	5·0 per cent
O	0·5 ,,
CO	37·5 ,,
CH_4	0·9 ,,
H	48·0 ,,
N	7·1 ,,

Such gas supplied to consumers is practically odourless.—*Journal of the American Chemical Society*, Vol. x., No. 9.

ESTIMATION OF TEA TANNIN.[*]

By JOHN TSAWOO WHITE.

So many and so various are the proposed methods of tannin-estimation, that in trying some samples of cutch or catechu it became necessary and important to choose a method of estimation. Therefore a reliable method, new or old, was necessary to be tried experimentally.

In looking round for a substance that would serve as a standard, the search chanced upon a sample of tea, commercially named Assam Pekoe Souchoung. The tannin in it was first determined by Lowenthal's method, acknowledged to be the best. Assuming with Rochleder that tea tannin is identical with quercitannic acid, and employing Neubauer and Oser's factor for this acid, it gave 11·9 per cent tannin. I must, however, say that the end reaction was not quite distinct, at least to my eyes. A solution, 4 grms. per litre, was used in all experiments; it was prepared by boiling 2 grms. of tea with a little less than 500 c.c. water for an hour, allowed to cool, diluted up to the mark, and filtered.

Then I tried precipitating tannin with a standard solution of acidified lead acetate. An excess of lead solution was used, and the excess determined in the filtrate. But as the composition of the lead precipitate is unknown, no results were obtained by these experiments. The acetic acid was added to keep up gallic acid. A solution containing enough of acetic acid to keep up a 4 grms. per litre solution of gallic acid from not precipitating, at first gave, however, a precipitate on being allowed to stand for a few hours.

My next trial was with ammoniacal zinc acetate, a reagent so characteristic and therefore so full of promise, a reagent used by Barbieri, Carpene, and Ferreil. A solution containing 100 grms. ZnO per litre was prepared. On adding ammonia to the zinc acetate there is a point where the first formed precipitate is almost entirely redissolved; 100 c.c. strong ammonia are now added, and then diluted to the litre mark: this solution gives a precipitate on diluting with water. Instead of dissolving the zinc tannate in sulphuric acid and oxidising it with $KMnO_4$, the precipitate was dried at 100° C, and the tannin calculated from its organic matter. This method I saw the late Dr. Romanis use occasionally; I do not know if it has been used by others. Zinc tannate is soluble in 14,600 parts of water at 21° C; and it is more insoluble in hot water—a single experiment gave its solubility as 1 part in 60,500 parts of water at 90° C. 100 c.c. of tea solution is precipitated in the cold with 10 c.c. zinc solution, allowed to stand an hour or two, filtered, and washed with hot water; boiling or allowing it to stand long will deposit an adherent coating of ZnO on the sides of the beaker, which is difficult to remove.

To avoid the troublesome and often annoying use of weighed filter-paper, the following method was adopted:—

After washing, the bulk of the undried precipitate is easily removed from within the folds of the filter: when dried, the precipitate sticks to the filter. The tannin is determined in this. Then the remainder of the tannate is ignited, and assuming that the precipitate is uniform, the total tannin is easily calculated. It is an advantage to use hydrochloric and hydrofluoric treated filter-papers like Schleicher and Schüll's; it will save correction for filter-ash. One experiment gave 19 per cent tannin, the tannate containing 54·53 per cent ZnO. Zinc tannate is more soluble in ammoniacal water: I did not try its solubility. The evidence of its solution may be seen by adding ammonia to some zinc tannate in suspension in water. The colour of the solution, previously slightly yellow, becomes at once dark coloured.

I next tried the tannin in 100 c.c. tea solution with the addition of 10 c.c. strong ammonia, often adding zinc acetate to make the strength equal to that of the zinc solution. The tannin was now 9·8 per cent, showing great solvent action, and the tannate contained 36·63 per cent ZnO. Instead of ammonia, 5 c.c. saturated solution of ammonium chloride was next added to prevent zinc oxide precipitating along with the tannate. The tannin was now 15·6 per cent, the tannate containing 34·02 per cent MO. This last and probably the best determination may be accepted as the amount of tannin obtained by this method. Before these experiments were tried I dissolved the tannate in acetic acid, precipitated the zinc with H_2S, evaporated the filtrate, and weighed the residue as pure tannin. Fairly constant, but low, results were obtained, viz., 8·2 per cent, 8·9 per cent, and 8·4 per cent tannin.

The evaporation values of a tannin solution evaporated with alcohol, with acetic acid, and with formic acid, were appreciably variable.

Zinc tannate is insoluble in methylated spirits, but it is difficult to wash with spirit.

As tannin is removed from solution by digesting with copper and zinc oxides, I tried digesting the tea solution with the dried oxides. The tea gave 31·9 per cent extract. The amount retained by the oxides was then determined by evaporation loss. Copper oxide acts more readily than zinc oxide. Alumina also removes tannin from its solution. As the moist oxide and hydrate may act more easily than when dry, some copper oxide and aluminium hydroxide were prepared by precipitation, and the tea solution was treated with copper oxide and aluminium hydrate in suspension in water. Copper oxide removed 18·9 per cent, and aluminium hydroxide 19·9 per cent and 19·6 per cent; thus a little over one half of the extract is absorbed.

Tannin is precipitated by aluminium acetate. A solution of aluminium acetate was prepared by digesting the hydroxide in 1 litre of water containing 100 c.c. acetic acid for a week, then diluting to 4 litres and filtering. The solution contains 2·7 grms. Al_2O_3 per litre. I find the acetic acid I use to contain 30 per cent anhydrous acid by titrating with potash and phenolphthalein. 100 c.c. of the tea solution are precipitated with 50 c.c. of the aluminium solution, filtered after an hour; the supernatant liquid is not always clear. It is washed with hot water; the precipitate washes easily. The tannin is then calculated from the loss on ignition after having dried and weighed it, the drying being done at 100° C. Three experiments gave 16·9 per cent, 15·3 per cent, and 16·4 per cent tannin, the tannate containing respectively 23·79 per cent, 26·57 per cent, and 20·17 per cent Al_2O_3. Gallic acid is not at first precipitated by aluminium acetate solution, but gives a blue colour due to traces of iron in the reagent. After some hours, however, a precipitate falls. I tried one experiment with gallic acid, a preparation of Messrs. Mottershead and Co. Only 77 per cent of the gallic acid is precipitated, the gallate containing 33·2 per cent Al_2O_3. The filtrate gave an intense blue colouration with ferric chloride. A trial with a sample of tannin, obtained from the Rangoon Medical Hall, with aluminium acetate gave the amount of tannin as 96·6 per cent, the tannate containing 25·07 per cent Al_2O_3.

Aluminium gallate dissolves easily in acetic acid. A solution of gallic acid, 4 grms. per litre, gave no precipitate with aluminium acetate containing additional acid of 50 c.c. per litre, even after standing over night—over fifteen hours. Tannin solution of the same strength is immediately precipitated. The tannate, however, dissolves when strongly acidified. 100 c.c. tea solution treated with 50 c.c. of aluminum acetate containing 50 c.c. additional acetic acid per litre, gave a slightly different result. The supernatant solution was clear, and it gave 13·5 per cent tannin, the tannate containing 14·5

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[*] Contribution from the Laboratory of the Chemical Examiner to Government, Burma.

per cent Al_2O_3. This is the latest determination of tea tannin with aluminium acetate. An advantage in using this reagent is this: that platinum crucibles may be used.

I intend to continue my experiments on other tannins and tannin containing bodies.

Aluminium acetate, like ferric acetate, the reagent of Handtke, might be found unsuited for some tannins. But may not tannins unprecipitated by aluminium acetate be unsuitable for tanning?

The above results are communicated as they may be of independent value and interest.

Rangoon, April 19, 1889.

THE TESTING OF LOGWOOD EXTRACTS.*

By T. C. PALMER.

The author remarked that he wished to call particular attention to the statement in his paper, that under the conditions of the test for strength of logwood extracts, with which the paper dealt, the compounds of tannin and copper oxide were nearly or quite colourless. This difference in behaviour between tannin and hæmatine was the more remarkable, since in many other respects the latter acts precisely as a tannin. This is even true with respect to its action on hide powder. An attempt to estimate the tannin in a pure extract of logwood, by means of filtration through powdered hide, had resulted in an apparent showing of twenty per cent of tannin, which loss was evidently due to an absorption of the hæmatine by the hide. In fact, the attraction of the hide for the colouring matter is quite as strong as it is for tannin. He here showed a column of hide powder deeply coloured by the passage through it of a very dilute clear solution of logwood.

The author also made some preliminary remarks on the faultiness of the tannin process of Hammer, as modified by Procter, giving data that show the amount of soluble matter in hide powder to depend very largely on the time the water is in contact with the hide, *i.e.*, in the rate of percolation. The hide powder, made by Schuchardt, gave to water an extract that left a residue on evaporation, ranging in amount, easily oxidisable, soluble in water, and with many of the reactions of the so-called coriin. The one fact above all that showed the faultiness of the process of Procter was that this residue, when re-dissolved in water, *was precipitated on addition of tannin solution.* Thus while the amount soluble in water could be only roughly estimated, the amount dissolved out by the tannin solution was simply unknowable, since at the top of the column, where the tannin is in abundance, there would be no dissolving out of the coriin, but as the liquor trickled down, losing tannin, it would dissolve more and more. The author stated that he expected shortly to bring before the Section his method of obviating this difficulty, retaining hide powder as the absorbent of tannin, but obtaining the tannin strength of the solution before and after filtration by an expedient that rendered evaporation of solutions or specific gravity determinations unnecessary.

ON THE COMPOUND $C_{21}Cl_{26}$.*

By EDGAR F. SMITH and HARRY F. KELLER.

In 1876† one of us (S.) described a compound containing only carbon and chlorine. It was obtained by the exhaustive chlorination of toluene exposed to sunlight, first at the boiling temperature and then in the cold. Several analyses of the purified product showed the presence of 21·40 per cent carbon and 78·6 chlorine. The only solvent employed at the time was chloroform, and from such a solution crystals, measuring one-half inch in length and one-fourth inch in breadth, were obtained. The forms were apparently orthorhombic. The melting-point, taken after each of a series of re-crystallisations, remained constant at 152°—153° C. To this rather interesting derivative the improbable formula $C_{21}Cl_{26}$ was ascribed. Nascent hydrogen acted with difficulty upon it. After an exposure of two months to the influence of zinc and sulphuric acid it was scarcely changed, inasmuch as an analysis of the product gave 21·69 per cent carbon, 77·76 per cent chlorine, and 1 per cent hydrogen.

Nothing further was done with the compound until about five years later, when a portion of it was treated in a sealed tube with an excess of aniline (*Am. Chem. Jour.*, vol. i., p. 150). By this treatment a base was formed, melting at 230° C. Its hydrochloric acid salt was analysed.

Crystals of the original compound, in its purest condition, were preserved for twelve years without undergoing any visible alteration, and it was but natural that we should be surprised, on fusing some of this same material, to find it melting at 101° C. This melting-point remained constant, even after re-crystallisation from pure chloroform. On heating a portion of the substance in a test-tube, we observed that hydrochloric acid gas was evolved. A combustion gave 22·8 per cent carbon and 2·2 per cent hydrogen. A vapour density determination was carried out, but, as we had evidence of decomposition, we place no reliance on the result. Every possible precaution was observed in the combustion, in order that we might arrive at the true hydrogen percentage, and that given above would indicate but slight change from the original constitution. Work is now being prosecuted with a view of obtaining the carbon chloride, when it is proposed to pay especial attention to the solution of its molecular formula and to the study of some of its derivatives. We therefore request those who may have entertained the idea of investigating this compound to postpone their work, and leave the field to us, at least, for a few months.

ON THE RE-DETERMINATION OF THE ATOMIC WEIGHT OF PALLADIUM.*

By Dr. E. H. KEISER.

The atomic weight of palladium has not been determined very carefully. The only data for the calculation of this constant, at the present time, are two analyses of the double chloride of palladium and potassium made by Berzelius in 1828. These two analyses do not agree very well. The first one gives 105·7, and the second one 106·2 for the atomic weight of palladium.

For the purpose of re-determining this atomic weight, metallic palladium in the form of foil was dissolved in aqua regia and the solution evaporated to dryness. The palladium chloride was then dissolved in dilute hydrochloric acid and the solution was filtered. Ammonia was added to the filtrate until the precipitate, which at first formed, was re-dissolved. After filtering the solution again, to remove any traces of ferric hydroxide, the filtrate was saturated with hydrochloric acid gas. The palladium is thus precipitated as palladium-di-ammonium chloride, $Pd(NH_3Cl)_2$, a yellow crystalline compound which is insoluble in water and acids, but which is readily soluble in dilute ammonia.

The yellow precipitate was re-dissolved in dilute

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* Chemical Section of the *Journal of the Franklin Institute*, April, 1889.

† "Dissertation." Goettingen, 1876; *Jahresbericht*, 1877, p. 421; *Am. Phil. Soc*,, xvii., p. 29.

* Chemical Section of the *Journal of the Franklin Institute*, April 1889.

ammonia, and the solution was filtered. If any rhodium had been present in the original sample of metallic palladium, it would have been separated by this process, because the rhodium di-ammonium chloride is insoluble in dilute ammonia. The filtrate was thereupon treated with hydrochloric acid and the palladium di-ammonium chloride thus precipitated was thoroughly washed with distilled water until all ammonium chloride was removed. The compound was carefully dried over sulphuric acid in a partial vacuum.

The compound was analysed by weighing off portions in platinum boats and heating up in a current of pure hydrogen. At a low temperature the yellow compound absorbs hydrogen, metallic palladium and ammonium chloride being formed.

$$Pd(NH_3Cl)_2+H_2=Pd+2NH_4Cl.$$

On raising the heat the ammonium chloride is completely volatilised, and spongy palladium remains behind. After the boat and its contents had cooled off somewhat, the hydrogen stream was replaced by one of dry air, and the boat was allowed to cool off completely in the air. By this means it was possible to avoid the retention of hydrogen by the palladium, and as the hydrogen stream was not displaced by air until the temperature of the palladium had fallen considerably below a low red heat, it was not possible that palladium oxide should have been formed.

Determination of Atomic Weight of Palladium.

I.—By ignition of $PdN_2H_6Cl_2$ in current of hydrogen.

No.	Weight of Substance.	Weight of Palladium.	Atomic Weight.
1.	0·83260	0·41965	106·459
2.	1·72635	0·86992	106·410
3.	1·40280	0·70670	106·355
4.	1·57940	0·79562	106·342
5.	1·89895	0·95650	106·321
6.	1·48065	0·74570	106·292
7.	1·56015	0·78585	106·322
8.	1·82658	0·92003	106·317
9.	2·40125	1·20970	106·355
10.	1·10400	0·55629	106·400
11.	0·93310	0·47010	106·366
Total ..	16·74583	8·43606	[106·3520]

Atomic weight = 106·35 H = 1· Maximum = 106·459
N = 14·01 Minimum = 106·292
Cl = 35·37 Difference = ·167
Atomic weight = 106·62, when o = 16.

The foregoing table contains the results of all the determinations that were made.

The investigation will be continued. It is intended to make a series of determinations by means of other palladium compounds.

NOTICES OF BOOKS.

A Dictionary of Explosives. By Major J. P. Cundill, R.A. Chatham: Royal Engineers' Institute. London: Hamilton, Adams, and Co.

The first point which must strike chemists and engineers in examining this eminently practical compilation is the multitude of explosives which have been suggested, patented, and often brought into use. We are no less struck by the absurdity of the names of some of these compounds or mixtures, and by the evident identity of many regarded as distinct by their inventors. The same idea, as Major Cundill remarks, has been patented and re-patented, and we may, perhaps, yet find a crop of litigation springing up not less luxuriant than that which occurred in connection with magenta.

The list of explosives practically used in this country is very limited. The author enumerates as such gunpowder, gun-cotton under various names, dynamite No. 1, blasting-gelatin, and gelatin dynamites. These two compounds are often confounded. Blasting-gelatin is a combination of nitro-glycerin and gun-cotton. Gelatin-dynamite is a thin blasting-gelatin mixed with nitrates, cotton, or charcoal.

We find in this work mention made of delusive experiments performed by manufacturers and their representatives to convince consumers or local authorities of the safety of their products. It is sometimes said that an explosive will burn away without explosion, and this may be true under certain circumstances. Thus, if a small quantity of gun-cotton is kindled or thrown into a fire it burns fiercely but quietly; yet if a fire breaks out in a magazine, part of the bulk having its temperature gradually raised reaches a point at which it explodes as destructively as if fired with a detonator. Dynamite may also be safely burnt in its ordinary unfrozen condition, but if it is gradually warmed in an oven or on a shovel over a fire, the result is generally a verdict of "Accidental Death." Major Cundill very justly says that in such cases the verdict should be suicide or manslaughter, as the case may be. The caution is also given that the compound which bears a blow without exploding may be made to detonate if previously heated. Attention is called to the effects of a glancing blow, combining percussion and friction. Such blows are likely to occur in charging a bore-hole, and they are far more effective than a much heavier blow given directly. Wearers or users of celluloid—that variety, at least, which consists largely of gun-cotton—may feel interested to learn that when heated it may be exploded by a shock.

The author classifies explosives in eight groups: gunpowder, ordinarily so-called, nitrate mixtures other than gunpowder, chlorate mixtures, nitro-compounds containing nitro-glycerin, nitro-compounds not containing nitro-glycerin, explosives in which picric acid or a picrate is a leading constituent, explosives of the Sprengel type, the essential feature of which is the admixture of a combustible with an oxidising agent, at the moment of or immediately preceding use, the constituents being non-explosive if taken separately, and lastly, miscellaneous explosives.

In a paragraph explaining the distinction between military and civil explosives we notice with profound regret a sentence which is perfectly true, but which may suggest to evil-disposed persons means for the most serious mischief.

The chlorated mixtures are very justly declared unsafe. This objection has been forcibly and distinctly put by Dr. Dupré, F.R.S.; Eissler and Berthelot concur in this opinion, and Major Cundill pronounces some of the compounds which he enumerates under this head to be "more or less dangerous haphazard mixtures." Some of them, *e.g.*, Augendre's "white powder," are capable of exploding even in the absence of one of the ingredients.

Melinite is mentioned, but its composition, not having transpired, is not given. It contains picric acid, and in the author's opinion it much resembles Turpin's explosive (Spec. No. 15,089, 1885). He thinks that nitro-benzol or some analogous material is also used. "A portion of the explosive as used to fill shells is said to be termed cresilite. Kresylic acid corresponds to carbolic acid, but contains the hypothetical radicle kresyle (C_7H_7) in place of phenyle (C_6H_5)."

The Sprengel explosives (Spec. No. 2642, 1871), and *Journal of the Chemical Society*, August and September, 1873) are a very interesting class of bodies. Whilst their power cannot be disputed, the circumstance that they have to be made on the spot forms not only a legal but a practical barrier to their extensive use.

In conclusion the author gives certain "words of caution" which, if attended to, would save much mischief:—

"The function of an explosive is to explode. Remember this in dealing with them. If an explosive is described as absolutely safe under all circumstances, do not treat it as some people treat a big dog, and try how much it will stand. There is no explosive, within my knowledge, in practical use which, when exploded in a confined space, does not give off noxious or deleterious gases. Do not expect the same class of explosive to do every variety of work. Different classes have their different functions. If using an explosive with which special instructions are issued, it is wiser to read them before an accident happens than to have to refer to them afterwards, to see if they are not issued for some good reason. Do not apply the sense of taste to explosives. In the case of nitro-glycerin and nitrobenzol compounds the consequences may be unpleasant."

Major Cundill's work will prove exceedingly valuable to all who manufacture, use, or study explosives.

Thirtieth Annual Report of the Inspector of Milk and Vinegar. From Jan. 1st to Dec. 31st, 1888. Boston: Rockwell and Churchill, City Printers.

The Inspector finds himself able to assert that in no large city in the world is the adulteration of milk suppressed to the degree which now prevails in Boston. This result reflects the greater credit upon the authorities since we are told that a few years ago 60 per cent of all samples were below the standard. For the year 1885 the percentage of poor samples was 30·64; for 1886, 18·55; for 1887, 12·54; and for 1888 only, 8·49. Every dealer is liable to have his milk tested on any day (Sundays included), and at any hour. The samples inspected, according to their merit, are either "passed" as good, "warned," or, in the worst cases, "reported" for prosecution. Of the 108 cases disposed of during the year, 87 cases were finally decided in favour of the prosecution. *Two* appeals seem to be allowed, firstly to the Superior Court, and secondly to the Supreme Court.

A preliminary examination of the samples is made by means of Feser's lactoscope, the results turning on the greater or less opacity of the sample, and by Pile's hydrometer, with correction for temperature. Instead of warming or cooling the milk to some standard degree, the sp. gr. is taken at any temperature, and then reduced to standard by calculation, the tables for which are here given.

If the results of this preliminary examination are condemnatory or doubtful, a chemical analysis follows, the points determined being total solids, solids not fat, fat, ash, milk-sugar (ascertained by means of the Ventzke-Scheibler polariscope), and albumenoids.

For the detection of annatto two methods are in use. The first is applicable to fresh, sweet milk only, and is as follows:—100 c.c. of the sample, rendered alkaline by the addition of 5 c.c. of solution of sodium carbonate (1 part in three of water), are poured into a glass jar, 1½ inches in diameter and 4—5 inches high. In this jar is placed a strip of white filter-paper (Schleicher and Schüll's No. 568) 5½ inches long and ½ inch wide. The jar is set aside for twelve hours in the dark, the paper is withdrawn and washed in running water, when, if annatto be present, and if, while still moist, it is dipped in a solution of stannous chloride, it appears of a pale salmon colour. If the milk is sour the colouring-matter of the annatto is precipitated, and escapes detection. The pink colour may be brought back to the original salmon tint by immersing the slip in a dilute solution of sodium carbonate. It is then well washed, dried in the cold, and further tested with dilute sulphuric acid (2 parts acid and 1 part water), which produces a bluish colour with annatto.

The second method, which is applicable to sour or stale milks, sets out with the precipitation of the caseine. Four fluid ozs. milk are coagulated in heat with a few drops of acetic acid. The colouring matter goes down in the caseine, which is then freed from serum by pressing and straining and ground up in a porcelain mortar with a fluid oz. of ether added in small portions, and is finally decanted off into a small globular separating apparatus having a stopper at the top and a stop-cock at the lower part. From 5 to 10 c.c. of dilute caustic lye (1 part sodium hydroxide in 100 of water) are added, and the whole is well shaken up. When the liquids have separated, the lower stratum of liquid, holding the annatto in solution, is drawn off into two small porcelain capsules of such size that the depth of the liquid in each may not exceed ¼ inch. In each capsule is then placed a disc of strong filter-paper, ⅝ in diameter, which are let stand for twelve hours in the dark and are then taken out and washed in fresh water, and may then be tested with stannous chloride or sulphuric acid as in the first method.

The detection of caramel, boracic acid, and salicylic acid and the microscopic examination of milk have also engaged the attention of the Inspector.

The oleomargarine question comes here to the front. The Inspector agrees with most eminent authorities that margarine is not injurious, and that it is objectionable only when sold under false names or when used in mixture with genuine butter. The only weak point in the law of Massachusetts on this subject seems to be that the name "butterine" is still tolerated.

Another question is the artificial colouration of butter, by which it is rendered possible to mix up different makes, good, bad, and indifferent, without the mixture being at once manifest to the eye of the purchaser. The colouring matter used is annatto, extracted by boiling or steeping in cotton-oil, linseed-oil, or whichever other oil happens to be the cheapest, and thus a considerable quantity of foreign fat is introduced into the butter. The manufacturers of these butter-colours—the names of whom are given boldly—assert that every gallon of their concoction used will increase the weight of the butter used by 8 lbs. The report contends—in our opinion with full justice—that the colouring of milk, butter, and margarine should alike be prohibited as opening the door for frauds indefinite in number.

On vinegar little is here said. During the last four years the percentage of poor vinegars sampled in Boston has fallen from 38·00 to 20·60 per cent. The author points out the distinguishing characters of cider-vinegar, which, when genuine, is not inferior to the white wine vinegar of France—now become rare—or to English sugar vinegars, and has an aroma never to be met with in alcohol or malt vinegars.

CORRESPONDENCE.

ALKARSIN.

To the Editor of the Chemical News.

Sir,—I find that by distilling chloride of acetyl, which is easily obtained by the distillation of concentrated hydrochloric with glacial acetic acid—

$$(HCl + C_2H_4O_2 = C_2H_3OCl + H_2O),$$

with an alloy of equal parts of zinc and arsenic, Zn_3As_2, an oily and fetid alkarsin is obtained, an acetide of arsenic. This liquid has an odour similar to arseniuretted hydrogen gas and acetic acid mixed, and seems to be decomposed by water or moisture into those two substances. If this be the case, therefore, the vapours of this alkarsin will act as deadly poison. When *I* made it, it did not fume or take fire in the air like ordinary alkarsin, viz., the mixture of kakodyle and its products of oxidation.

The alkarsin that I have discovered is merely an acet*ide* of arsenic, because the last part of the formula will not be O_2, as in other acetates. It may, however, combine with oxygen to form the *acetate*.—I am, &c.,

G. W. Blythe, M.P.S.

5, Alderley Road, Hoylake,
Cheshire.

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. cviii., No. 18, May 7, 1889.

On the Origin of Bronze, and on the Sceptre of Pepi I., King of Egypt.—M. Berthelot.—In view of the comparative rarity of tin, the author agrees with the opinion of many archæologists that the use of pure copper must have preceded that of bronze. The sceptre of Pepi I., preserved in the British Museum, dates back to 3500—4000 years B.C. It is a small hollow cylinder of copper, covered with hieroglyphics. Through the intervention of the French ambassador M. Berthelot has obtained 0·0248 grm. of filings from the interior of the cylinder, which, on analysis, proved to be pure copper, free from tin and zinc, but containing a doubtful trace of lead. M. Berthelot thinks that the introduction of bronze does not date back beyond fifty to sixty centuries B.C.

On the Thionic Series. Action of Alkalies.—M. Berthelot.—The general theory of condensed anhydrides gives an exact explanation, at once chemical and thermochemical, of the constitution, the conditions of reaction, and the transformations of the thionic compounds. This applies equally to the metaphosphoric and pyrophosphoric acids, compounds condensed with loss as to their capacity of saturation compared with the normal tribasic phosphoric acid.

Researches on the Application of the Measure of Rotatory Power to the Study of the Compounds formed by the Action of Neutral Magnesium and Lithium Molybdates upon Solutions of Tartaric Acid.—D. Gernez.—The simplest combinations produced in aqueous solution by tartaric acid, and the neutral molybdates and tungstates which correspond to a maximum rotatory power, are formed by the union of the acid to the salt molecule to molecule.

The Atomic Weight of Ruthenium.—A. Joly.—Assuming O = 15·960 the author finds Ru = 101·49. Ruthenium has been freed from osmium, the atomic weight of which (191 according to the latest determinations of Seubert) is nearly double.

The Manganese Oxides obtained in the Moist Way.—A. Gorgen.—Hydrated manganous oxide, held in suspension in a mother-liquor containing an excess of manganese salt and submitted to the action of air, produces saturated manganite, $MnO_2,2MnO$, combined with variable quantities of water. Hydrated manganous oxide in alkaline liquors absorbs larger proportions of oxygen. On this fact depends the process of regeneration of oxides of manganese, as proposed by Weldon.

On Oxycinchonine-α.—E. Jungfleisch and E. Lèger.—This compound crystallises out of alcohol in colourless flattened prisms. It is insoluble in water but readily soluble in dilute alcohol and acetone, and more abundantly in strong alcohol, benzene, and chloroform. If saline solutions are not fluorescent they are precipitated by ammonia, but the precipitate re-dissolves in excess. It is isomeric with homoquinine, apoquinine, and apoquinidine, as well as with the oxycinchonines of Schutzenberger and Strecker.

The Alcoholic Fermentation of the Juice of the Sugar-cane.—V. Marcano.—The crude cane-spirit differs from other industrial alcohols by the presence of notable quantities of methylic alcohol, by the absence of the higher alcohols, and by the presence of an acid, *sui generis*.

Action of Zinc Chloride upon Isobutylic Alcohol in Presence of Hydrochloric Acid. Part of Isobutyl Chloride. Properties of Polybutylene.—MM. Malbot and Gentil.—Not adapted for useful abstraction.

The Determination of Organic Nitrogen by the Kjeldahl Process.—E. Aubin and L. Alla.—The authors prefer the Kjeldahl process to that of Will and Varrentrapp on the following grounds:—The dryness of the matter to be analysed. Many agricultural substances contain 15 to 40 per cent of moisture, and on mixing it with soda-lime there is sometimes an escape of ammonia. The liquid or pastey state is also inconvenient, as milk, beer, urine, drainings of dunghills, &c. The low sp. gr. of certain industrial waste and their hygroscopic quality. The heterogeneous character of certain materials; the difficulty of pulverisation. In the Kjeldahl process these properties do not interfere.

On an Artificial Silk.—M. de Chardonnet.—The author forms a nitrocellulose, dissolves it in a mixture of alcohol and ether, removes a portion of the nitrogen by immersion in nitric acid at sp. gr. 1·32 at a temperature falling from 35° to 25°. It is said to take up colours like natural silk.

Biedermann's Central-Blatt fur Agricultur Chemie. Vol. xviii., Part 5.

Disposal of Refuse by Irrigation or Removal.—E. Reichardt.—The author, whilst advocating irrigation, admits that considerable quantities of potash and nitrogen are carried off into the rivers. For the disinfection of manure-heaps he recommends peat litter.

The Transformation of Nitrates in the Soil.—M. Berthelot.—From the *Comptes Rendus*.

The Production of Farmyard Manure.—A. Müntz and Ch. Girard (*Annales Agronomiques*).—The experiments relate principally to sheep. The authors find that a litter of earth retains the nitrogen of the excreta of these animals considerably better than does straw. Of 23·01 kilos. of nitrogen supplied to the sheep in their food (a straw litter being used) 1·67 kilos. were retained in the bodies, 8·90 were secured in the manure, and 12·44 (=51 per cent) were lost. P. P. Dehérain considers that had the authors used a larger proportion of straw the loss would have been smaller.

Manurial Experiments Conducted at the Pennsylvania State College.—W. Frear.—From the *Agricultural Bulletin of the Pennsylvania State College*, No. 14.

Influence of Manures on the Composition of Barley.—M. Krandauer (*Hopfenzeitung*).—The nitrogenous manure did not cause any marked increase in the nitrogen of the barley.

The Influence of Salt on the Digestibility of Protein in Various Articles of Cattle-food.—Prof. Sievert.—The addition of common salt appears to have no effect.

Variations in the Composition of Milk.—Harald Faber (*Tidskrift for Landökonomi*).—(See p. 253).

Influence of Petroleum-Steep upon the Germination of Maize.—Prof. Gustav Wilhelm (*Oest. Land. Wochenblatt.*—If the seed is steeped in petroleum germination is, and the growth of the plants is rather, delayed, and a smaller percentage of the seeds come up. But the injury is not so great as to necessitate the disuse of this experiment where the attacks of vermin are to be expected.

Researches on Inosite.—L. Maquenne.—From the *Bulletin de la Société Chimique*.

The Rational Feeding of Horses.—Prof. E. Wolff, Prof. Seiglin, and Dr. C. Riess.—At the conclusion of a long report on the experiments conducted in Paris in 1886-87 it is admitted that the question of the nutritive value of cellulose is not decided.

NOTES AND QUERIES.

₊ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Molecular Weight.—Will some reader supply an answer to the following:—Explain how it is possible to determine the molecular weight of a substance by its influence in lowering the melting-point of a solvent.—S. J.

Viscous Liquids.—All viscous liquids, as far as I can make out, the fluidity being increased by increase of temperature, vary considerably in viscosity with ordinary variations of temperature. I shall be grateful to learn where, if possible, I may find a record of any observations on this subject, and whether there exists such a thing as a tolerably viscous liquid, which is but slightly affected by ordinary variations of temperature.—R. Snowdon.

MEETINGS FOR THE WEEK.

Monday June 3rd.—Society of Chemical Industry, 8. "Naphthalin Derivatives of Technical Importance," by W. P. Wynne. "Purification of Alcohol by means of Hydrocarbon Oils," by Dr. W. S. Squire.

—— Royal Institution, 5. General Monthly Meeting.

Tuesday, 4th.—The "Faraday Lecture," by Prof. Mendeleeff, will be delivered in the Theatre of the Royal Institution, Albemarle Street, at 8.30 p.m. (Fellows of the Chemical Society desiring extra tickets for ladies or gentlemen are requested to apply to the Secretary).

—— Royal Institution, 3. "Some Recent Biological Discoveries," by E. Ray Lankester.

Wednesday, 5th.—Geological, 8.

Thursday, 6th.—Royal Institution, 3. "Chemical Affinity," by Professor Dewar.

—— Royal, 4.30.

—— Chemical, 8. "Experimental Researches on the Periodic Law," by Dr. B. Brauner. "The Amylodextrin of W. Naegali," by H. T. Brown and G. H. Morris. "The Determination of the Molecular Weights of the Carbohydrates (Part II.)," by H. T. Brown and G. H. Morris. "Researches on Silicon Compounds (Part IV.)," by Prof. Emerson Reynolds, F.R.S. "The Isomerism of the Alkyl Derivatives of Mixed Diazoamido Compounds," by Prof. Meldola and F. W. Streatfeild. "The Atomic Weight of Zinc," by Dr. Gladstone and W. Hibbert. "The Amount of Nitric Acid in the Rain-water at Rothamsted, with Notes on the Analysis of Rain-water," by R. Warington, F.R.S. "The Product of the Action of Sulphur on Resin," by G. H. Morris.

Friday, 7th.—Royal Institution, 9. "Recent Researches into the Origin and Age of the Highlands of Scotland and the West of Ireland," by Archibald Geikie, F.R.S.

—— Geologists' Association, 8.

Saturday, 8th.—Royal Institution, 3. "Idealism and Experience in Philosophy and Literature," by Prof. W. Knight.

—— Physical, 3. "On a Method of Suppressing Sparking in Electric Currents," by Prof. S. P. Thompson, D.Sc. "On a Shunt Transformer," by E. W. Smith. "Notes on Geometrical Optics:—(1) On the Deduction of the Elementary Theory of Mirrors and Lenses from Wave Principles; (2) On a Dioptric Spherometer; (3) On the Formula of the Lenticular Mirror; (4) On the Use of the Focal Circle in Mirror and Lens' Problems," by Prof. S. P. Thompson, D.Sc. "On the Use of the Biquartz," by A. W. Ward.

THE CHEMICAL NEWS.

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RESEARCHES IN THE CHEMISTRY OF SELENIC ACID AND OTHER SELENIUM COMPOUNDS.*

By Sir CHARLES A. CAMERON, M.D., F.R.C.S.I., V.P.I.C.,
Professor of Chemistry and Hygiene, R.C.S.I.;
and JOHN MACALLAN, F.I.C.,
Demonstrator of Chemistry, R.C.S.I.

(Concluded from p. 260).

The Action of Heat upon Selenic Acid.

Action of Heat in a Vacuum.—The effect of heating dilute selenic acid in a vacuum up to 180° has already been described—dilute acid distils until that temperature is reached, when the anhydrous acid remains.

The result of further heating is merely for a time to raise the temperature; the acid does not distil in the anhydrous condition. At about 200° it begins to decompose slowly, and at higher temperatures rapidly, into selenium dioxide, oxygen, and water. The latter serves to dilute a portion of the remaining acid, which then at once distils. In order to examine the effect of distilling the anhydrous acid destructively in a vacuum, a portion was heated in a flask connected with a condensing arrangement until rapid decomposition took place. The residue always consisted of a mixture of anhydrous selenic acid with selenium dioxide, the proportion of the latter increasing with the rise of temperature and length of time of heating. The former was proved to be present by dropping in a crystal of anhydrous acid, when the liquid froze, and it also gave a colouration in the cold with the selenium test for the same acid, which will be described hereafter. A portion which had been distilled for some time left a residue of which 0·7107 grm. neutralised 18·50 c.c. of semi-normal soda solution, using litmus as indicator, equivalent to 94·27 per cent of acid calculated as selenic—a result which might be expected, owing to the influence of the selenium dioxide in diminishing the acidity, as has been already pointed out. The distillate consisted of selenium dioxide mixed with selenic acid. The latter was in a dilute state, since it would not solidify on addition of a crystal of anhydrous acid, nor would it respond to the selenium test: 0·4703 grm. neutralised 11·11 c.c. of seminormal soda solution, equivalent to 85·46 per cent of acid calculated as selenic. Taking into account the diminution of acidity caused by the selenium dioxide, it is evident that a very concentrated, although not anhydrous, acid distils over.

Action of Heat under Ordinary Pressures.—When dilute selenic acid is boiled at ordinary pressures nothing but water is evolved until 205° is reached, at which temperature it has the composition of the monohydrated acid. In these respects it behaves like dilute sulphuric acid. After passing 205° the distillate contains at first mere traces of selenic acid, but its strength gradually increases. A portion of acid distilled between 205° and 227° yielded a distillate of which 0·6826 grm. neutralised 0·10 c.c. of seminormal soda solution, equivalent to 0·53 per cent of selenic acid. On further heating from 227° to 260° a distillate was obtained, of which 0·3818 grm. neutralised 0·32 c.c. of seminormal soda solution, equivalent to 3·03 per cent of selenic acid. At the latter temperature the acid commenced to distil over in white fumes. 0·6878 grm. of the residue left at 260° neutralised 17·76 c.c. of seminormal soda solution, equivalent to 93·41 per cent of selenic acid. At higher temperatures a portion of the acid is decomposed, the distillate being kept weak by the water continuously set free in the decomposition; and at still higher temperatures much selenium dioxide also distils over. A portion of acid which commenced to boil at 235° was heated until the temperature rose to 325°: 2·1542 grms. of the distillate neutralised 3 c.c. of seminormal soda solution, equivalent to 5·04 per cent of selenic acid. The residue was then further heated until the geater part of the acid was decomposed, and the strength of the distillate taken: 1·6176 grm. neutralised 16·5 c.c. of seminormal soda solution, equivalent to 36·90 per cent of acid calculated as selenic, but much of the acidity was due to selenious acid, a large amount of which was present in the distillate. It is thus seen that the selenic acid which distils under ordinary pressures is always highly dilute.

When anhydrous selenic acid is strongly heated under ordinary pressures a portion of it is decomposed into selenium dioxide, oxygen, and water, the latter serving to dilute the remaining acid. It will then no longer solidify on addition of a crystal of the anhydrous acid. After further heating it becomes sufficiently dilute to distil over in the manner already described. It is instructive to compare with this the action which takes place in the case of anhydrous sulphuric acid. Marignac found (*Annales de Chimie et Physique* (1853), 39, 184) that the latter when heated gives off sulphuric anhydride until the remaining acid is reduced to the same strength as that yielded by a more dilute acid on prolonged ebullition—about 98·66 per cent. In the case of selenic acid the anhydride is evidently unable to exist free at elevated temperatures, but breaks up into selenium dioxide and oxygen.

It is worthy of note that a remarkable coincidence exists between the temperature at which selenic acid is decomposed, and that at which selenium dioxide sublimes. The latter is not stated very definitely in any of the chemical text-books; we have found, however, that at 280° rapid sublimation takes place, while at 250° volatilisation proceeds slowly. When selenic acid is kept for some time at the latter temperature it is always found to contain traces of selenium dioxide, while at 280° decomposition proceeds with rapidity. It is probable that a connection exists to a considerable extent between the phenomena, and that the explanation of the coincidence may be that the comparatively weak affinities which bind the molecule of selenic acid are unable to prevent its disruption when once a temperature is reached at which the tendency of its constituents to separate is aided by the expansion attending a change to the gaseous condition. We have seen that both phenomena are affected by the temperature; they are also dependent to some extent upon the pressure. Anhydrous selenic acid commences to dissociate in a vacuum at about 200°. We found that when selenious acid was heated under similar circumstances water was quickly evolved, and after prolonged heating of the residue a distinct white ring of selenium dioxide was deposited on the cold portion of the neck of the flask.

The Action of Sulphur upon Selenic Acid.

When powdered sulphur is mixed with liquid anhydrous selenic acid, there is no action in the cold; but if the mixture be heated to 63°, the sulphur dissolves in the acid with production of an exceedingly deep indigo-blue colour. There is some action, but slight, at 58°. The body which is produced is very unstable, since it begins to decompose at the temperature at which it is formed, with evolution of sulphur dioxide, and reduction of the selenic acid to selenious acid. If water be added when the colour has first developed, sulphur is deposited in soft yellow flakes; but after decomposition has commenced, the addition of water throws down red selenium chiefly, owing to the reaction between the sulphurous and selenious acids which are formed.

A similar action has long been known to occur between sulphur and sulphuric acid. In 1804 Buchholz (Gehlen's *Neues Journal der Chemie*, 3, 7) discovered that sulphur dissolved in the latter acid with the formation of a blue

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* A Paper read before the Royal Society, May 2, 1889.

colour, the sulphur being re-precipitated on addition of water. This reaction was subsequently investigated by Vogel, Schweigger, Berzelius, Wach, and Stein, and in 1875 Weber succeeded in isolating the blue compound (Poggendorff's *Annalen der Physik und Chemie*, 156, 531), and discovered it to be a sesquioxide of sulphur, S_2O_3, but very unstable, decomposing at ordinary temperatures with evolution of sulphur dioxide.

The Action of Selenium upon Selenic Acid.

A reaction takes place between selenium and anhydrous selenic acid in the cold. The selenium dissolves in the acid with production of an intense and beautiful green colour. The presence of a minute quantity of water prevents the colour from developing fully until the acid is warmed. The acid is capable of dissolving a considerable quantity of selenium. If kept in a closed vessel the colour thus produced is very permanent, being unaffected for months during summer weather, but if the acid be heated to 75° the colour disappears, and the selenic acid is found to be partly reduced to selenious acid. Addition of water, when the colour has developed, throws down a voluminous red precipitate of selenium; and exposure to the air in an open vessel for a few minutes is sufficient, from the same cause, to change the green colour to red. It will be shown hereafter that this green colour is probably caused by the formation of a new oxide of selenium. Its production with the anhydrous acid affords a test for the latter, which we have already made use of in examining the effect of heat upon selenic acid.

In 1827 Magnus found that selenium was dissolved by strong sulphuric acid with development of a green colour, and was re-precipitated on addition of water. Berzelius and Fischer subsequently investigated the reaction, and in 1875 Weber (Poggendorff's *Annalen der Physik und Chemie*, 156, 545) isolated the green compound, and found it to be a sulphoxide of selenium, $SeSO_3$. The colour given by selenium with sulphuric acid is a dark green, not so bright as that which it produces with selenic acid.

The Action of Tellurium upon Selenic Acid.

Like selenium, tellurium reacts upon anhydrous selenic acid in the cold, but with production of a purple red colour. Even when the acid is not perfectly anhydrous, it will still give a colouration in the cold. The compound thus formed is probably very unstable, since the colour disappears at so low a temperature as 19°, the selenic acid being partly reduced to selenious acid. If water be added when the colour has developed, tellurium is thrown down in sooty flakes, and exposure to moist air produces the same effect.

Tellurium reacts in a similar manner with strong sulphuric acid with development of a red colour, and re-precipitation on addition of water. This was first observed by Müller von Reichenstein. In 1798 the same reaction was investigated by Klaproth, and afterwards by Magnus and Fischer. The red compound was isolated by Weber in 1882 (*Journal fur Praktische Chemie*, 25, 218), and soon afterwards independently by Divers and Shimosé (*Journal of the Chemical Society*, Transactions, 43, 319), and was ascertained to be tellurium sulphoxide, $TeSO_3$.

Comparison of Sulphoxides with Selenoxides.

The coloured compounds first formed by the action of sulphur, selenium, and tellurium upon sulphuric acid were subsequently produced by the action of the same bodies upon sulphuric anhydride, and were isolated by forming them in the latter manner, and then removing the excess of anhydride. As has been already mentioned, they were found to be sulphoxides having the composition respectively, SSO_3, $SeSO_3$, and $TeSO_3$. Considering the similarity of the reactions which produce them, and of the decompositions to which they are liable, it is very probable that the coloured bodies formed with selenic acid are selenoxides, analogous to the sulphoxides already known, the sulphur in the latter being replaced by selenium. A comparison of the formulæ of the two series of bodies as represented in the following table, leads to some interesting considerations:—

Colour of compound.	Sulphoxides.	Selenoxides.
Blue	SSO_3	$SSeO_3$
Green	$SeSO_3$	$SeSeO_3$
Red	$TeSO_3$	$TeSeO_3$

The green body formed by the action of selenium upon selenic acid is, in all probability, a new oxide of selenium, having the composition Se_2O_3, analogous to the sesquioxide of sulphur formed by the action of sulphur upon sulphuric acid.

The colour of the above compounds appears to be almost entirely due to the element which is added on to the anhydride; the sulphur or selenium in the residual portion of the molecule has scarcely any effect upon the colour.

The green body $SeSO_3$ must be metameric with the blue compound $SSeO_3$, and consequently the atoms of sulphur and selenium in each of these bodies must occupy dissimilar positions in the molecule.

The Possible Existence of Selenic Anhydride.

A consideration of the foregoing facts leads to the conclusion that selenic anhydride, which has not up to the present time been obtained, is yet capable of existing in a free condition. Just as the sulphoxides are direct addition compounds of sulphur, selenium, and tellurium respectively with sulphuric anhydride, so the selenoxides must be regarded as addition compounds of the elements mentioned, with selenic anhydride. It is difficult to conceive that bodies so constituted are capable of existing free, and that the anhydride is unable to do so. On the other hand, it is probable that it dissociates at a comparatively low temperature, but one that is higher than 75°—the highest temperature at which the most stable of the selenoxides has been as yet found to exist. Selenious anhydride is always obtained, and not selenic, under similar conditions to those which produce sulphuric anhydride, and involving a high temperature.

We have examined the action of heat upon various selenates. Those selected for the purpose were the selenates of antimony, bismuth, platinum, lead, and silver, and also ferric and mercuric selenates. In no instance was selenic anhydride obtained, but selenious anhydride was evolved in all cases when the above selenates were strongly heated.

Von Gerichten (*Liebig's Annalen der Chemie* for 1873, p. 214) endeavoured to form selenic anhydride in a similar manner to that by which sulphuric anhydride is usually obtained—by leading a mixture of oxygen and the vapour of selenious anhydride through red-hot platinum sponge. He states that in one experiment a white deposit was obtained which consisted partly of selenious anhydride, but probably also contained selenic anhydride, since it dissolved in water with a hissing sound, and the solution was found to contain selenic acid. In subsequent experiments a decidedly negative result was obtained, since only selenious anhydride was found in the product.

In order to examine if selenic anhydride is produced in the manner just described, the following experiments were made:—

Some platinum sponge was introduced into a combustion-tube, and a quantity of selenious anhydride placed behind it. The platinum sponge was kept at a red heat, and the selenious anhydride was also heated until it sublimed. Oxygen, which was first dried by passing through a series of tubes containing calcium chloride and sulphuric acid, was led through the platinum sponge, carrying the vapour of the selenious anhydride with it. A white deposit formed in front of the platinum sponge, which, on examination, was found to consist solely of selenious anhydride.

The last experiment was repeated, substituting selenium for selenious anhydride. The vapour of the selenium, on passing through the platinum sponge, was oxidised to selenious anhydride, but no selenic anhydride was formed.

The next experiment was similar to the first, but platinum black was substituted for platinum sponge. As before only selenious anhydride was deposited.

In the next experiment selenious anhydride was mixed with platinum sponge, and placed within a tube arranged in such a way that it could be placed in an oil-bath. The temperature was then raised gradually to 250°, oxygen being led through continuously. At the temperature mentioned a sublimate formed, and this as well as the platinum sponge was treated with water and tested, but no selenic acid was found.

The next experiment was similar to the last, except that the selenious anhydride was mixed with platinum black instead of platinum sponge, but, as before, nothing but selenious anhydride was obtained.

As may be seen from the above experiments, we have been unable to confirm the observation made by Von Gerichten.

We have found that oxygen in the active condition is unable to oxidise selenious anhydride. Oxygen, which was first passed through a series of drying tubes, was ozonised by means of a Houzeau's ozoniser, and then led slowly through a tube containing selenious anhydride for three hours and a half. At the end of that time the tube was disconnected, the ozone displaced by a current of dried air, and the contents of the tube dissolved in water and tested for selenic acid, but no trace of it was detected.

The Selenates of Antimony, Bismuth, and Platinum.

In the examination of the action of heat upon selenates, the three above mentioned were included. We have been unable to find any published account of these, and accordingly give here a short description of them.

Antimonious Selenate.—This body was formed by heating metallic antimony with selenic acid until it dissolved, and then continuing the heating until the excess of acid was driven off. It forms a white crystalline mass, which under the microscope is seen to consist of minute prisms. It is not very soluble in acids, but on boiling with selenic acid for some time it dissolves slightly, but apparently without formation of an acid salt, as the crystals deposited on evaporating the solution have the same shape and size as the original salt. It is not decomposed on boiling with water, nor is it soluble; if, however, the excess of selenic acid has not been expelled in its preparation, a little of it dissolves in the weak acid formed, and crystallises out again on cooling.

Bismuthous Selenate.—This was prepared by boiling bismuthous carbonate with selenic acid, and continuing the heating until the excess of acid was expelled. It crystallises in minute white prisms. It is insoluble in water, and is not decomposed by it on boiling, but if selenic acid be present it dissolves. It is also soluble in sulphuric acid on boiling, and readily in hydrochloric and nitric acid. Potash and soda decompose it, uniting with the selenic acid.

Platinic Selenate.—This was prepared by heating platinic chloride with selenic acid until the hydrochloric and excess of selenic acid were expelled. It is a dark brown body, which dissolves slightly in water on boiling, forming a yellowish brown solution. It is insoluble in alcohol. It dissolves readily in hydrochloric acid, and leaves metallic platinum on ignition.

The Action of Phosphoric Anhydride upon Selenic Acid.

When sulphuric acid is heated strongly with phosphoric anhydride sulphuric anhydride is evolved; on the other hand, the effect of heating a mixture of anhydrous selenic acid and phosphoric anhydride to a high temperature is, that selenious anhydride is given off, and not selenic. In order to see if a different reaction occurs between the latter two bodies at a lower temperature, some anhydrous acid was mixed with phosphoric anhydride in a flask, which was then tightly closed and placed in the water-oven. After heating for some time a clear solution was obtained, and the flask was then removed and allowed to stand in the cold. Crystals were slowly deposited, which under the microscope were seen to be transparent cubes. The acid liquid was drained off, and the crystals examined. So far as an analysis could be carried out the results agree with the view that the body thus obtained is selenic anhydride, SeO_3, but the quantity of material at our disposal at the time was too small to admit of its satisfactory separation and examination. We are, however, at present engaged in operating upon larger quantities, and hope, at no distant date, to submit our results to the Royal Society.

Selenium Oxychloride.

It may be useful here to mention a reaction, hitherto undescribed, by which selenium oxychloride can be obtained. It consists in distilling a mixture of sodium chloride and selenium dioxide. The reaction is a simple one—

$$2SeO_2+2NaCl=Na_2SeO_3+SeOCl_2.$$

Half the selenium remains as sodium selenite.

THE ACCURATE DETERMINATION OF CARBONIC ACID AND MOISTURE IN AIR.

By J. S. HALDANE, M.A., M.B.,
and M. S. PEMBREY, Pell Exhibitioner of Christ Church, Oxford.

(Continued from p. 258).

We at first directed our attention to the errors connected with weighing. The glass flasks hitherto used weighed from 110 to 115 grms., and on account of their weight had not been weighed on a very fine balance. The glass stoppers of the flasks had not been greased, and we suspected that the sulphuric acid had escaped at the sides of the stopper, and so given rise to errors. The flasks were also of an awkward shape for carrying about, and easily broken; and since it was essential to make the apparatus easily portable we decided to substitute for the flasks large test-tubes. Accordingly test-tubes (6 inches × 1 inch) were filled with soda-lime and pumice saturated with sulphuric acid, and provided with double bored corks. Through each cork there passed a longer glass tube reaching to the bottom of the test-tube, and a shorter one only passing downwards as far as the cork. The cork was covered with paraffin inside and out. Before use the tubes were carefully washed, and dried with a clean cloth. Each tube weighed about 70 grms. The weighings were done on a long-arm Oertling balance weighing with certainty to less than 0·0001 grm. The balance previously used was apt to give slightly different indications each time the knife edge was brought down. The precaution was also taken of leaving the tubes in the balance-room for at least half an hour before weighing, and placing them on the balance with as little handling as possible, so as to prevent the temperature being altered by the warmth of the hand. Even with the old balance better results were obtained on taking these precautions than previously. Thus in three experiments the second sulphuric acid tube varied −0·0005, −0·0004, and +0·0006. In two experiments on the absorption of CO_2 the test absorption-tubes in one case weighed exactly the same after the experiment as before, and in another case they lost 0·0020. In the following experiment all the weighings were made very carefully on the fine balance. 32 litres of air were aspirated through the tubes in thirty-three minutes.

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* Read before the Royal Society, May 2, 1889. (From the Physiological Laboratory, Oxford).

Tube 1	+0·1986	
„ 2	+0·0001	
„ 3	−0·0049	together = +0·0207.
„ 4	+0·0256	
„ 5	−0·0197	together = +0·0006.
„ 6	+0·0203	

Since even the new test absorption-tubes sometimes gained and sometimes lost in weight, we determined to study the causes of these variations. It was of course a matter of the utmost importance for the method to eliminate as far as possible "errors of weighing," as otherwise it would be necessary in making analyses to aspirate inconveniently large quantities of air.

We at first thought that the errors of weighing might be due chiefly to alterations in the pressure and temperature of the air occurring between the weighings. A simple calculation shows that the difference from this cause in the weight of the air displaced by the apparatus must be very distinctly appreciable with a balance weighing to decimilligrms. We therefore weighed absorption-tubes at intervals, noting at the same time the variations in the height of the barometer and in the temperature of the room. The variations in weight did not, however, at all correspond with the variations in barometric pressure and temperature. These variations in weight occurred so rapidly at times that almost every swing of the balance showed a slight alteration in weight, and this alteration went on hour after hour, the change being sometimes in the direction of gain and sometimes in the direction of loss of weight. Occasionally there was no sensible change for two or three hours. The alteration occurred whether the tubes were stoppered or not, and amounted frequently to about 10 decimilligrms. in the course of several hours. Similar alterations were found to occur in a dry empty tube.

Probably the alterations were partly due to the varying state of saturation of the air with moisture, and consequent variations in the amount of moisture condensed on the outside of the glass tubes, and partly to diffusion of moisture into the tubes. We did not, however, pursue the inquiry further, since we found that the "error of weighing" could be entirely eliminated by the plan of weighing against a counterpoise consisting of a tube made exactly like a sulphuric acid or a soda-lime absorption-tube, and of about the same weight. This counterpoise is always kept in the same place as the absorption-tubes. It is left stoppered when they are stoppered,[*] and unstoppered when they are unstoppered. As during an experiment the absorption-tubes may have been cooled or warmed more than the counterpoise by the air passing through them, the weighing must be deferred for half an hour, so as to allow their temperatures to become equal again. The tubes are weighed unstoppered. Before weighing, the stoppers are removed from the whole of the tubes, including the counterpoise, and not replaced until the last tube has been weighed. No absorbent is kept inside the balance case. With these precautions we found that the tubes do not vary in apparent weight within twenty-four hours by more than 3 decimilligrms. at the most, and usually agree to a decimilligrm. Our weights, although apparently in good preservation, showed disagreements with one another which amounted with different combinations of weights to 2 decimilligrms., so that slight apparent remaining variations in weight of the tubes might be set down as mostly due to imperfections in the weights.

After the error of weighing had thus been disposed of, we proceeded to make new test experiments.

Experiment No. 1.

The tubes were arranged in series in the following order:—1, sulphuric acid; 2, sulphuric acid; 3, soda-lime; 4, sulphuric acid; 5, soda-lime; 6, sulphuric acid. 90 litres were aspirated through in ninety minutes. The aspirator in this and the following experiments was a Bunsen water-pump, and the air was measured by a gas-meter.

Tube 1	+0·5142	
„ 2	±0·0000	
„ 3	+0·0463	together+0·0868.
„ 4	+0·0405	
„ 5	−0·0221	together−0·0001.
„ 6	+0·0220	

Experiment No. 2.

Repetition of No. 1, 90 litres aspirated in ninety-one minutes.

Tube 1	+0·4712	
„ 2	+0·0002	
„ 3	+0·0372	together = +0·0721.
„ 4	+0·0349	
„ 5	−0·0164	together = −0·0007.
„ 6	+0·0157	

At the end of this experiment some particles of soda-lime were found in the tubing connecting tubes 5 and 6. Evidently a little soda-lime had been blown over during the experiment, and what had been left in the rubber tubing was doubtless the cause of the loss in weight of 5 and 6 together. To prevent a repetition of this loss some cotton-wool was placed in the soda-lime tubes between the soda-lime and the cork.

Experiment No. 3.

Repetition of No. 1, 90 litres aspirated in ninety-seven minutes.

Tube 1	+0·5742	
„ 2	+0·0011	
„ 3	+0·0360	+0·1198
„ 4	+0·0838	
„ 5	−0·0828	+0·0004
„ 6	+0·0832	

In this experiment there was an escape of moisture from tube No. 1; this tube had been used for a number of experiments in addition to those recorded above. It was not used again except as a counterpoise.

The experiment described seemed to show that a certain proportion of CO_2 escapes absorption by soda-lime, and is absorbed by baryta solution. Although we felt sure this was not the case, we, nevertheless, chiefly for the sake of testing the tube method of Pettenkofer, repeated the experiment with the following precautions:—

In addition to the six Pettenkofer tubes through which the air was passed, six others were taken, washed, and charged with the same quantity of baryta solution in exactly the same way as the first set. These dummy tubes were kept stoppered during the experiment. All the tubes were washed before the experiment, first with dilute nitric acid (1 to 10), then three times with tap water, and, finally, with distilled water; they were then dried in the usual way. 60 litres of air were aspirated in an hour. At the end of the experiment the baryta from each set of Pettenkofer tubes was poured into a ½-litre flask, and at once corked and allowed to stand for the night; during this process every precaution was taken to avoid unnecessary contact with the baryta-water.

Sulphuric acid, pair 1[*]	+0·4183
Soda-lime, pair 1. ..	+0·0554

Baryta from first set of Pettenkofer tubes ..	(1) 40 c.c.	= 39·9 c.c. standard oxalic.
	(2) „	= 39·9 „ „

Loss of water by same tubes by evaporation 0·8408 grm.

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[*] The stoppers used are the ordinary ones, consisting of a short piece of black rubber closed at one end by a piece of glass rod.

[*] The tubes were arranged in pairs, as described below.

Baryta from dummy set of Pettenkofer tubes .. .. .. (1) 40 c.c. = 39·65
(2) ,, = 39·75

Mean .. .. 39·7

Standard baryta-water, 40 c.c. = 40·25.
Loss of alkalinity in first set = 6 × 0·35 = 2·1 c.c. standard oxalic.
Loss by evaporation .. .. = 0·84

2·94 c.c.

Loss of alkalinity in dummy set = 6 × 0·55 = 3·30 c.c. oxalic solution.

The dummy tubes had thus actually lost slightly more in alkalinity than the tubes through which the air was passed. This result explains the loss in alkalinity in the baryta-water in the previous experiments.

The loss in the dummy tubes is equal to what would be caused by the absorption of 0·0033 grm. of CO_2, or the CO_2 contained in about 4 litres of air. Considering the scrupulous precautions which were taken, such a loss could hardly be due to the baryta-water coming in contact with air during the manipulations necessary. We thought that possibly the loss might be mostly due to the action of the glass on the baryta-water; and our experience called to mind a statement of Pflüger[*] that he found in making the titrations for Kjeldahl nitrogen determinations that it was impossible to titrate accurately in flasks which had been previously washed with acid. The glass seemed to retain part of the acid, and give it up again slowly during the analysis. We made several experiments as regard the bearing of this point on the Pettenkofer method, but the results were conflicting.

The above experiments proved that the absorption both of moisture and CO_2 was practically complete by the respective absorption-tubes, although the Experiment No. 3 seemed to show the escape of a scarcely weightable trace of CO_2. The absence of variation in weight of tube 2 in the first two experiments, and in others noted below, proves the groundlessness of the supposition of Hlasiwetz and others that CO_2 or any other gas present in air is absorbed by the sulphuric acid. Such an absorption is *primâ facie* highly improbable. The coefficient of absorption of sulphuric acid for CO_2 is, according to Setschenow, about equal to that of water, and a simple calculation shows that the variations in the amount of CO_2 occurring in any air ordinarily met with are too small to produce a weighable effect upon the amount held in absorption by the sulphuric acid. The case is of course quite different when large quantities of CO_2 are present, as in the gases from a combustion.

These experiments also show that there is no appreciable escape of CO_2 or moisture from outside through the junctions of the tubing into the air current. Pettenkofer believed that there is such an escape when the pressure in the tubing is negative, and therefore he drove the air through the absorption-tubes of his respiration apparatus instead of aspirating. Possibly, however, the escape observed by him may have been through the walls of the long pieces of rubber tubing connecting his absorption apparatus.

In order to save time and trouble in weighing, we now resolved to weigh tubes 1 and 2 and 3 and 4 together. The tubes were therefore made permanently connected in pairs. The final form given to them was shown by a drawing. The following are the details :—The test-tubes are 4 × 1 inch, and made of thin glass. Each tube is provided with a double-bored cork about $\frac{1}{2}$ inch thick, which is fitted with glass tubing of about $\frac{3}{16}$ inch internal diameter, and in the form shown in the drawing.[†] The tubing must fit tightly; and the corks must be covered with a layer of paraffin inside and out. They are pushed down a very little below the top of the tube, the end of the tube being first warmed to soften the paraffin, and so facilitate the entrance of the cork. To prevent pieces of pumice or soda-lime getting into the tube during this operation a passage should first be cleared in the pumice or soda-lime with a piece of glass rod. Should, however, any soda-lime get into the tube and produce an obstruction, this can be easily pushed down from the outside by a piece of wire. As the figure showed, a plug of cotton-wool is placed between the surface of the soda-lime and the cork. A layer of paraffin is spread smoothly over the top of the cork until it is just level with the edges of the tube. In this way the risk is avoided of pieces of paraffin being knocked off during the weighings. The apparatus must be tested for tightness by means of an aspirating bottle or other simple arrangement, and should allow air to pass perfectly freely when suction is applied.

The pumice is sifted through a wire sieve with meshes $\frac{1}{8}$-inch apart, and shaken in a fine one to remove the powder. It is then heated to redness by playing on it with a large blowpipe flame, and thrown still hot into sulphuric acid ("pure re-distilled.") The superfluous acid is then poured off, and the pumice preserved for use in a stoppered bottle. Before using the tubes for experiments we have always taken the precaution of washing them out with air. The air passed through them at first usually tastes slightly of sulphurous acid.

The soda-lime we have hitherto used was made by heating together in a copper vessel 2 litres of 60 per cent caustic soda solution, and the product obtained by shaking to a fine powder 1000 grms. of quick-lime. The heating was continued until the soda-lime became capable of being broken up into fragments in a mortar. The fragments were rapidly sifted in a wire sieve with meshes $\frac{1}{16}$ inch apart, and the product freed from powder by sifting in a finer sieve. We have also tried commercial soda-lime similarly sifted, and found that it absorbed CO_2 nearly as well.

Each pair of tubes weighs, when filled, about 80 grms.

The aspirator used was arranged as follows :—Two bottles, each holding about 3200 c.c. up to a mark on the neck, were provided with corks, the one with two holes bored in it, the other with three. Through each cork passed a long piece of tubing about $\frac{1}{4}$-inch in internal diameter, and a short bent tube of a somewhat less diameter, the long pieces in the two bottles being connected together by a piece of stout, non-collapsing rubber tubing provided with a screw-clip and a burette-clip. The screw-clip is for regulating the flow of water once for all to about a litre per minute. The burette-clip is for stopping the flow during an experiment. The temperature of the water is measured by means of a thermometer inserted in a third hole in one of the corks. To prevent breakage, this thermometer should not project beyond the cork. The bottles are covered outside with a layer of felt, to keep the temperature of the air and water equal during an experiment, and also to prevent breakage. A vertical strip on each bottle is, however, left uncovered, so that the height of the water may be watched during an experiment. It is convenient to graduate the bottles roughly by passing strips of paper at intervals of half a litre up the uncovered strip of glass. With the help of this graduation it is easy to ascertain that the aspirator is running at about the proper rate.

To graduate the aspirator, one of the bottles is allowed to drain for a minute, and is then weighed. The two bottles are then connected and filled, so that both of the bottles are full to the mark, and the tubing is also full of water. The cork of the weighed bottle is removed, care being taken to let no water escape from the end of the long piece of glass tubing. The bottle filled with water is then weighed again, and by deducting this weight from that of the empty bottle, and allowing for air displaced, &c., as in the graduation of a measuring flask, the

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[*] Pflüger's *Archiv.*, vol. xxxvi., p. 105.

[†] The longer piece of glass tubing in the first sulphuric acid absorption-tube is made somewhat shorter than the corresponding tubing in the other absorption-tubes. The inconvenience arising from the collection of water in the first tube is thus avoided.

amount of water held by the bottle filled to the mark with the tubing in it is obtained. The difference between this amount, and some round number of c.c., such as 3000, is then measured into the bottle, which has been previously emptied and drained for a minute. The cork is then replaced, care being taken, as before, not to spill any of the water in the tubing. The aspirator is now ready for use.

The short piece of glass tubing of the bottle which is filled to the mark, is attached by rubber tubing to the absorption apparatus. The other bottle is then placed 2 or 3 feet below, and the burette-clip opened. It is always desirable to test the tightness of the whole apparatus before each experiment by opening the clip while the stopper is on the inlet tube of the absorption apparatus. The water is allowed to flow until the lower bottle is full exactly to the mark on the neck. The bottles are then reversed, if necessary, and the process repeated as often as required. In very foul air, such as that of ordinary schools without mechanical ventilation, one bottleful of air will be sufficient, as a rule. In free air, several bottlesful will be required, the number varying according to the accuracy aimed at.[*]

The thermometer must be read during the aspiration. It is doubtless well to have the temperature of the water as near as practicable to that of the air to be examined, but we found that with the felt jacket, a thermometer suspended in the air above the water, kept within 0·25 of a degree of the temperature of the water during the emptying of the aspirator, and for some minutes longer. This was on a windy day, and with the temperature of the water 6° C. above that of the air. The temperature of the water itself varies very slowly, but must be observed at intervals and the mean taken in a long experiment.

(To be continued).

NOTE ON THE

METHOD OF DETERMINING THE ATOMIC WEIGHT OF OXYGEN ADOPTED BY MR. W. A. NOYES.

By G. STILLINGFLEET JOHNSON.

In this paper, reprinted from the *American Chemical Journal* (vol. ii., No. 3) in the Chemical News (vol. lix., p. 224), a method is described for determining the atomic weight of oxygen by weighing the water formed on reducing copper oxide in hydrogen in the same vessel in which the reduction has taken place.

One source of error in the determination is indicated as possibly operating in his experiments by the author himself, viz., the retention by the copper (which has escaped complete re-oxidation) of hydrogen, occluded by the metal during its reduction in hydrogen gas. Other sources of error are clearly indicated in a paper of mine "On the Occlusion of Hydrogen by Copper," which was published in the *Journal of the Chemical Society*, May, 1879. As Mr. Noyes is evidently ignorant of the work done by Englishmen in this direction, and as the results obtained by me may prove interesting to some of the readers of the Chemical News, I have epitomised my work so far as it relates to the paper under discussion.

Four sources of error are perceptible to me in Mr. Noyes's method of experimentation, two of which are proved in my paper quoted above to be certainly operative, whilst the remaining two would come into play in case the copper employed contained sulphur.

1. The first certainly operative source of error is the one indicated by Mr. Noyes himself, *i.e.*, the retention of occluded hydrogen by incompletely re-oxidised copper. Mr. Noyes found it impossible to re-oxidise his copper completely, and he records two results which indicate a gradual oxidation of occluded hydrogen.

There are numerous experiments in the paper to which I have referred, in which it is clearly proved that copper will retain occluded hydrogen when heated to redness in a vacuum, but yields up its occluded hydrogen as water by combustion in carefully dried air.

2. The second source of error which in my opinion would certainly vitiate the accuracy of Mr. Noyes's results appears to have escaped his notice altogether. When copper oxide is reduced in hydrogen gas at temperatures below 700° C. I have found and recorded (*loc. cit*) that not only hydrogen, but actual water, is occluded by the reduced copper, and as this water was not carried away by a stream of hydrogen at the temperature of reduction, it would in all probability escape removal *in vacuo* at the same temperature. This retained water was, in my experiments, collected and weighed after its expulsion from the copper by ignition in pure nitrogen. Now, I find no record in Mr. Noyes's paper of the *temperature* at which his copper oxide was reduced, but I should gather from his description of the apparatus employed that it could not have exceeded 700° C., otherwise his glass bulb would have been in jeopardy.

As regards the third and fourth sources of error, they would operate only in case the copper employed contained sulphur. I am induced, however, to mention them, because the only guarantee given by Mr. Noyes of the purity of his copper oxide is that it was "Kahlbaum's best in wire form." Now, as I have never seen a specimen of commercial copper, even that obtained by electrolytic methods, which gave a negative result when tested for sulphur by solution in nitric acid and treatment with solution of baric nitrate, though in some cases the mixture must stand for some hours before the $BaSO_4$ comes down, I always conclude that sulphur is present until its absence has been proved by direct testing.

When sulphur is present in the copper, not only is the S not expelled completely during oxidation, but it is also retained in the metal after reduction in hydrogen, and, when the reduced copper is subsequently re-oxidised, H_2SO_4 is formed. All this is described in my paper (*loc. cit.*), and further, I proceed to describe the preparation of a sample of copper oxide free from sulphur, and to show that the metal obtained by reduction of this oxide in hydrogen occluded none of that gas, so that I would recommend the use of such copper oxide to future experimenters in this field.

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ON THE

DETERMINATION OF THE ORGANIC NITROGEN IN NATURAL WATERS BY THE KJELDAHL METHOD.[*]

By THOMAS M. DROWN, M.D., and HENRY MARTIN, S.B.

The justification for the almost universal practice of determining the organic nitrogen in waters in the form of albumenoid ammonia is to be found in the great simplicity of the Wanklyn process. The amount of nitrogen obtained in the form of ammonia by the action of alkaline permanganate on nitrogenous organic matter in water bears no known relation to the total nitrogen present, and chemists report widely differing results in consequence of differing practice. In the case of colourless waters, with small amount of organic matter, the differences are not usually great, but in most surface

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[*] About 30 c.c. of air are contained in the sulphuric acid absorption-tubes, and in some experiments it may be necessary to make an allowance for this air in calculating the results for CO_2. Such air contains, on an average, about 19 vols. of CO. per 10,000 of air.

[*] From the *Technology Quarterly*, Boston, vol. ii., No. 3.

waters, with considerable organic matter in suspension and solution, the results often differ fifty or one hundred per cent. Some water analysts stop the distillation for albumenoid ammonia when 150 c.c. have distilled over; others continue until 250 c.c. are obtained, and others, again, strive to get all the ammonia they can by the addition of more alkaline permanganate, or by replacing the water which has distilled over.

There can be no doubt that the determination of the total organic nitrogen would be generally practised in place of the determination of the albumenoid ammonia, if there was available a short, easily executed, and accurate method for this purpose.

As the result of a very large number of experiments with the Kjeldahl nitrogen process, we think it may be safely said that this method leaves little, if anything, to be desired in these respects.

The modifications of the process, as usually practised, to adapt it to the determination of organic nitrogen in waters, are in the direction of its simplification. Thus the amount of organic matter in water is ordinarily so very small that the use of solid potassium permanganate for the final and complete oxidation of the organic matter is probably never necessary. In most of the analyses which we have made, we have continued to use it as a matter of precaution, but in the comparative experiments, with and without its use, the results have not differed. The volumetric determination of the ammonia by titration with very dilute standard acid was found to be less accurate and less convenient than the Nesslerisation of the distillate, in the usual method employed in water analysis. Further, the same flask is used for both the digestion and the distillation.

Professor W. R. Nichols experimented with the Kjeldahl process for the determination of the nitrogen in sewage with satisfactory results,[*] but the process has not yet, as far as we know, been used in regular water analysis.

The examination is conducted as follows:—500 c.c. of the water is poured into a round-bottom flask, of about 900 c.c. capacity, and boiled until 200 c.c. have been distilled off. The "free ammonia" which is thus expelled may, if desired, be determined by connecting the flask with a condenser. To the remaining water in the flask is added, after cooling, 10 c.c. of pure concentrated sulphuric acid.[†] After shaking, the flask is placed in an inclined position on wire gauze, on a ring-stand, or other convenient support, and boiled cautiously, in a good-drawing hood, until all the water is driven off and the concentrated sulphuric acid is white or a very pale yellow. The flask is then removed from the flame, and a very little powdered potassium permanganate added until, on shaking, the liquid acquires a green colour, showing that an excess of the permanganate has been added. Should the colour be purple instead of green, it shows that the water has not all been driven off. After cooling, 200 c.c. of water free from ammonia are added, the neck of the flask being washed free from acid, and then 100 c.c. of sodium hydrate[‡] solution. The flask is immediately connected with the condenser, and then shaken to mix the contents.

The distillation at the start is conducted rather slowly, and the first 50 c.c. are condensed in very dilute hydrochloric acid.[§] The contents of the flask may then be boiled more rapidly until 150 c.c. to 175 c.c. have altogether been collected. The total distillate is made up to 250 c.c. with water free from ammonia, well mixed, and 50 c.c. taken for Nesslerisation. No serious difficulty has been encountered from bumping when boiling the alkaline solution. The use of metallic zinc in the flask to facilitate the boiling is, of course, inadmissible, on account of the reduction of nitrates and nitrites, should they be present, to ammonia.

Any efficient condensing arrangement may be used for the collection of the ammonia. We have used with great satisfaction the condenser devised by Prof. S. W. Johnson, of the Connecticut Agricultural Experiment Station, which is described in *Bulletin* No. 12 of the United States Department of Agriculture, Division of Chemistry. It consists of a copper tank, 20 inches high, 32 inches long, 3 inches across the bottom, widening to 6 inches at the top. The tank is provided with an adequate supply of running water, entering at the bottom, and accommodates 6 or 7 block-tin condensing-tubes, three-eighths inch internal diameter, which enter the tank through holes in the front side near the top, above the level of the overflow, and pass down vertically through the tank and out through rubber stoppers tightly fitted into holes in the bottom. They project about 2 inches below the tank, and are connected by means of rubber tubes to straight glass calcium chloride tubes with a bulb at the upper end. These glass tubes dip into 250 c.c. flasks which receive the distillate. The distilling-flasks are connected with the tin condensing-tubes by means of rubber stoppers which carry a bulbed glass tube bent at right angles. This tube and its rubber stopper remain permanently connected with the tin tube.

The flasks rest on iron rings, and are heated with the free flame of a Bunsen burner. They should be carefully selected as to size and height. And the fixtures should be so arranged that all parts are interchangeable. There is then never any difficulty in putting the flasks promptly into place and connecting them with the condenser.

It is a good plan to have flasks, partly filled with water free from ammonia, connected with the condensing-tubes when not in use.

Before beginning a determination the water in the flask is boiled until the distillate shows, on Nesslerisation, that the apparatus is completely free from ammonia. Into the flask which receives the distillate there is put 1 c.c. of the dilute hydrochloric acid and 50 c.c. of water. The delivery tube dips into this liquid only during the collection of the first 50 c.c. of the distillate. The flask is then lowered so that the tube remains above the liquid for the remaining time of the distillation.

In carrying out the operation, the most scrupulous care must be observed in preventing access of ammonia from any source. The acid solutions will absorb ammonia from the air of the laboratory or from the dust of the room if they are allowed to remain uncovered for any length of time. This source of error has been found at times to be very large; quite enough to render a determination valueless. One experiment gave a gain of ammonia in twenty hours, by leaving the flask which contained the concentrated sulphuric acid uncovered, equivalent to 0·5 c.c. of the standard ammonium chloride solution, and at another time the gain was 3 c.c.

The operation should therefore be carried out without interruption, and for every determination, or set of determinations, a blank analysis with ammonia-free water should be made for a correction for the ammonia in the reagents and that accidentally introduced in the process.

We have not found that the presence of nitrates and nitrites in waters interferes with the accurate determination of the organic nitrogen. The error which has been found by Kjeldahl and Warington[*] to be caused by nitrates in the determination of organic nitrogen seems to disappear under the conditions of great dilution which we have in natural waters.

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[*] *Franklin Institute Journal*, August, 1885.

[†] It is necessary to have for this purpose sulphuric acid which is very nearly, if not quite, free from nitrogen in any form. Baker and Adamson, of Easton, Penn., make an acid for this purpose which contains only 0·005 m.grm. of ammonia in 10 c.c.

[‡] The sodium hydrate solution is made by dissolving 200 grms. of commercial caustic soda of good quality in 1·25 litres of distilled water, adding 2 grms. of potassium permanganate, and boiling down to somewhat less than a litre. When cold, the solution is made up to a litre. The addition of the permanganate is to oxidise any organic matter which may be present in the caustic soda.

[§] This acid should be free from ammonia; 1 c.c. of the acid is equivalent to 0·5 m.grm. of ammonia.

[*] Chemical News, lii., p. 162.

The following experiments bear on this point:—

1500 c.c. standard ammonium chloride solution (= 15 m.grms. NH_3) and 10 c.c. of standard potassium nitrite solution (= 1 m.grm. N) were boiled with 10 c.c. of sulphuric acid, and the vapours condensed. This distillate contained only 0·15 m.grm. nitrogen as ammonia and nitrous acid. The residue in the flask was made alkaline and distilled, and the ammonia obtained was precisely the amount taken, namely, 1500 c.c. The experiment was repeated, using a nitrate in place of the nitrite, and under the same conditions the 1500 c.c. of ammonia were recovered.

When a smaller amount of ammonia was used, we still failed to observe any loss. Thus when 10 c.c. standard ammoniun chloride solution and 10 c.c. potassium nitrite solution (= 0·1 m.grm. N) were treated as above, there was obtained ammonia equivalent to 10·5 c.c. Another experiment with the same quantities gave precisely 10 c.c. of ammonia regained. With potassium nitrate instead of nitrite, in the same proportions as in the foregoing experiment, 10·5 c.c. of ammonia were obtained.

The attempt to collect all the nitrous and nitric acids in the distillate was unsuccessful. The flask and condenser were connected by ground joints, so that the distillation could be continued after the sulphuric was concentrated. Owing, probably, to the shape of the flask, the acids were condensed, in part, in the neck of the flask, for after a second and a third addition of water and a renewal of the distillation more nitrous and nitric acids were obtained in the distillate. To see whether there was any loss of ammonia from ammonium sulphate in presence of sulphurous acid from the action of sulphuric acid on carbonaceous matter, the following experiments were tried:—10 c.c. of standard ammonium chloride solution were treated with 10 c.c. of sulphuric acid and a weighed amount of Swedish filter-paper. Deducting for the nitrogen in the paper, determined in a blank analysis, 10·5 c.c. of ammonia were obtained. In a duplicate experiment the ammonia obtained was 10 c.c.—precisely the amount taken. In still another experiment with 50 c.c. of standard ammonium chloride solution and filter-paper, 51 c.c. were obtained.

No attempt has been made to compare, as regard the results obtained, the above-described method of determining the organic nitrogen with the combustion method of Frankland and Armstrong. But the following experiments on very dilute solutions of organic substances of known composition may serve to confirm the accuracy of the method.

One hundred m.grms. of pure crystals of urea were dissolved in one litre of water free from ammonia. Ten c.c. of this solution were added to 500 c.c. of water, and the analysis conducted as above described. There was obtained 0·494 m.grm. of nitrogen, the theoretical amount being 0·466. In a duplicate experiment no solid potassium permanganate was added to complete the oxidation, and the result was 0·486 m.grm.

A solution of uric acid in dilute potassium hydrate was made of the same strength as the urea, and 10 c.c. taken for analysis. There was found 0·326 m.grm. of nitrogen; required, 0·333 m.grm. In a duplicate experiment without the permanganate, precisely the same amount was obtained.

A solution of naphthylamine, 100 m.grms. to the litre, was dissolved by the aid of dilute hydrochloric acid. An analysis of 10 c.c. gave 0·082 m.grm. nitrogen; required, 0·097. Here again the result obtained by the omission of the permanganate agreed precisely with the determination in which the permanganate was used.

The following series of experiments, made on a sample of Cochituate water, shows the very close agreement of results in the determination of organic nitrogen under varying conditions. From a large bottle of water freshly drawn from the tap were taken five portions of 500 c.c. each.

Comparison of Albumenoid Ammonia and Organic Nitrogen in Natural Waters.

I. *Surface Waters.*

Water.	Colour.	Albumenoid ammonia.	Organic nitrogen calculated as ammonia.
Arlington, Reservoir—			
June	0·8	0·0256	0·0560
July	0·3	0·0274	0·0560
Boston Supply, Basin 4—			
June	1·0	0·0226	0·0470
July	0·7	0·0234	0·0400
August	0·9	0·0254	0·0460
Boston Supply, Basin 2—			
June	1·4	0·0350	0·0590
July	1·3	0·0294	0·0450
August	0·85	0·0234	6·0440
Boston Supply, Basin 3—			
June	1·9	0·0392	0·0790
July	1·7	0·0336	0·0540
August	0·8	0·0278	0·0590
Boston Supply, Lake Cochituate—			
June	0·35	0·0176	0·0420
July	0·10	0·0192	0·0390
August	0·10	0·0196	0·0420
Boston Supply, Mystic Lake—			
June	0·20	0·0252	0·0590
July	0·10	0·0244	0·0560
August	0·15	0·0212	0·0420
Bridgewater, Taunton River—			
June	2·3	0·0248	0·0520
July	1·0	0·0210	0·0440
August	0·7	0·0212	0·0390
Brockton, Reservoir—			
June	0·9	0·0234	0·0570
July	0·9	0·0260	0·0490
August	0·7	0·0310	0·0610
Brookline, Charles River—			
June	1·20	0·0320	0·0520
July	0·60	0·0216	0·0470
August	0·45	0·0208	0·0380
Cambridge, Fresh Pond—			
June	0·20	0·0162	0·0370
July	0·15	0·0170	0·0390
August	0·0	0·0172	0·0390
Clinton, Nashua River—			
June	0·1	0·0072	0·0230
July	0·2	0·0144	0·0360
August	0·2	0·0124	0·0320
Fitchburg, Reservoir—			
June	0·1	0·0124	0·0250
July	0·1	0·0158	0·0340
August	0·1	0·0146	0·0240
Great Barrington, Housatonic River—			
June	0·1	0·0122	0·0320
July	0·1	0·0120	0·0270
August	0·0	0·0134	0·0320
Nashua, Merrimac River—			
June	0·4	0·0120	0·0320
July	0·2	0·0132	0·0290
August	0·2	0·0106	0·0290
Lowell, Merrimac River—			
June	0·30	0·0142	0·0420
July	0·10	0·0148	0·0280
August	0·25	0·0134	0·0320
Haverhill, Merrimac River—			
June	0·40	0·0164	0·0490
July	0·20	0·0170	0·0420
August	0·20	0·0163	0·0348

Water.	Colour.	Albumenoid ammonia.	Organic nitrogen calculated as ammonia.
Lake Winnepesaukee—			
June	0·0	0·0090	0·0230
July	0·0	0·0082	0·0190
August	0·0	0·0080	0·0200
Hyde Park, Neponset River—			
June	0·6	0·0286	0·0520
July	0·8	0·0432	0·1100
Lynn, Birch Pond—			
June	0·45	0·0194	0·0420
July	0·35	0·0216	0·0410
August	0·25	0·0174	0·0410
Malden, Spot Pond—			
June	0·3	0·0216	0·0440
July	0·2	0·0198	0·0390
August	0·2	0·0216	0·0390
Montague, Connecticut River—			
June	0·15	0·0120	0·0220
July	0·20	0·0118	0·0250
Springfield, Connecticut River—			
June	0·4	0·0132	0·0390
July	0·15	0·0146	0·0320
August	0·15	0·0170	0·0380
New Bedford, Acushnet River—			
June	2·3	0·0296	0·0540
July	1·8	0·0278	0·0540
Northboro, Assabet River—			
June	0·7	0·0192	0·0490
July	0·4	0·0216	0·0380
August	0·4	0·0174	0·0410
Salem, Wenham Lake—			
June	0·10	0·0132	0·0320
July	0·05	0·0118	0·0290
August	0·00	0·0130	0·0260
Springfield, Ludlow Reservoir—			
June	0·10	0·0222	0·0460
	0·20	0·0214	0·0440
July	0·10	0·0220	0·0420
August	0·05	0·0198	0·0390
	0·10	0·0206	0·0370
Wayland, Reservoir—			
June	1·5	0·0272	0·0590
July	0·9	0·0364	0·0660
August	0·4	0·0244	0·0540
Whitman, Hobart's Pond—			
June	1·7	0·0538	0·0990
July	1·5	0·0426	0·0990
August	0·9	0·0342	0·0740
Wilmington, Shawsheen River—			
June	0·8	0·0242	0·0640
July	0·15	0·0114	0·0370
August	1·00	0·0316	0·0570
Woburn, Horn Pond—			
June	0·35	0·0290	0·0570
July	0·25	0·0324	0·0590
August	0·10	0·0240	0·0440
Worcester, Blackstone River—			
June	—	0·0350	0·1350
July	—	0·0440	0·1550
August	—	0·0830	0·3800

II. *Ground Water.*

(Without Colour).

Water.	Albumenoid ammonia.	Organic nitrogen as ammonia.
Brookline, Filter Gallery—		
June	0·0046	0·0190
July	0·0046	0·0220
August	0·0042	0·0170
Newton, Filter Gallery—		
June	0·0044	0·0190
July	0·0072	0·0160
August	0·0052	0·0100
Revere, Wells—		
June	0·0018	0·0034
July	0·0034	0·0070
August	0·0018	0·0100
Revere, Reservoir—		
June	0·0034	0·0130
July	0·0046	0·0150
August	0·0060	0·0190
Waltham, Filter Gallery—		
June	0·0030	0·0170
July	0·0050	0·0160
August	0·0056	0·0150
Waltham, Reservoir—		
June	0·0042	0·0230
July	0·0042	0·0180
August	0·0060	0·0160

The first portion was treated by the usual method, already described.

The second portion was treated like the first, except that the addition of solid permanganate was omitted.

The third portion received 10 c.c. of standard potassium nitrate solution, equivalent to 0·1 m.grm. of nitrogen.

The fourth portion received 1 c.c. of potassium nitrite solution, equivalent to 0·01 m.grm. of nitrogen.

The fifth portion contained ten times the amount of potassium nitrite as the fourth portion, or 0·1 m.grm.

The third, fourth, and fifth portions were treated in all respects like the first portion.

The results, expressed in organic nitrogen, parts per 100,000, were—

No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
0·0354	0·0354	0·0354	0·0365	0·0365

It may be of interest to give a few of the results obtained in the determination of the organic nitrogen by this method in natural waters in comparison with the results obtained as albumenoid ammonia. In the Table will be found the analyses of some Massachusetts waters during three successive months, June, July, and August, 1888.

In the first column is a record of the colour, based on a comparison with the Nesslerisation of a known amount of ammonium chloride. Thus a colour 1 means that the water possessed a colour corresponding in depth and tint to 1 c.c. of standard ammonium chloride solution (=0·00001 grm. NH_3) when Nesslerised; a colour of 2 is twice the depth of colour, and 0·1 is one-tenth the colour of one. In the second column is the albumenoid ammonia obtained by the adding 40 c.c. of alkaline permanganate to the water in the flask, after boiling off 150 c.c. for free ammonia, and then distilling over 250 c.c. In the third column is the organic nitrogen determined by the Kjeldahl process, converted into ammonia to make the figures comparable with the second column. All the determinations were made on the waters filtered through paper in the laboratory.

It will be noted that the organic nitrogen in the surface waters is in general about double the albumenoid ammonia. The average of all the analyses of these waters given above is 0·0214 for the albumenoid ammonia, and 0·0476 for the organic nitrogen. In the ground waters the relation of the albumenoid ammonia to the organic nitrogen is still less. Too much importance must not, however, be given to this relation in the case of the ground waters, for it is probable that the figures given for the organic nitrogen are all a little high, owing to the fact that all of the sources of error were not fully known when most of the analyses were made. The proportional excess in case of the surface waters is believed to be insignificant, but with the smaller content of nitrogen in the ground waters the error is perhaps proportionately large.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

May 25, 1889.

Prof. Reinold, F.R.S., President, in the chair.

Mr. T. A. Lawson was elected a member.

The thanks of the Society were given to Mr. T. H. Blakesley for presenting to the library a copy of the second edition of his work on "Alternate Currents."

The following papers were read :—

"*On a Relation Existing between the Density and Refraction of Gaseous Elements and Some of their Compounds.*" By Rev. T. Pelham Dale.

In a previous communication the author pointed out a relation between the specific refractive energies of sulphur and selenium, and the present paper deals with similar relations in gaseous bodies. On calculating out the values of—

$$\frac{\mu - 1}{d}$$

for the elements H, O, N, Cl, S, P, it was noticed that the logarithms were nearly integral multiples of half the logarithm for H, those for N, Cl, and P being double and S and O three times that number. The value of $\mu - 1$ for different elements is compared with the $\mu - 1$ for H, the resulting numbers being for oxygen 2, mercury 7, arsenic 8, and sulphur 12 nearly. Similar calculations are made for the compounds N_2O, NO, CO, SO_2, Cy, NH_3, HCl, H_2S, CH_4, and C_2H_4, but as the data obtainable are very rough the numbers are not so closely integral. The author hopes that better data will be furnished by persons having greater facilities than himself for experimental research.

Prof. Rücker thought the results obtained pointed towards some relation between the volumes of the molecules of different elements, and, at the close of the meeting, announced that on working out the relation he found the relative volumes to be a series of numbers in geometrical progression.

"*On a Waterspray Influence Machine.*" By Mr. George Fuller.

The apparatus is made up of four similar sections, each consisting of a nozzle, a metal ring, and a metal dish or receiver, arranged about a vertical axis. Pressure water issues from perforations 1-100th inch in diameter in the nozzles, and passes through the ring into the insulated receiver below. The rings are placed at such a distance below the nozzles as to be about the point where the streams break into spray, and the receivers empty themselves automatically. Calling the consecutive sections 1, 2, 3, 4, respectively, the rings of 1 and 3 are connected to the receiver of 4, and those of 2 and 4 to the receiver of 1. The discharge points are connected with the receivers 2 and 3, and a rapid succession of sparks passes when the water is turned on.

Prof. S. P. Thompson enquired whether the length of the spark was limited by leakage along the glass rods, or by the spray passing between the receivers, and in reply

Mr. Fuller said he thought the former leakage the most important.

"*Notes on Polarised Light. (a) On the Transition Tints of Various Orders. (b) Lecture Illustrations of the Rotation of Circularly Polarised Light. (c) On the Rotation of Circularly Polarised and Non-polarised Light.*" By Prof. S. P. Thompson.

The first note described an enquiry as to what thickness of quartz gives the best "sensitive tint" for polarimetric work. Biot gave the name to the tint produced by a quartz 3¾ m.m. thick in a bright field, whereas, in most modern polarimeters, the name is given to that produced by 7½ m.m. quartz in a dark field. The transition tints of various orders were exhibited on a diagram of Newton's scale of colours and by a wedge of selenite. Experiments were made on quartzes of 3¾ and 11¼ m.m., giving tints of the first and second order respectively in the bright field, and with a 7½ m.m. quartz in a dark field. The 3¾ was more sensitive than the 11¼ to small rotations, but the 7½ m.m. seemed the best of the three. Prismatic analysis of the light transmitted by each led to the same conclusion, a new square-ended direct vision prism, built up of a glass prism (angle 140°) immersed in cinnamic ether, being used for that purpose. The author pointed out that the "sensitive tints" of German opticians are decidedly redder than Biot's and those generally used in England.

In the first apparatus described under (*b*) the ray of light is represented by a stretched cord thrown into promiscuous vibration by a tuning-fork, and the polariser and analyser are each represented by two plates of glass mounted parallel to each other about a millimetre apart, between which the cord passes. Between the polariser and analyser the vibrations are in one plane, and they are transmitted or cut off by the analyser according as its plates are parallel or perpendicular to those of the polariser. By blowing across one side of the spindle-shaped vibrating segment between the crossed plates the plane of vibration is slightly rotated and part is transmitted through the analyser. Other experiments illustrating rotation of the plane of polarisation were shown or described, the most conclusive being a bar of heavy glass placed along with a fish-eye lens between crossed Nicols. On starting a current in a helix surrounding the glass the black cross formed by the fish lens is seen to turn round as the current grows. Another piece of apparatus to illustrate Fresnel's view of the circularly polarised waves in quartz consists of two equal co-planar discs rotating in opposite directions, and carrying pins on which the extremities of a double pantograph arrangement are pivotted. The middle point of the linkwork describes a line perpendicular or inclined to the line of centres of the discs according as the phases of the pins are the same or different.

Note (*c*).—In speaking of rotary polarisation it is customary to say that the plane of polarisation is rotated, but the author thinks it is equally correct to say that the light itself is rotated. Prof. Stefan's and Prof. Abbé's experiments bearing on the subject were described, and to demonstrate that ordinary light may be rotated, a bi-quartz was placed between a Fresnel bi-prism and the screen on which the interference fringes were formed. By using quartzes of thickness sufficient to rotate each beam 45° the interference fringes are caused to disappear, and on inserting a bar of heavy glass in each of the pencils and magnetising one of them the fringes re-appear.

Mr. Glazebrook thought the reason why 3¾ m.m. quartzes were more sensitive than 11¼ might be seen by considering the sector-shaped spectrum in which the rays are spread out by the quartz, for with the thick piece the angle of the sector will be three times that in the thin one, and hence, in the latter case, a greater change of colour is produced by a given small rotation.

Mr. Ward strongly condemned the use of bi-quartzes for rotation experiments, for he found it impossible to get them cut with such accuracy as to give a uniform tint, and if the light be slightly elliptically polarised considerable error may be introduced. Speaking of magnetic rotation, he thought Fresnel's explanation unsatisfactory, and considered it probable that the rotary character of the magnetic field increases the period of one and decreases that of the other circular wave, their velocities remaining the same. As regards quartz, he believes the rotary action due to the light itself (probably an effect of the longitudinal wave) and not to any peculiar crystalline structure of the quartz, for liquids exhibit similar phenomena.

Dr. Thompson, in reply, said Mr. Glazebrook's explanation of the difference in sensibility of the quartzes of various thicknesses was not quite satisfactory, for the reasoning would lead one to expect the 3¾ m.m. to be most sensitive, whereas experiment showed that the 7½ m.m. was best. He quite agreed with Mr. Ward about the defects of the bi-quartz, and thought the shadow method preferable in many cases. On the other hand, he was disposed to believe that the rotary power of quartz was a result of its crystalline structure, for fused quartz possessed no such property. As regards liquids, Dr. Thompson thought the rotation due to some kind of skew symmetry possessed by the molecules, the average effect of which is observed.

"*On the Molecular Weight of Caoutchouc and other Colloid Bodies.*" By Dr. J. H. Gladstone, F.R.S., and Mr. W. Hibbert, F.I.C.

This paper gives the results of determinations made by Raoult's method, the reliability of which was first tested by preliminary experiments on substances of known molecular weights, and found to be fairly satisfactory. The experiments on caoutchouc give a very high value (above 6000), thus confirming the authors' previous impression that it was a colloid. Similar experiments were made on gum-arabic, caramel, albumen, and ferric and aluminic hydrates, all of which were found to have high molecular weights. All the experiments confirm the belief that the molecule of a colloidal substance is an aggregate of a very great number of atoms.

CORRESPONDENCE.

SEPARATION OF SILICA AND SAND.

To the Editor of the Chemical News.

Sir,—In an article on "Indigo Stem Ash" (Chemical News, vol. lix., p. 244) Mr. John Tsawoo White questions the possibility of perfectly separating silica from sand, after the mixture has been ignited, by means of sodium carbonate solution.

I can entirely confirm Mr. White's suspicions, for my own experience tells me that if silica has been ignited at a temperature sufficiently high to ensure the expulsion of the last traces of water (the use of the blowpipe, or, better, a muffle is necessary), it will by no means completely dissolve in sodium carbonate, even on long digestion. It is therefore needful to effect the separation while the silica is still in the hydrated condition.—I am, &c.,

Bertram Blount.

Laboratory, Broadway, Westminster, S.W.,
April 28, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 19, May 13, 1889.

Thionic Series. Action of Acids upon the Hyposulphites.—M. Berthelot.—The author studies thermochemically the displacement of hyposulphurous acid by boric acid, which in the cold is nil; by acetic acid, which has only a very minute effect; by sulphuric and hydrochloric acids.

On Mesocamphoric Acid.—C. Friedel.—Mesocamphoric acid is an isomer of camphoric acid obtained by heating dextro-camphoric acid to 140°—160° for thirty hours with an aqueous solution of hydriodic or hydrochloric acid. So far from being an inactive acid, it is split up by mere crystallisation into two acids, one dextro- and the other lævo-, of equal rotatory powers, but differing in their physical properties.

The Study of the Electro-conductivity of Saline Solutions applied to the Problems of Chemical Mechanics. Acid Salts.—P. Chroustchoff.—The author gives a table of the electro-conductivities of watery solutions, each containing merely a single salt.

Action of Air on Manganese Carbonate. Question if this Reaction can give Rise to any Manganese Dioxide.—A. Gorgen.—Experiment seems to show that at the common temperature manganese carbonate or oxide cannot absorb, in contact with air or aërated water, a proportion of oxygen greater than that present in the compound MnO_2MnO; hence we cannot assume that in nature manganese carbonate, deposited from its carbonic solutions, can give rise to deposits of manganese dioxide

On Platinic Chloride.—L. Pigeon.—The author has succeeded in obtaining platinum chloride by operating on a mixture of platinum and selenium in a stout glass tube partly filled with arsenic chloride, traversed by a rapid current of dry chlorine, and gradually heated to a boil in an oil-bath. The matter first obtained is a compound of platinum chloride and selenium chloride. On heating to 200° the latter sublimes, and platinic chloride remains. Platinum chloride is stable, at least up to 360°.

Certain Compounds of Nitric Oxide and of Hypoazotide with Anhydrous Chlorides.—Nitric oxide reacts with a great liberation of heat upon anhydrous antimony pentachloride, yielding a yellow crystalline body, $2SbCl_5NO_2$. Nitric oxide gives also direct combinations with anhydrous bismuth chloride and with anhydrous ferric and aluminic sesquichlorides. All these bodies are decomposable by water. Hypoazotide (NO_4) also forms analogous combinations under similar circumstances.

The Solubility of Salts. Reply to M. Le Chatelier.—H. W. Bakhuis Roozeboom.

The Solubility of Salts. New Reply to M. Roozeboom.—H. Le Chatelier.—A continuation of the controversy which we have already noticed.

Action of Borax upon the Polyatomic Alcohols.—Aug. Lambert.—The author concludes that the polyatomic alcohols possessing the primary function, and they only, can combine with boric acid to form energetic conjugated acids capable of decomposing carbonates, but becoming dissociated if diluted. The polyglucosides (saccharose, lactose, &c.) do not contain primary alcoholic groups, and have, consequently, a molecular constitution analogous to that of quercite and mannite.

Action of Borax on the Polyatomic Phenols.—Aug. Lambert.—If a small quantity of borax is added to a strong solution of pyrogallol, sodium monoborate is formed and a boro-conjugated acid capable of decomposing carbonates. Pyrogallol acts upon borax, as do glycerin and the mannites. Pyrocatechine, the gallates, and the tannates behave in a similar manner, but there is no action with orcine, resorcine, or hydroquinone.

On the Richness of Wheat in Gluten.—E. Gatellier and L. L'Hote.—The author thinks that it may be possible both to obtain a heavier crop and an increase in the proportion of gluten.

Biedermann's Central-Blatt fur Agricultur Chemie. Vol. xviii., Part 5.

On Paragalactine and γ-Galactan.—Prof. E. Schulze, Dr. E. Steiger, and Dr. E. von Lippmann.—

Paragalactin forms about 25 per cent of lupin-seeds extracted with water, alcohol, and ether. Like β-galactan, it is converted into galactose if it is heated with dilute sulphuric acid. γ-Galactan, $C_6H_{10}O_5$, obtained from the residues of beet-sugar, is strongly dextro-rotatory, and on boiling with dilute acids it yields galactose.

On the Glucoses obtained from Raffinose, and on Crystalline Saccharolactonic Acid.—Dr. Hädicke, J. Gans, Dr. Sohst, and Prof. B. Tollens.—From *Liebig's Annalen.*

Detection of Nitric Acid in Waters and Soils.—E. Bréal (*Annales Agronomiques*).—Nitrates dissolved in water accumulate by means of capillarity where evaporation is most rapid. The author therefore uses strips of white filter-paper, which must be previously freed from nitrates by careful washing—which he places with one end in the water to be examined whilst the other end is in the air. The nitrate gradually rises and accumulates at the extremity of the paper. Even if nitric acid is present in very minute traces in from twelve to fifteen hours they will all have collected in the extreme 1—2 m.m. of the paper. This is then cut off, put in a porcelain capsule, let dry, and then touched with a small drop of sulpho-phenol. If nitric acid is present the paper turns blood-red, and, on the addition of ammonia, becomes blue or green.

Action of the Alkaline and Earthy-Alkaline Metals upon the Animal Organisms.—A. Curci.

The Resistance of Pollen.—P. Rittinghaus (*Naturforscher*).—Most kinds of pollen can bear a temperature of 90° in dry air for fifteen minutes without losing its vitality. In moist air it is more easily destroyed. The plasma of pollen is generally more susceptible to antiseptics than are micro-organisms.

The Signification of the Colouring-matter of Chlorophyll.—A. Hansen.—The author considers that this pigment attracts carbonic acid, forms with it an unstable compound, and hands it over again to the assimilating plasma of the chlorophyll granules. It is, therefore a carrier of carbonic acid.

Action of the Alkaloids on the Animal and Vegetable Kingdoms.— A. Marcacci.—Seeds, roots, and plants all experience more or less the influence of certain alkaloids. From this point of view there is no sharp line of distinction to be drawn between animal and vegetable protoplasm. Still less can poisons be classified as acting upon animals or upon plants.

Ericaceæ on Calcareous Soils.—Prof. Julius Kühn.—The dictum that representatives of the ericaceous family never grow on calcareous soils is incorrect. *Rhododendron hirsutum* grows only on lime soils, whilst its near ally, *R. ferrugineum*, grows only on soils poor in lime. *Calluna vulgaris* (to which we may add *Erica tetralix*) and *E. cinerea*) avoid lime, whilst *E. carnea* grows in abundance on dolomitic soils.

MEETINGS FOR THE WEEK.

Tuesday, 11th.—Royal Institution, 3. "Some Recent Biological Discoveries," by E. Ray Lankester.
—— Royal Medical and Chirurgical, 8.30.
Wednesday, 12th.—Microscopical, 8.
Thursday, 13th.—Royal Institution, 3. "Chemical Affinity," by Professor Dewar.
—— Mathematical, 8.
Friday, 14th.—Royal Institution, 9. "Quartz Fibres," by C. V. Boys, F.R.S.
—— Astronomical, 8.
—— Quekett Club, 8.
Saturday, 15th.—Royal Institution, 3. "Idealism and Experience in Art and Life," by W. Knight, LL.D.

TO CORRESPONDENTS.

T. and R. W. Bower.—An electric spark would inflame coal-gas if passed across it in a space to which the air had access. If in a space entirely enclosed, and supposing the sparks to be frequent and of great intensity, the gas would be decomposed with deposition of carbon.

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2.—The Progress of Economic Botany in England during the last Fifty Years (1837-1887).
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TO MANUFACTURING CHEMISTS and OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 1575 tons of MANGANATE OF SODA, to be delivered at the rate of not less than 100, nor more than 200 tons per week, from the 1st July, 1889.

Persons tendering will be required to declare in their Tender that they pay such rates of wages, and observe such hours of labour, as are generally accepted as fair in the trade.

The Specification, Form of Tender, and other particulars may be obtained on application to the Chemist of the Council at the office, Spring Gardens, until Monday, the 17th June, 1889. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., must be endorsed Tender for Manganate, and be sent in not later than 10 o'clock on Tuesday morning, the 18th inst.

The Council does not bind itself to accept the lowest or any Tender.

H. de la HOOKE,
Clerk of the Council.

Spring Gardens, S.W.,
6th June, 1889.

TO MANUFACTURING CHEMISTS and OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 1375 tons of SULPHURIC ACID, to be delivered as required, from the 1st July, next.

Persons tendering will be required to declare in their Tender that they pay such rates of wages, and observe such hours of labour, as are generally accepted as fair in the trade.

The Specification, Form of Tender, and other particulars may be obtained on application to the Chemist of the Council, at the office, Spring Gardens, until Monday, the 17th June, 1889. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., must be endorsed Tender for Sulphuric Acid, and be sent in not later than 10 o'clock on Tuesday morning, the 18th inst.

The Council does not bind itself to accept the lowest or any Tender.

H. de la HOOKE,
Clerk of the Council.

Spring Gardens, S.W.,
6th June, 1889.

THE CHEMICAL NEWS.

Vol. LIX. No. 1542.

NOTES OF RECENT AND FUTURE RESEARCH. THE SYNTHESIS OF URIC ACID.

By SAMUEL E. PHILLIPS, F.C.S.

In a paper read before the British Association, 1877, I recommended the simple and easy synthesis of uric acid, which had so long been a bone of contention with chemists, and further elucidation was referred to in the Chemical News, vol. xxxii., p. 209, and vol. xxxix., p. 28.

It was not a matter of numerical guess-work, but an estimate of reactions, supported by the widest and clearest evidence, and confirmed by every item of M. Grimaux's numerous ureide syntheses.

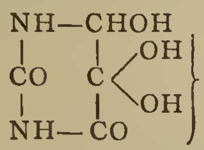
My contention was that uric acid would prove to be an ultimate of tartronic acid di-ureide. That as tartronyl anhydride + urea – 2HO gave tartronyl urea, miscalled dialuric acid on its empirical discovery; so tartronyl urea + urea – 4HO would give the elements of uric acid, thus:—

$$\begin{aligned}(\mathrm{CO})_2\ 6\ 1\ 6\ \mathrm{H_3N_2}+\mathrm{CO_2H_4N_2} &= (\mathrm{CO})_4\ (\mathrm{C_6H_1O_6})\ \mathrm{H_7N_4}\ (a)\\ -2\mathrm{HO} &= (\mathrm{CO})_2\mathrm{Cy}\ (6\ 1\ 6)\ \mathrm{H_5N_3}\ (b)\\ -2\mathrm{HO} &= \mathrm{Cy_2}\ (6\ 1\ 6)\ \mathrm{H_3N_2}\ (c)\end{aligned}$$

(*a*) being the normal di-ureide, (*b*) pseudo-uric acid, and (*c*) the ultimate, uric acid.

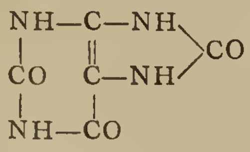
Nature of May 16th announces with much interest that M. Behrend has now synthesised uric acid, which proves to be *in the strictest accordance with the above.* But let us remark that in the meantime M. Horbaczewski had actually produced this so-called acid, by a very complex high temperature reaction from glycocine and urea. But my impression of its extreme vagueness seemed confirmed by the latest opinions formed of that reaction, that it was a ureide derivative of acrylic acid. Then we find that "glycocine, leucine, aspartic acid, as well as urea itself, when brought into the organism of fowls, are changed into uric acid, as found in the urine." Added to all this we find that certain reactions with uric acid lead to the formation of tartronyl compounds; so much so that some eminent chemists have maintained that it must be a derivative of tartronic acid or of tartronyl urea.

We now compare this with the synthesis of M. Behrend. It is a very round-about process, but as tartronyl urea has long been known and identified we may well pass over, as quite superfluous, the first five stages; and, commencing with No. 6, we have malonyl urea (barbituric acid = $(\mathrm{CO})_2\ 6\ 1\ 4\ \mathrm{H_3N_2}$) oxidised by bromine-water to tartronyl urea or dialuric acid, $(\mathrm{CO})_2\ 6\ 1\ 6\ \mathrm{H_3N_2}$, which is notated:—



$(a) = (\mathrm{CO_2})\ 6\ 1\ 6\ \mathrm{H_3N_2}+2\mathrm{HO}$.

(7) " $(a)+\text{urea}-3\mathrm{H_2O}=\text{uric acid}$."

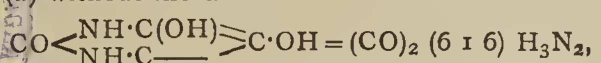


which, being fairly interpreted, means:—Tartronyl urea + urea – 4HO = uric acid. Thus:—

$$\begin{aligned}(\mathrm{CO})_2\ 6\ 1\ 6\ \mathrm{H_3N_2}+(\mathrm{CO})_2\mathrm{H_4N_2} &= (\mathrm{CO})_4\mathrm{C_6H_1O_6}\,\mathrm{H_7N_4}\ (a)\\ -2\mathrm{HO} &= (\mathrm{CO})_2\mathrm{Cy}\ 6\ 1\ 6\ \mathrm{H_5N_3}\ (b)\\ -2\mathrm{HO} &= \mathrm{Cy_2}\ 6\ 1\ 6\ \mathrm{H_3N_2}\ (c)\end{aligned}$$

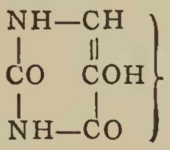
(*a*) the normal di-ureide, (*b*) pseudo-uric acid, and (*c*) = the ultimate, uric acid.

In the early part of 1888 M. Behrend notated tartronyl urea (*a*) without the 2HO:—



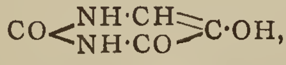
$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{NH\cdot C(OH)}}{\mathrm{NH\cdot C}}{>}\mathrm{C\cdot OH} = (\mathrm{CO})_2\ (6\ 1\ 6)\ \mathrm{H_3N_2},$$

calling it iso-dialuric acid, and that it crystallises with 4HO, two passing off at 100°, and the remainder at 150°; also that his present iso-barbituric acid (malonyl urea)—



$= (\mathrm{CO})_2\ (6\ 1\ 4)\ \mathrm{H_3N_2}$.

was then—



$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{NH\cdot CH}}{\mathrm{NH\cdot CO}}{>}\mathrm{C\cdot OH},$$

"iso-barbituric acid is the ureide of dihydroxyacrylic acid."

This curious adherence to old terms and ideas certainly needs further elucidation.

I propose shortly to moot the bearing of all this upon the future synthesis of the vegetable alkaloid caffeine.

Wokingham Road, Reading
May 25, 1889.

WALNUT OIL.

By THOMAS T. P. BRUCE WARREN.

This oil, which I obtained from the fully ripened nut of the *Juglans regia*, has so many excellent properties especially for mixing with artists' colours for fine art work, that I am surprised at the small amount of information available on this interesting oil.

Walnut oil is largely used for adulterating olive oil, and to compensate for its high iodine absorption it is mixed with pure lard oil olein, which also retards the thickening effect due to oxidation. The marc left on expression of the oil is said to be largely used in the manufacture of chocolate. Many people, I am told, prefer walnut oil to olive oil for cooking purposes.

The value of this oil for out-door work has been given me by a friend who used it for painting the verandas and jalousies of his house (near Como, Italy) some twenty years ago, and which have not required painting since. In this country, at least, walnut oil is beyond the reach of the general painter, and I do not know that the pure oil is to be obtained as a commercial article, even on a small scale.

It was in examining the properties of this and other oils, used as adulterants of olive oil, that I was obliged to prepare them so as to be sure of getting them in a reliable condition as regards purity. The walnuts were harvested in the autumn of 1887, and kept in a dry airy room until the following March. The kernels had shrunk up and contracted a disagreeable acrid taste, so familiar with old olive oil, in which this has been used as an adulterant. Most oxidised oils, especially cotton-seed oil, reveal a similar acrid taste, but walnut oil has, in addition, an unmistakable increase in viscosity. The nuts were opened and the kernels thrown into warm water, so as to loosen the epidermis; they were then rubbed in a coarse towel, so as to blanch them. The decorticated nuts were wiped dry and rubbed to a smooth paste in a marble mortar. The paste was first digested in $\mathrm{CS_2}$, then placed in a percolator and exhausted with the same solvent, which was evaporated off. The yield of oil was small, but probably, if the nuts had been left to fully ripen on the trees without knocking them off the yield might have been greater. It is by no means improbable that oxidation may have rendered a portion of the oil insoluble. The decorticated kernels gave a perfectly sweet, inodorous, and almost colourless oil, which rapidly thickens to an almost colourless, transparent, and perfectly elastic skin or film, which does not darken or crack easily by age. These are properties which, for fine art painting, might be of great value in preserving the tinctorial purity and freshness of pigments.

Sulphur chloride gives a perfectly white product with the fresh oil, but, when oxidised, the product is very dark, almost black. The iodine absorption of the fresh oil thus obtained is very high, but falls rapidly by oxidation or blowing. A curious fact has been disclosed with reference to the oxidation of this and similar oils. If such an oil be mixed with lard oil, olive oil, or sperm oil, it thickens by oxidation but is perfectly soluble. Such a mixture is largely used in weaving or spinning. Commercial samples of linseed oil, when cold drawn, have a much higher iodine absorption, probably due to the same cause. Oils extracted by CS_2 are very much higher than the same oils, especially if hot pressed.

THE FREE CAUSTIC ALKALI OF SOAP.

By J. A. WILSON.

In a previous note on the same subject in the Chemical News (vol. lix., p. 221) I pointed out that there is a source of error in the spirit method, and this error is due to the simultaneous presence of free alkali and free fat or oil.

When high class soaps are analysed, containing no free glycerides, the spirit method gives very accurate results, but any analyst who has to deal with soaps of any quality, and made in the most imperfect manner, will find the alcohol process perplexing. Hence I have no hesitation in saying that the determination of free caustic alkali in some soaps is one of the *most difficult problems* met with in practice. The conditions necessary to ensure the stability of the soap (*i.e.*, the decomposition into an acid soap and free caustic alkali) are just those conditions necessary to ensure the absolute saponification of the *glycerides* by the *free caustic alkali present*. To any expert in soap analysis the presence of free alkali and glycerides in the sample simultaneously is easily seen; on the addition of alcohol with phenolphthalein the colour goes deep, then gradually fades and may disappear altogether.

The method depending on insolubility of soap in strong brine has been proved to give the most inaccurate results, whilst that depending on precipitation of the alkali by carbonic dioxide gas, the solvent for the soap being alcohol, gives the same conditions necessary for complete saponification as stated above; hence this process is of no use. It is necessary to bear these facts in mind in these days, when we hear so much about the absence of free alkali in certain soaps.

In using the alcohol process for determining free caustic alkali it is necessary to use nearly or, better, absolute alcohol and to conduct the operation with the least possible access of air; moreover, the alcohol should be used largely and in due regard to the percentage of water in the soap.

In these cases, on account of the presence of free fat, the alcohol process must be abandoned if good results are required, and better state the results in this form :—

Alkali in Total, %. Alkali combined with Fatty Acids, %.

If the alkali existing as silicate and carbonate be very carefully determined some idea may be gained of the alkali actually present as sodium hydrate. Supposing palmnut or cocoanut oil to have been used in the fabrication of the soap, the determination of the Na_2O required to neutralise the fatty acids becomes quite inaccurate, owing to the solubility of the lower fatty acids, hence another complication arises.

In order to show the differences between the above methods let me quote a few analyses of mine :—

Nature of the Sample.	Alkali (Na_2O) by Titration. Per Cent.	Alkali by Titration of the Insoluble Fatty Acids.	Alkali by Alcohol Test.
1. Palm oil Soap, Cold Process..	5·00	4·59	0·00
2. Highly Watered Soap from Bone-fat.. ..	3·51	·71	0·31
3. Palm oil Soap similar to No. 1	5·61	5·39	0·00
4. Common Soap for Calico-printers	6·95	6·31	·38
5. Soap from Tallow and Cocoanut Oil	3·59	2·52	0·107
6. Washing Soap sold in North of England	7·33	7·70	0·017

Finally, as interesting, let me notice the article sold for calico-printers' use, known as soluble oil, which is made from castor oil, consisting therefore of the soda salt of ricinoleic acid. This material is required to be as neutral as possible; hence some makers, after saponification, add hydric chloride to neutralise the excess of alkali, which of course is overstepped, and free fatty acid results. Its usual composition is—

Free fatty acid as ricinoleic acid	4·75	per cent.
Total fatty acids	20·50	,,
Total alkali..	1·67	,,

On decomposition of this soap with subsequent titration of the washed fatty acids the number of c.c. of alkali used for neutralisation must be corrected by that required to neutralise the free fatty acids. Samples No. 1 and 3 in the table contained matured glycerides easily detected as previously mentioned. That the figure 0·31 per cent, corresponding to soap No. 2, is incorrect, was proved by estimation of the carbonate and silicate in the soap. The last soap in the table actually gave results higher in the third column than in the total column. The analysis especially, as in the others, was conducted most carefully with identical results. Accordingly, I sent a sample from the same to a well-known analyst, who certified as follows:—Alkali as soap, 7·66; alkali in total, 7·51; free alkali by alcohol, 0·02.

It is thus seen that he got results agreeing with mine in the main question, although he got higher results for the direct titration, usually stated as total. These results seem inexplicable, since free fat cannot possibly have any influence. That the estimation of *free caustic alkali* in soap is not so *easy* as is generally supposed will, I think, be admitted.

Laboratory, Tottington,
near Bury.

AN AUTOMATIC FUMIGATOR.

By H. N. WARREN, Research Analyst.

This form of apparatus is specially indicated both for scientific and commercial purposes, in the former ranking far superior to any form of apparatus designed for the purpose of evolving sulphurous anhydride, the usual method employed in the laboratory being that of decomposing the strongest oil of vitriol either by the aid of metallic copper or ordinary wood-charcoal contained in a flask or suitable apparatus, and applying a continued heat. Both these substances, however, present considerable drawbacks, the copper in the first instance forming with the strong acid a difficultly soluble salt, causes an annoyance both by surrounding the remaining metal by incrustation, and thus retarding further action, or seriously endangering a fracture of the vessel by incessant bumping. In using the new apparatus, a small dish containing pieces of ordinary roll sulphur after being well lighted, which is best performed by applying a heated iron to the same, is introduced with its contents into a metallic draught, or furnace piece, and a dome with its chimney projection, which is composed either of glass or metal, placed directly over it; a strong draught is at once formed, and the combustion of the sulphur is maintained until the whole is consumed, thus liberating a plentiful supply of sulphur dioxide. By connecting a tube or metallic pipe, as the case may be, bent at right angles with the projecting chimney, and terminating with a refrigerative worm surrounded by a powerful freezing-mixture, a large quantity of liquid sulphurous anhydride may be speedily manufactured, thus rendering the apparatus a useful piece for the lecture table. By connecting with the chimney projection a metallic vane-shaped cap, which is intended to distribute or to allow of the gas intermixing more uniformly with the atmosphere when desired, the apparatus at once furnishes a most efficient fumigator or deodoriser, being also applicable for bleaching purposes.

Everton Research Laboratory,
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THE TERRESTRIAL ORIGIN OF THE OXYGEN RAYS IN THE SOLAR SPECTRUM.

By J. JANSSEN.

M. Eiffel having placed the tower in the Champ de Mars at the author's disposal for the experiments and observations which he wished to institute there, he has utilised the powerful source of light installed there for certain studies of the terrestrial spectrum, with especial reference to the origin of the oxygen rays in the solar spectrum.

It is now known that there exist in the solar spectrum several groups of rays due to the oxygen contained in our atmosphere. But it may be asked if these groups are due exclusively to the action of our atmosphere, and if the sun's atmosphere takes no part in them at all, or, if their origin is twofold; in a word, are they purely terrestrial or terrestrial-solar?

To decide this question several methods are possible. One of the most certain is that of vibrations, the origin of which may be traced to the fine conception of M. Fizeau, and which has been applied by M. Thollon, and improved by M. Cornu. In the present case, however, its application would seem to be very difficult.

We may also observe the decrease of intensity which the groups undergo as we rise in the atmosphere. By the most careful comparisons, and by extended observations, we may judge if the decrease in the intensity of the rays warrants us in inferring their complete disappearance at the bounderies of the atmosphere. This is the method employed in the last expedition to the ridge of Mont Blanc (Grands Mulets). Or we may proceed by a comparison of equality; arranging a powerful light, with a continuous spectrum, at a distance from the instrument, such that the atmospheric stratum traversed may represent the action of the earth's atmosphere upon the sun's rays about the zenith.

These conditions are very happily realised by the repective positions of the Eiffel tower and the observatory of Meudon. The intervening distance is about 7700 metres, which represents approximately the thickness of an atmosphere, having the same weight as the terrestrial atmosphere, and a density which is uniform and equal to that of the atmospheric stratum near the sun. Besides the considerable power of the luminous apparatus installed at the summit of the tower permitted the use of the instrument which the author had employed at Meudon and on the Grands Mulets for the sun. He has also used a collecting-lens before the slit, so as to give the spectrum an intensity comparable to that of the solar spectrum in the same instrument. With these arrangements the spectrum appeared extremely bright. The field extended beyond A. The group B appeared as intense as with the summer sun at noon. The group A was also strongly manifest. Other groups were also distinguished, especially that of watery vapour; their intensity seemed to agree with the hygrometric condition of the atmospheric stratum traversed.

The author wished to study the oxygen groups with the great spectrometer of MM. Brunner and with M. Rowland's grating, but the limited time during which the light was supplied did not permit.

No oxygen band appeared in the visible spectrum. Still, the thickness of the stratum of oxygen traversed was equivalent to a column of more than 260 metres of oxygen, at a pressure of six atmospheres. This shows that for oxygen the rays follow quite a different law from the bands. Whilst for the rays the recent experiment shows that it seems indifferent whether we use a column of gas of constant density or a column equivalent in weight but of variable density; for the bands, on the contrary, the absorption taking place according to the square of the density, there would be required on the surface of the sun an atmospheric thickness of more than 50 kilometres for their production.

M. Janssen considers his experiment as merely supplying an additional fact which requires to be fixed with precision and developed. The height at which the tower of the Champ de Mars enables the luminous focus to be placed, and the power of this focus, promises us further experiments of high interest.—*Comptes Rendus*, vol. cviii., p. 1035.

A METHOD FOR THE DETECTION OF CHLORINE, BROMINE, IODINE, AND SULPHUR IN ORGANIC COMPOUNDS.

By CHARLES W. MARSH.

In testing for sulphur according to Schönn* by heating an organic substance with metallic sodium in a closed tube, dissolving the sodium sulphide formed in water, and adding a solution of sodium nitroprusside, the inconvenience of working with sodium and the precautions necessary in heating the sodium and substance and in adding water to the contents of the tube led the writer to look for another metal to replace the sodium. This metal, when heated with organic bodies, should decompose them and combine with the halogens and sulphur, or, if the substance were decomposed by heat, would enter into like combination.

Magnesium in fine powder has also been recommended by Schonn,† but only for the estimation of sulphur. He heats the substance with powdered magnesium in a hard glass tube, allows it to cool, adds a little water, and heats. The liquid is filtered and a solution of sodium nitroprusside added, and this reacts for sulphur by giving a reddish violet colouration.

Powdered zinc having the property of decomposing organic substances when heated with them, it seemed that this might be a ready substance to decompose organic bodies, and at the same time to unite with the halogens to form chloride, bromide, or iodide, as the case

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* *Zeit. Anal. Chem.*, viii., 52

† *Ibid.*, viii., 398.

might be, all of which are soluble in water. From the water solution the corresponding silver salt would be precipitated, which would aid to identify the halogen in the substance treated.

The substances containing sulphur in any form of combination would, on heating with zinc, form zinc sulphide. This could be decomposed by the addition of hydrochloric acid direct to the tube containing the zinc and charred residue of the organic substance, if any, and the sulphuretted hydrogen gas then tested for at the mouth of the tube by means of a narrow slip of filter-paper moistened with lead acetate solution.

The method of procedure outlined was tried on many organic substances containing chlorine, bromine, iodine, and sulphur, and gave the expected results. Several organic substances containing no chlorine, bromine, or iodine, were treated in the same manner, and a white precipitate invariably appeared on the addition of nitric acid and silver nitrate solution. The distilled water was tested, but gave no reaction for chlorine. A small quantity of zinc was shaken with water, the liquid poured on a filter, and to the filtrate nitric acid and silver nitrate solution were added, and immediately a white precipitate appeared, which was soluble in ammonium hydrate and re-precipitated by nitric acid, showing the presence of a large quantity of chlorine in the zinc. The test for sulphur was made as described, a brown colour being obtained on the lead acetate paper, showing the presence of a small amount of sulphur. The zinc was some used in the organic laboratory work, and came in the form of powder. As the zinc used contained chlorine and sulphur, the tests already made were valueless.

Another sample of fine zinc used in the reduction of ferric iron solutions was treated for chlorine and gave no reaction. It also gave no reaction for sulphur. This zinc comes in a spherical form, the diameters of which are mostly half a millimetre. The experiments made with the impure zinc were repeated with the pure sample, and also on several other compounds. The test on substances containing no chlorine, bromine, iodine, nor sulphur were made, and in no case was a distinct reaction obtained. In but one case an opalescence appeared after the addition of nitric acid and silver nitrate solution, while in all the others the solution remained perfectly clear. No trace of sulphur could be detected. This proved that the decomposition of organic substances on heating would not give reactions similar to the ones characteristic of the elements sought.

The substance was heated in about the same manner in every case, with a few exceptions, which will be described. Many of the tests were made in small hard-glass closed tubes, such as are used in blowpipe analysis, having an internal diameter of five millimetres and a length of sixty millimetres. Four-inch test tubes were found to give as satisfactory results.

The exact details of manipulation are as follows:—

The substance is first introduced into the tube and then the zinc is added in about equal volume. They are intimately mixed by shaking. The tube is held in a slanting position, with the lower end in the flame, and heated slowly. In many cases the substance volatilises, condenses in the upper end of the tube, and runs down upon the hot zinc, when it is decomposed. In others it carbonises and a watery coloured liquid distils.

If combustible gases or vapours are given off, they are lighted. It is better not to heat the tube red hot, for in that case the zinc would melt to a globule and inclose some of the zinc salt formed. At the same time the zinc chloride, bromide, and iodide would be volatilised and thus cause a loss. Zinc sulphide is not volatile.

If a liquid is under examination it is better to use a test-tube, as the mouth is wider. The liquid is first added to the test-tube, which moistens the sides, so that when the zinc is added it will adhere to the inner walls and some remain near the mouth. The test-tube, held in a wooden holder, is slightly heated, and the vapours, if inflammable, are ignited, while the tube is held in a position nearly horizontal. The heat is so regulated that the flame will be as small as possible, and will tend to burn down in the tube and there act upon the zinc adhering to the sides. With the liquids methyl iodide, ethyl iodide, and carbon disulphide, this was the only method by which reactions for iodine and sulphur could be obtained. With para-dichlor-benzene this last method gave good results, whereas the general method of heating gave no reaction for chlorine.

After heating with zinc the residue in the tube is cooled and treated as follows:—

For Chlorine.—About one cubic centimetre of distilled water is added direct to the test-tube, the whole shaken and allowed to stand, while a small filter is fitted to a funnel. The liquid is now poured on the filter and caught in a short test-tube placed underneath. The filtrate is acidified with nitric acid and a solution of silver nitrate added. A white precipitate of silver chloride, soluble in ammonium hydrate and re-precipitated by nitric acid, was obtained from the following substances tested:—

Liquids.—Chloroform, acetyl chloride, ethylene chloride, allyl chloride.

Solids.—Mono-chlor-crotonic acid, para-dichlor-benzene, trichlor-phenol.

For Bromine.—The contents of the tube are treated with water and filtered, as in the test for chlorine. The filtrate is divided into two parts. In one part nitric acid and silver nitrate solution are added, when the light yellow precipitate of silver bromide appears. To the other part of the filtrate nitric acid is added and a few drops of carbon disulphide. The carbon disulphide is coloured brown from the bromine liberated. In several cases the precipitate of silver bromide was very slight, but in every case the carbon disulphide was strongly coloured.

The following substances gave the reactions described:—

Liquids.—Acetyl bromide, amyl bromide, isobutyl-bromide, brom-toluene.

Solids.—Tribrom-aniline, ortho-nitro-dibrom-phenyl-propionic acid, dibrom-benzene, mono-brom-camphor, dibrom-camphor, eosine, dibrom-gallein, dibrom-anthraquinone, dibrom-anthracene.

For Iodine.—The filtrate is divided and treated as in the case of bromine. Yellow silver iodide is obtained in the first instance, and the carbon disulphide coloured violet by the iodine freed from the zinc by the nitric acid in the second.

Iodine was thus detected in the following substances:—

Liquids.—*Methyl iodide, ethyl iodide, allyl iodide, isobutyl iodide.

Solids.—Iodoform.

For Sulphur.—To the tube containing the residue after heating the substance with zinc a few drops of hydrochloric acid are added, and the hydrogen sulphide generated identified as it escapes from the mouth of the tube by filter-paper moistened with lead acetate solution. The paper is turned brown almost immediately. There is no necessity for heating the tube. The compounds in the list gave distinct reactions.

Liquids.—Carbon disulphide, allyl mustard oil, ethyl sulphocyanate.

Solids.—Sulpho-urea, potassium amyl sulphate, sulphanilic acid, ammonium diphenyl-amidazo-benzene sulphonate, saccharin, sodium beta-naphthol-disulphonate, mono-sodium anthraquinone sulphonate, morphine sulphate.

It is claimed that, by using the process described, chlorine, bromine, iodine, and sulphur can be accurately and rapidly detected in organic compounds by the use of

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* The liquid iodides used were more or less decomposed and coloured by iodine set free. In order to work upon undecomposed chemicals, they were each separately shaken with potassium hydrate solution, to take up the iodine, and the resulting colourless alcoholic iodide was repeatedly washed with water. The iodides thus treated were used for the experiments.

apparatus and chemicals ordinarily found in chemical laboratories.—*American Chemical Journal*, vol. xi., No. 4.

ALUMINIUM.*

By Sir HENRY ROSCOE, M.P., D.C.L., LL.D., V.P.R.S.

Chemists of many lands have contributed to our knowledge of the metal aluminium. Davy, in 1807, tried in vain to reduce alumina by means of the electric current. Oerstedt, the Dane, in 1824, pointed out that the metal could be obtained by treating the chloride with an alkali metal; this was accomplished in Germany by Wöhler in 1827, and more completely in 1845, whilst in 1854, Bunsen showed how the metal can be obtained by electrolysis. But it is to France, by the hands of Henri Ste.-Claire Deville, in the same year, that the honour belongs of having first prepared aluminium in a state of purity, and of obtaining it on a scale which enabled its valuable properties to be recognised and made available, and the bar of "silver-white metal from clay" was one of the chemical wonders in the first Paris Exhibition of 1855. Now England and America step in, and I have this evening to relate the important changes which further investigation has effected in the metallurgy of aluminium. The process suggested by Oerstedt, carried out by Wöhler, and modified by Deville, remains in principle unchanged. The metal is prepared, as before, by a reduction of the double chloride of aluminium and sodium, by means of metallic sodium in presence of cryolite; and it is therefore not so much a description of a new reaction as of improvements of old ones of which I have to speak.

I may perhaps be allowed to remind my hearers that more than 33 years ago, Mr. Barlow, then secretary to the Institution, delivered a discourse in the presence of M. Deville on the properties and mode of preparation of aluminium, then a novelty. He stated that the metal was then sold at the rate of £3 per ounce, and the exhibition of a small ingot, cast in the laboratory by M. Deville, was considered remarkable. As indicating the progress since made, I may remark that the metal is now sold at 20s. per lb., and manufactured by the ton, by the Aluminium Company, at their works at Oldbury, near Birmingham. The improvements which have been made in this manufacture by the zeal and energy of Mr. Castner, an American metallurgist, are of so important a character, that the process may properly be termed the Deville-Castner process.

The production of aluminium previous to 1887, probably did not exceed 10,000 lbs. per annum, whilst the price at that time was very high. To attain even this production required that at least 100,000 lbs. of double chloride, and 40,000 lbs of sodium should be manufactured annually. From these figures an idea of the magnitude of the undertaking assumed by the Aluminium Company may be estimated, when we learn that they erected works having an annual producing capacity of 100,000 lbs. of aluminium. To accomplish this, required not only that at least 400,000 lbs. of sodium, 800,000 lbs. of chlorine, and 1,000,000 lbs. of double chloride, should be annually manufactured, but in addition that each of these materials should be produced at a very low cost, in order to enable the metal to be sold at 20s. per lb.

The works now cover a space of nearly five acres. They are divided into five separate departments, viz., 1st, sodium; 2nd, chlorine; 3rd, chloride; 4th, aluminium; and 5th, foundry, rolling, wire mills, &c.

In each department an accurate account is kept of the production each day, the amount of material used, the different furnaces and apparatus in operation, &c. In this manner it has been found possible to ascertain each day exactly how the different processes are progressing, and what effect any modification has, either on cost, quantity, or quality of product. By this means a complicated chemical process is reduced to a series of very simple operations, so that whilst the processes are apparently complicated and difficult to carry out successfully, this is not the case now that the details connected with the manufacture have been perfected, and each operation carried on quite independently until the final materials are brought together for the production of the aluminium.

Manufacture of Sodium.

The first improvement occurs in the manufacture of sodium by what is known as the "Castner Process." The successful working of this process marks an era in the production of sodium, as it not only has greatly cheapened the metal, but has enabled the manufacture to be carried out upon a very large scale with little or no danger. Practically, the process consists in heating fused caustic soda in contact with carbon whilst the former substance is in a perfectly liquid condition. By the process in vogue before the introduction of this method, it was always deemed necessary that special means should be taken to guard against actual fusion of the mixed charges, which, if it were to take place, would to a large extent allow the alkali and reducing material to separate. Thus, having an infusible charge to heat, requiring the employment of a very high temperatue for its decomposition, the iron vessels must be of small circumference to allow the penetration of the heat to the centre of the charge without actually melting the vessel in which the materials are heated. By the new process, owing to the alkali being in a fused or perfectly liquid condition in contact directly with carbon, the necessity of this is avoided, and consequently, the reduction can be carried on in large vessels at a comparatively low temperature. The reaction taking place may be expressed as follows:—

$$3NaHO+C=Na_2CO_3+3H+Na.$$

The vessels in which the charges of alkali and reducing material are heated are of egg-shaped pattern, about 18 inches in width at their widest part and about 3 feet high, and are made in two portions, the lower one being actually in the form of a crucible, while the upper one is provided with an unright stem and a protruding hollow arm. This part of the apparatus is known as the cover. In commencing the operation, these covers are raised in the heated furnace through apertures provided in the floor of the heated chamber, and are then fastened in their place by an attachment adjusted to the stem; the hollow arm extends outside the furnace. Directly below each aperture in the bottom of the furnace are situated the hydraulic lifts, attached to the top of which are the platforms upon which are placed the crucibles to be raised into the furnace. Attached to the hydraulic lifts are the usual reversing valves for lowering or raising, and the platform is of such a size as, when raised, completely to fill the bottom aperture of the furnace. The charged crucible, being placed upon the platform, is raised into its position, the edges meeting those of the cover, forming an air-tight joint which prevents the escape of gas and vapour from the vessel during reduction, except by the hollow arm provided for this purpose. The natural expansion of the iron vessels is accommodated by the water-pressure in the hydraulic lifts, so that the joint of the cover and crucible are not disturbed until it is intended to lower the lift for the purpose of removing the crucible.

The length of time required for the first operation of reduction and distillation is about two hours. At the end of this time the crucibles are lowered, taken from the platforms by a large pair of tongs on wheels, carried to a dumping pit, and thrown on their side. The residue is cleaned out, and the hot pot, being again gripped by the tongs, is taken back to the furnace. On its way, the charge of alkali and reducing material is thrown in. It is again placed on the lift and raised in position against

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* A Lecture delivered at the Royal Institution of Great Britain, May 3, 1889.

the edges of the cover. The time consumed in making the change is one and a half minutes, and it only requires about seven minutes to draw, empty, recharge, and replace the five crucibles in each furnace. In this manner the crucibles retain the greater amount of their heat, so that the operation of reduction and distillation now only requires one hour and ten minutes. Each of the four furnaces, of five crucibles each, when in operation, are drawn alternately, so that the process is carried on night and day.

Attached to the protruding hollow arm from the cover are the condensers, which are of a peculiar pattern specially adapted to this process, being quite different from those formerly used. They are about 5 inches in diameter, and nearly 3 feet long, and have a small opening in the bottom about 20 inches from the nozzle. The bottom of these condensers is so inclined that the metal condensed from the vapour issuing from the crucible during reduction, flows down and out into a small pot placed directly below this opening. The uncondensed gases escape from the condenser at the further end, and burn with the characteristic sodium flame. The condensers are also provided with a small hinged door at the further end, by means of which the workmen from time to time may look in to observe how the distillation is progressing. Previous to drawing the crucibles from the furnace for the purpose of emptying and recharging, the small pots each containing the distilled metal are removed, and empty ones substituted. Those removed each contain on an average about 6 lbs. of metal, and are taken directly to the sodium casting shop, where it is melted and cast, either into large bars ready to be used for making aluminium, or in smaller sticks to be sold.

Special care is taken to keep the temperature of the furnaces at about 1000° C., and the gas and air valves are carefully regulated, so as to maintain as even a temperature as possible. The covers remain in the furnace from Sunday night to Saturday afternoon, and the crucibles are kept in use until they are worn out, when new ones are substituted without interrupting the general running of the furnace. A furnace in operation requires 250 lbs. of caustic soda every one hour and ten minutes, and yields in the same time 30 lbs. of sodium, and about 240 lbs. of crude carbonate of soda. With the four furnaces at work 120 lbs. of sodium can be made every seventy minutes, or over a ton in the twenty-four hours. The residual carbonate, on treatment with lime in the usual manner, yields two-thirds of the original amount of caustic operated upon. The sodium, after being cast, is saturated with kerosene oil, and stored in large tanks holding several tons, placed in rooms specially designed both for security against either fire or water.

Chlorine Manufacture.

This part of the works is connected with the adjacent works of Messrs. Chance Bros. by a large gutta-percha pipe, by means of which from time to time hydrochloric acid is supplied direct into the large storage cisterns, from which it is used as desired for making the chlorine. For the preparation of the chlorine gas needed in making the chloride, the usual method is employed: that is, hydrochloric acid and manganese dioxide are heated together when chlorine gas is evolved with effervescence, and is led away by earthenware and lead pipes to large lead-lined gasometers, where it is stored.

The materials for the generation of the chlorine are brought together in large tanks, or stills, built up out of great sandstone slabs, having rubber joints, and the heating is effected by the injection of steam. The evolution of gas, at first rapid, becomes gradually slower, and at last stops; the hydrochloric acid and manganese dioxide being converted into chlorine and manganous chloride. This last compound remains dissolved in the "spent still liquor," and is re-converted into manganese dioxide, to be used over again, by Weldon's Manganese Recovery Process. Owing to the difficulty of keeping up a regular supply of chlorine under a constant pressure directly from the stills, in order that the quantity passed into the sixty different retorts in which the double chloride is made can be regulated and fed as desired, four large gasometers were erected. Each of these is capable of holding 1000 cubic feet of gas, and is completely lined with lead, as are all the connecting mains, &c., this being the only available metal which withstands the corrosive action of chlorine. The gasometers are filled in turn from the stills, the chlorine consumed being taken direct from a gasometer under a regular pressure until it is exhausted, the valves being changed, the supply is taken from another holder, the emptied one being re-filled from the still.

Manufacture of the Double Chloride.

Twelve large regenerative gas furnaces are used for heating, and in each of these are fixed five horizontal fire-clay retorts about 10 ft. in length, into which the mixture for making the double chloride is placed. These furnaces have been built in two rows, six on a side, the clear passage-way down the centre of the building, which is about 250 ft. long, being 50 ft. in width. Above this central passage is the staging, carrying the large lead-mains for the supply of the chlorine coming from the gasometers. Opposite each retort and attached to the main are situated the regulating valves, connected with lead and earthenware pipes, for the regulation and passage of the chlorine to each retort. The valves are of peculiar design, and have been so constructed that the chlorine is made to pass through a certain depth of liquid, which not only, by opposing a certain pressure, allows a known quantity of gas to pass in a given time, but also prevents any return from the retort into the main, should an increase of pressure be suddenly developed in the retorts.

The mixture with which the retorts are charged is made by grinding together hydrate of alumina, salt, and charcoal. This mixture is then moistened with water, which partially dissolves the salt, and thrown into a pug-mill of the usual type for making drain-pipes, excepting that the mass is forced out into solid cylindrical lengths upon a platform alongside of which a workman is stationed with a large knife, by means of which the material is cut into lengths of about three inches each. These are then piled on top of the large furnaces to dry. In a few hours they have sufficiently hardened to allow of their being handled. They are then transferred to large wagons, and are ready to be used in charging the retorts.

The success of this process is in a great measure dependent, 1st, on the proportionate mixture of materials; 2nd, on the temperature of the furnace; 3rd, on the quantity of chlorine introduced in a given time; and 4th, on the actual construction of the retorts. I am, however, not at liberty to discuss the details of this part of the process, which have only a commercial interest. In carrying on the operation the furnaces or retorts, when at the proper temperature, are charged by throwing in the balls until they are quite full, the fronts are then sealed up, and the charge allowed to remain undisturbed for about four hours, during which time the water of the alumina hydrate is completely expelled. At the end of this time the valves on the chlorine main are opened, and the gas is allowed to pass into the charged retorts. In the rear of each retort, and connected therewith by means of an earthenware pipe, are the condenser boxes which are built in brick. These boxes are provided with openings or doors, and also with earthenware pipes, connected with a small flue for carrying off the uncondensed vapours to the large chimney. At first the chlorine passed into each retort is all absorbed by the charge, and only carbonic oxide escapes into the open boxes, where it burns. After a certain time, however, dense fumes are evolved, and the boxes are then closed, while the connecting pipe between the box and the small flue serves to carry off the uncondensed vapours to the chimney.

The reaction which takes place is as follows:—

$$Al_2O_3+2NaCl+3C+6Cl=2AlCl_3NaCl+3CO.$$

The chlorine is passed in for about seventy-two hours in varying quantity, the boxes at the back being opened from time to time by the workmen to ascertain the progress of the distillation. At the end of the time mentioned the chlorine valves are closed and the boxes at the back of the furnace are all thrown open. The crude double chloride, as distilled from the retorts, condenses in the connecting pipe and trickles down into the boxes, where it solidifies in large irregular masses. The yield from a bench of five retorts will average from 1600 to 1800 lbs., which is not far from the theoretical quantity. After the removal of the crude chloride from the condenser boxes the retorts are opened at their charging end, and the residue, which consists of a small quantity of alumina, charcoal, and salt, is raked out and re-mixed in certain proportions with fresh material, to be used over again. The furnace is immediately re-charged and the same operations repeated, so that from each furnace upwards of 3500 lbs. of chloride are obtained weekly. With ten of the twelve furnaces always at work the plant is easily capable of producing 30,000 lbs. of chloride per week, or 1,500,000 lbs. per annum.

Owing to the presence of iron, both in the materials used (viz., charcoal, alumina, &c.) and in the fire-clay composing the retorts, the distilled chloride always contains a varying proportion of this metal in the form of ferrous and ferric chlorides. When it is remembered that it requires 10 lbs. of this chloride to produce 1 lb. of aluminium by reduction, it will be quite apparent how materially a very small percentage of iron in the chloride will influence the quality of the resulting metal. I may say that, exercising the utmost care as to the purity of the alumina and the charcoal used, and after having the retorts made of special fire-clay containing only a very small percentage of iron, it was found almost impossible to produce upon a large scale a chloride containing less than 0·3 per cent of iron.

This crude double chloride, as it is now called at the works, is highly deliquescent, and varies in colour from a light yellow to a dark red. The variation in colour is not so much due to the varying percentage of iron contained as to the relative proportion of ferric or ferrous chlorides present, and although a sample may be either very dark or quite light, it may still contain only a small percentage of iron if it be present as ferric salt, or a very large percentage if it is in the ferrous condition. Even when exercising all possible precautions, the average analysis of the crude double chloride shows about 0·4 per cent of iron. The metal subsequently made from this chloride, therefore, never contained much less than about 5 per cent of iron, and, as this quantity greatly injures the capacity of aluminium for drawing into wire, rolling, &c., the metal thus obtained required to be refined. This was successfully accomplished by Mr. Castner and his able assistant Mr. Cullen, and for some time all the metal made was refined, the iron being lowered to about 2 per cent.

The process, however, was difficult to carry out, and required careful manipulation, but as it then seemed the only remedy for effectively removing the iron, it was adopted and carried on for some time quite successfully, until another invention of Mr. Castner rendered it totally unnecessary. This consisted in purifying the double chloride before reduction. I cannot now explain this process, but I am able to show some of the product. This purified chloride, or pure double chloride, is, as you see, quite white, and is far less deliquescent than the crude, so that it is quite reasonable to infer that this most undesirable property is greatly due to the former presence of iron chlorides. I have seen large quantities containing upwards of 1½ per cent of iron, or 150 lbs. to 10,000 of the chloride, completely purified from iron in a few minutes, so that, whilst the substance before treatment was wholly unfit for the preparation of aluminium, owing to the presence of iron, the result was, like the sample exhibited, a mass containing only 1 lb. of iron in 10,000, or 0·01 per cent. The process is extremely simple, and adds little or no appreciable cost to the final product. After treatment, this pure chloride is melted in large iron pots and run into drums similar to those used for storing caustic soda. As far as I am aware it was generally believed to be an impossibility to remove the iron from anhydrous double chloride of aluminium and sodium, and few, if any, chemists, have ever seen a pure white double chloride.

Aluminium Manufacture.

I now come to the final stage of the process, viz., the reduction of the pure double chloride by sodium. This is effected, not in a tube of Bohemian glass, as shown in Mr. Barlow's lecture in 1856, but in a large reverberatory furnace, having an inclined hearth about six feet square, the inclination being towards the front of the furnace, through which are several openings at different heights. The pure chloride is ground together with cryolite in about the proportions of two to one, and is then carried to a staging erected above the reducing furnace. The sodium, in large slabs or blocks, is run through a machine similar to an ordinary tobacco-cutting machine, where it is cut into small thin slices; it is then also transferred to the staging above the reducing furnace.

Both materials are now thrown into a large revolving drum, when they become thoroughly mixed. The drum being opened and partially turned, the contents drop out into a car on a tramway directly below. The furnace having been raised to the desired temperature, the dampers of the furnace are all closed to prevent the access of air, the heating gas also being shut off. The car is then moved out on the roof of the furnace until it stands directly over the centre of the hearth. The furnace roof is provided with large hoppers, and through these openings the charge is introduced as quickly as possible. The reaction takes place almost immediately, and the whole charge quickly liquefies. At the end of a certain time the heating gas is again introduced and the charge kept at a moderate temperature for about two hours. At the end of this period the furnace is tapped by driving a bar through the lower opening, which has previously been stopped with a fire-clay plug, and the liquid metal run out in a silver stream into moulds placed below the opening. When the metal has all been drawn off, the slag is allowed to run out into small iron wagons and removed. The openings being again plugged up, the furnace is ready for another charge. From each charge, composed of about 1200 lbs. of pure chloride, 600 lbs. of cryolite, and 350 lbs. of sodium, about 115 to 120 lbs. of aluminium is obtained.

The purity of the metal entirely depends upon the purity of the chloride used, and without exercising more than ordinary care the metal tests usually indicate a purity of metal above 99 per cent. On the table is the metal run from a single charge, its weight is 116 lbs., and its composition, as shown by analysis, is 99·2 aluminium, 0·3 silicon, and 0·5 iron. This I believe to be the largest and the purest mass of metal ever made in one operation.

The result of eight or nine charges are laid on one side, and then melted down in the furnace to make a uniform quality, the liquid metal, after a good stirring, being drawn off into moulds. These large ingots, weighing about 60 lbs. each, are sent to the casting shop, there to be melted and cast into the ordinary pigs, or other shapes, as may be required for the making of tubes, sheets, or wire, or else used directly for making alloys of either copper or iron.

The following Table shows approximately the quantity of each material used in the production of one ton of aluminium:—

Metallic sodium	6,300 lbs.
Double chloride	22,400 ,,
Cryolite	8,000 ,,
Coal	8 tons

To produce 6300 lbs. of sodium is required:—

Caustic soda	44,000 lbs.
Carbide made from pitch, 12,000 lbs., and iron turnings, 1000 lbs. ..	7,000 ,,
Crucible castings	2½ tons
Coal	75 ,,

For the production of 22,400 lbs. double chloride is required:—

Common salt	8,000 lbs.
Alumina hydrate	11,000 ,,
Chlorine gas	15,000 ,,
Coal	180 tons

For the production of 15,000 lbs. of chlorine gas is required:—

Hydrochloric acid	180,000 lbs.
Limestone dust	45,000 ,,
Lime	30,000 ,,
Loss of manganese..	1,000 ,,

(These figures were rendered more evident by the aid of small blocks, each cut a given size so as to represent the relative weights of the different materials used to produce one unit of aluminium).

It might seem, on looking over the above numbers, as if an extraordinary amount of waste occurred, and as if the production is far below that which ought to be obtained, but a study of the figures will show that this is not the case. I would wish to call attention to one item in particular, viz., fuel, it having been remarked that the consumption of coal must prevent cheap production. I think when it is remembered that coal, such as used at the works, costs only 4s. per ton, while the product is worth £2240 per ton, the cost of coal is not an item of consequence in the cost of production. The total cost of the coal to produce one ton of metal being £50; the actual cost for fuel is less than sixpence for every pound of aluminium produced. The ratio of cost of fuel to value of product is indeed less than is the case in making either iron or steel. In concluding my remarks as to the method of manufacture and the process in general, I may add that I do not think it is too much to expect, in view of the rapid strides already made, that in the future, further improvements and modifications will enable aluminium to be produced and sold even at a lower price than appears at present possible.

Properties of Aluminium.

In its physical properties aluminium widely differs from all the other metals. Its colour is a beautiful white, with a slight blue tint. The intensity of this colour becomes more apparent when the metal has been worked, or when it contains silicon or iron. The surface may be made to take a very high polish, when the blue tint of the metal becomes manifest, or it may be treated with caustic soda and then nitric acid, which will leave the metal quite white. The extensibility or malleability of aluminium is very high, ranking with gold and silver if the metal be of good quality. It may be beaten out into thin leaf quite as easily as either gold or silver, although it requires more careful annealing.

It is extremely ductile and may be easily drawn, especial care only being required in the annealing.

The excessive sonorousness of aluminium is best shown by example (large suspended bar being struck). Faraday has remarked, after experiments conducted in his laboratory, that the sound produced by an ingot of aluminium is not simple, and one may distinguish the two sounds by turning the vibrating ingot.

After being cast it has about the hardness of pure silver, but may be sensibly hardened by hammering.

Its tensile strength varies between 12 and 14 tons to the inch (test sample which was shown having been broken at 13 tons or 27,000 lbs.), ordinary cast iron being about 8 tons. Comparing the strength of aluminium in relation to its weight, it is equal to steel of 38 tons tensile strength. The specific gravity of cast aluminium is 2·58, but after rolling or hammering this figure is increased to about 2·68.

The specific gravity of aluminium being 1, copper is 3·6, nickel 3·5, silver 4, lead 4·8, gold 7·7.

The fusibility of aluminium has been variously stated as being between that of zinc and silver, or between 600° and 1000° C.

As no reliable information has ever been made public on this subject, my friend Professor Carnelley undertook to determine it. I was aware, from information gained at the works at Oldbury, that a small increase in the percentage of contained iron materially raised its point of fusion, and it has been undoubtedly due to this cause that such wide limits are given for the melting-point. Under these circumstances two samples were forwarded for testing, of which No. 1, containing ½ per cent of iron, had a melting-point of 700° C.; whereas No. 2, containing 5 per cent of iron, does not melt at 700°, and only softens somewhat above that temperature, but undergoes incipient fusion at 730°.

According to Faraday, aluminium ranks very high among metallic conductors of heat and electricity, and he found that it conducted heat better than either silver or copper. The specific heat is also very high, which accounts for length of time required for an ingot of the metal to either melt or get cold after being cast.

Chemically, its properties are well worthy of study.

Air, either wet or dry, has absolutely no effect on aluminium at the ordinary temperature, but this property is only possessed by a very pure quality of metal, and the pure metal in mass undergoes only slight oxidation even at the melting-point of platinum.

Thin leaf, however, when heated in a current of oxygen, burns with a brilliant bluish white light. (Experiment shown). If the metal be pure, water has no effect on it whatever, even at a red heat. Sulphur and its compounds also are without action on it, while, under the same circumstances, nearly all metals would be discoloured with great rapidity. (Experiment shown using silver and aluminium under the same conditions).

Dilute sulphuric acid and nitric acid, both diluted and concentrated, have no effect on it, although it may be dissolved in either hydrochloric acid or caustic alkali. Heated in an atmosphere of chlorine it burns with a vivid light, producing aluminium chloride. (Experiment shown). In connection with the subject it may be of interest to state the true melting-point of the double chloride of aluminium and sodium, which has always been given at 170° to 180° C., but which Mr. Baker, the chemist of the works, finds lies between 125° and 130° C.

Uses of Aluminium.

Its uses, unalloyed, have heretofore been greatly restricted. This is, I believe, alone owing to its former high price, for no metal possessing the properties of aluminium could help coming into larger use if its cost were moderate. Much has been said as to the impossibility of soldering it being against its popular use, but I believe that this difficulty will now soon be overcome. The following are a few of the purposes to which it is at present put:—Telescope tubes, marine glasses, eyeglasses, and sextants, especially on account of its lightness. Fine wire for the making of lace, embroidery, &c. Leaf, in the place of silver leaf, sabre sheaths, sword handles, &c., statuettes, and works of art, jewellery, and delicate physical apparatus, culinary utensils, harness fittings, metallic parts of soldiers' uniforms, dental purposes, surgical instruments, reflectors (it not being tarnished by the products of combustion), photographic apparatus, aëronautical and engineering purposes, and especially for the making of alloys.

Alloys of Aluminium.

The most important alloys of aluminium are those made with copper. These alloys were first prepared by Dr. Percy, in England, and now give promise of being largely used. The alloy produced by the addition of 10 per cent of aluminium to copper, the maximum amount that can be used to produce a satisfactory alloy, is known as aluminium bronze. Bronzes, however, are made which contain smaller amounts of aluminium, possessing in a degree the valuable properties of the ten per cent bronze. According to the percentage of aluminium up to 10 per cent, the colour varies from red gold to pale yellow. The 10 per cent alloy takes a fine polish, and has the colour of jewellers' gold. The 5 per cent alloy is not quite so hard, the colour being very similar to that of pure gold. I am indebted to Prof. Roberts-Austen for a splendid specimen of crystallised gold, as also for a mould in which the gold at the Mint is usually cast, and in this I have prepared ingots of the 10 and 5 per cent alloy, so that a comparison may be made of the colour of these with a gold ingot cast in the same mould (for the loan of which I have to thank Messrs. Johnson, Matthey, and Co.), all of which are before you.

I have also ingots of the same size, of pure aluminium, from which an idea of the relative weights of gold and aluminium may be obtained.

To arrive at perfection in the making of these alloys, not only is it required that the aluminium used should be of good quality, but also that the copper must be of the very best obtainable. For this purpose only the best brands of Lake Superior copper should be used. Inferior brands of copper or any impurities in the alloy give poor results. The alloys all possess a good colour, polish well, keep their colour far better than all other copper alloys, are extremely malleable and ductile, can be worked either hot or cold, easily engraved, the higher grades have an elasticity exceeding steel, are easily cast into complicated objects, do not lose in re-melting, and are possessed of great strength, dependent, of course, on the purity and percentage of contained aluminium. The 10 per cent alloy, when cast, has a tensile strength of between 70,000 and 80,000 lbs. per square inch, but when hammered or worked, the test exceeds 100,000 lbs. (A sample shown broke at 105,000 lbs.)

An attempt to enumerate either the present uses or the possible future commercial value of these alloys is beyond my present purpose. I may, however, remark that they are not only adapted to take the place of bronze, brass, and steel, but they so far surpass all of those metals, both physically and chemically, as to make their extended use assured. (Sheets, rods, tubes, wire, and ingots shown),

But even a more important use of aluminium seems to be its employment in the iron industry, of which it promises shortly to become a valuable factor, owing to certain effects which it produces when present, even in the most minute proportions. Experiments are now being carried on at numerous iron and steel works, in England, on the Continent, and in America. The results so far attained are greatly at variance, for whilst in the majority of cases the improvements made have encouraged the continuance of the trials, in others the results have not been satisfactory. On this point I would wish to say to those who may contemplate making use of aluminium in this direction, that it would be advisable before trying their experiments to ascertain whether the aluminium alloy they may purchase actually contains any aluminium at all, for some of the so-called aluminium alloys contain little or no aluminium, and this may doubtless account for the negative results obtained. Again, others contain such varying proportions of carbon, silicon, and other impurities, as to render their use highly objectionable.

It seems to be a prevailing idea with some people, that because aluminium is so light compared with iron, that they cannot be directly alloyed, and furthermore, that for the same reason, alloys made by the direct melting together of the two metals would not be equal to an alloy where both metals are reduced together. Now, of course, this is not the case, and the statement has been put forward by those who were only able to make the alloys in one way.

Aluminium added to molten iron and steel lowers their melting-points, consequently increases the fluidity of the metal, and causes it to run easily into moulds and set there, without entrapping air and other gases, which serve to form blow-holes and similar imperfections. It is already used by a large number of steel founders, and seems to render the production of sound steel castings more certain and easy than is otherwise possible.

One of the most remarkable applications of this property which aluminium possesses of lowering the melting-point of iron has been made use of by Mr. Nordenfelt in the production of castings of wrought iron.

Aluminium forms alloys with most other metals, and although each possess peculiar properties which in the future may be utilised, at present they are but little used.

In conclusion, I beg to call your attention to the wood models on the table, one being representative of aluminium, the other aluminium bronze. The originals of these models are now in the Paris Exhibition, each weighing 1000 lbs. With regard to the aluminium bronze, I cannot speak positively, but the block of pure aluminium is undoubtedly the largest casting ever made in this most wonderful metal.

I have to thank the Directors of the Aluminium Company, and especially Mr. Castner, for furnishing me with the interesting series of specimens of raw and manufactured metal for illustrating my discourse.

NOTICES OF BOOKS.

The Chemistry of Chlorophyll. By Edward Schunck, Ph.D., F.R.S., F.C.S. (Reprinted from *Annals of Botany*, February, 1889).

Notwithstanding much eloborate research, the nature of chlorophyll is as yet so imperfectly known that different authorities return discordant answers to the question, what is to be understood by the term? Pelletier and Caventon, its sponsors, consider chlorophyll as simply an organic colouring-matter, like indigo or alizarine. Some chemists define it as the sum of the coloured constituents of green leaves, soluble in alcohol and ether, but insoluble in water. Physiologists have applied the term chlorophyll to "the complex of substances contained in living green cells which take part in the process of assimilation, and of which the colouring matter constitutes a portion." Dr. Schunck, in this investigation, adheres very closely to the definition of Pelletier and Caventon, and means "simply the substance, or, it may be, the mixture of substances, to which the pure green colour of ordinary healthy leaves and other vegetable organs is due."

In speaking of the isolation of chlorophyll the author shows that it is an unstable compound, very sensitive to the action of acids. Hence, Berzelius, Mulder, Morot, and Fremy, who used hydrochloric acid in preparing chlorophyll, obtained and studied decomposition-products.

Arm. Gautier in preparing chlorophyll uses neutral solvents only. Hansen treats the alcoholic extract with caustic lye to saponify fatty matters, the residue being then successively extracted with petroleum ether and with ordinary ether, the pure chlorophyll being finally obtained by crystallisation from a mixture of alcohol and ether. Dr. Schunck, however, cannot accept Hansen's conclusions, as the product obtained, unlike ordinary chlorophyll, is readily soluble in water. He is further led to the conclusion that chlorophyll is modified by the action of alkalies, that it has not yet been obtained in a state of purity, and that in the plant it probably exists in an amorphous state. An approximately pure solution of chlorophyll may be obtained by mixing the alcoholic extract of grass with twice its volume of water, and agitating with ether. The ether takes up the chlorophyll (though not alone), whilst certain yellow colouring-matters are left in the watery solution.

The solutions of chlorophyll in alcohol, ether, &c. have a bright green colour, a red fluorescence, and a well-known absorption spectrum. Nitrogen, according to the otherwise discordant analyses of both Gautier and Hansen, is present to the amount of 4—5 per cent. Iron, the author considers, is not an essential constituent.

In Dr. Schunck's opinion, the bands at the blue end of the absorption spectrum do not belong to chlorophyll, in his sense of the term.

The question is next raised whether chlorophyll is a homogeneous body or a mixture of several substances very similar in their properties? But, on this point, an absolute conclusion has not yet been reached. The decompositions of chlorophyll are then considered—that occurring on mere exposure to air and light, and that induced by the action of acids. Its behaviour with alkalies, which is very interesting, has been studied by Dr. Russell, F.R.S., and Mr. Lapraik. The most remarkable of the products obtained by the author is phyllotannin, concerning which Dr. Schunck remarks:—"There are few natural colouring-matters or derivatives which surpass phyllotannin and its derivatives with regard to beauty, combined with absorption spectra of singular elegance."

The action of aniline on chlorophyll is a new branch of enquiry which the author hopes to resume.

The occurrence of chlorophyll in the animal organism is admitted on the authority of Prof. Ray Lankester, of Dr. McMunn, and of Pocklington. Its function is probably respiratory. As regards its duties in plants he considers that the carbonic acid, which forms one of its constituents, "being held more loosely combined than in an ordinary carbonate, and yet in a state of greater condensation than it would be in a mere watery solution, would be in a favourable condition for transfer to the assimilating plasma which effects its decomposition with elimination of oxygen." The chlorophyll then takes up fresh quantities of CO_2, acting, therefore, as a carrier of carbonic acid in the plant, just as hæmoglobin conveys oxygen in the animal economy.

In this memoir, which is illustrated with figures of absorption spectra, Dr. Schunck has not merely given an excellent summary of our present knowledge of the chemistry of chlorophyll, but he has added some novel facts of value and has pointed out paths for further research. The physicist, the chemist, and the biologist will alike read his results with interest.

On the Pentane Standard and Pentane Lamps. By A. V Harcourt, M.A., F.R.S., with an Appendix by W. Stepney Rawson. Birmingham: J. Wright and Co.

Now photometry has become an operation of constantly recurring necessity, the question of a standard which shall be convenient, trustworthy, and shall always give comparable results has become one of grave importance. The standard source of light legally recognised in this country is the sperm candle of a fixed size and weight. But, unfortunately, however carefully they may be prepared the quantity of light which they give out is not absolutely uniform. Spermaceti itself is not a definite chemical individual, and in practice the manufacturer adds to it a small proportion of beeswax—four or five per cent. Hence, the melting-point of the sperm as used is not absolutely constant. There is no definition given by the Acts of the number and size of the threads of the wick, the closeness of the plaiting of the strands, and the degree of tightness to which the threads are stretched, though all these conditions affect the light of the candle. Series of tests made with different samples of candles, both coming within the parliamentary definition, gave results differing by five or six per cent. The methods of using them admit also of variations which affect the results.

Hence, an amended standard appears desirable, and such is accordingly proposed by Mr. Vernon Harcourt. He suggests a pentane lamp, otherwise known as an "air-gas flame," as a normal source of light. Full instructions are here given for the preparation and use of this mixture.

From the experiments here mentioned it appears that the results obtained with the air-gas flame are decidedly more constant than those with the normal candle. We read that Mr. W. G. Wood, one of the official gas examiners, was instructed in Mr. Harcourt's method, and on that and the following day made a series of testings of a stored coal-gas alternately with Mr. H. B. Dixon. Mr. Wood made eight readings of the illuminating power, the lowest being 16·6 and the highest 16·9. Mr. Dixon made eleven readings, of which the lowest was 16·6 and the highest 16·8. Their mean results differed by less than $\frac{1}{10}$ candle.

In view of such satisfactory results the propriety of adopting the pentane lamp in place of the standard candle ought to be taken into serious consideration.

Water-Works Statistics, 1889. Edited by Charles W. Hastings.

Gas-Works Statistics, 1889. Edited by Charles W. Hastings.

The Gas and Water Companies' Directory, 1889. London: Hazell, Watson, and Viney.

Of these three useful compilations the "Water-Works" is the least complete. Not, it would evidently appear, from any neglect on the part of the Editor, but from the disinclination of the officials to fill up the schedules of inquiry. Why they should be less communicative than the authorities of gas-works it is not easy to see. We still find no returns from Aylesbury, Tring, Kingston, and Salford. This is the more striking as the Chiltern Hills Company, who supply the two former towns, have no reason to be ashamed of the quality of the water which they furnish. On page 4 is the intimation that a certain water requires to be hardened—a very unusual complaint, except for dyeing-blacks. The "character" of the waters is often given very vaguely. Thus, one water supply calls itself "softer than chalk-water generally."

We do not see that any gas-work has, this year, achieved the feat of selling more gas than it has made, but one little town has sold exactly the quantity which it produced. In the illuminating power of gas Scotland still takes the lead. Many are given at 30-candle power, Tain at 32, Stow and Banchory at 33, and Colinsburgh (oil-gas) at 65! We see no mention of the production of water-gas, which is, we believe, already manufactured on the large scale, and which has a great future before it if the difficulty of the possible escape of carbon monoxide can be prevented.

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. cviii., No. 20, May 20, 1889.

On the Terrestrial Origin of the Oxygen Rays in the Solar Spectrum.—J. Janssen.—(See p. 281).

The Impossibility of Diamagnetic Bodies.—P. Duhem.—The author concludes that the existence of diamagnetic bodies is incompatible with the principles of thermodynamics. To explain the existence of diamagnetic bodies in nature he reverts to the hypothesis of E. Becquerel, admitting that the supposed diamagnetic bodies are merely magnetic substances immersed in a medium more strongly magnetic.

The Variations of the Acid Function in Stannic Oxide.—Leo Vignon.—The author concludes that there exists an entire series of stannic acids, the first term of which is the soluble acid and the last is the ignited metastannic acid. These acids are formed by successive condensations, effected, not by the elimination of water, but by molecular transpositions coinciding with a gradual decrease in the intensity of the acid function.

On Oxalomolybdic Acid and the Oxalomolybdates.—A. Péchard. — Molybdic acid dissolves readily at a boiling heat in oxalic acid, yielding a syrupy liquid which crystallises on evaporation. The paper includes a description of the silver, barium, and sodium oxalomolybdates. Oxalomolybdic acid, if moist, turns blue on exposure to the sun's rays. Characters traced on paper with a solution of the acid on exposure to the sun quickly take an indigo-blue colour. This blue colour disappears on contact with water. If characters traced upon paper with the acid are very strongly heated they turn black, and are then no longer effaced by water.

On Phosphorous Acid. — L. Amat. — An aqueous solution of sodium pyrophosphite is converted into an acid phosphite the more rapidly as the solution is stronger and the temperature higher. The presence of an acid accelerates the transformation.

Action of the Alkaline Meta-, Pyro-, and Ortho-Arseniates upon the Alkaline Earthy Oxides.—M. Lefèvre.—In the researches it is found that calcium has a greater tendency to form chloro-arseniates than barium. On the other hand, barium has a greater tendency to form simple compounds than calcium, strontium taking an intermediate position.

On the Ammonium Malonates.—M. Massol.—A thermo-chemical paper, not admitting of useful abstraction.

The Proportion of Nitrates Contained in the Rain Water of Tropical Regions.— A. Müntz and V. Marcano.—One of the stations of observation selected by the authors is at Caracas (Venezuela), in 10° 3′ N. Lat., and at the elevation of 922 metres. The mean temperature is 21·8°, the rain-fall is irregular, and the storms severe and frequent. The observations extend over two years, and refer to 121 samples. The general mean of nitric acid was 2·23 m.grms. per litre. On one occasion it rose to 16·25 m.grms., and on another it was as low as 0·20 m.grms. On the contrary, at Liebfrauenberg, in Alsace, Boussingault found a mean of only 0·18 m.grm. nitric acid per litre, and at Rothamsted Messrs. Lawes and Gilbert obtained a mean of 0·42 m.grm. If we compare the total quantity of nitric acid thus brought down to the ground yearly, the difference appears still greater, as in tropical countries the annual depth of rain is generally greater than in temperate climates. At Caracas the rain-fall is about 1 metre. The quantity of nitrogen brought to the soil in the state of nitrate is 5·782 kilos. per hectare, whilst in Alsace it is only 0·330 kilo. and at Rothamsted 0·830 kilo. In the Island Reunion the mean nitric acid per litre of rain is 2·67 m.grms., or, taking the rain-fall at 1 metre, 6·93 kilos. of nitric nitrogen per hectare. In such climates the rain-fall alone supplies a nitrogenous manuring equal to about 50 kilos. of nitrate of soda yearly.

On the Richness of Wheat in Gluten.—E. Gatelier and L. L'Hote.—The authors conclude that the gross yield of grain and the proportion of gluten may be simultaneously increased by proper manuring and by the selection of suitable varieties.

The Alcoholic Fermentation of Milk.— M. Martinand.— Under certain conditions the alcoholic fermentation of milk, and its coagulation, may be effected with all kinds of yeast.

MISCELLANEOUS.

Pharmaceutical Society.—At a meeting of the Council of this Society on June 5th, Mr. Michael Carteighe was for the eighth time re-elected President. Mr. Alexander Bottle was re-elected Vice-President, and Mr. John Robbins Treasurer.

Action of the Alkaline and Earthy-Alkaline Metals upon the Animal Organisms.—A. Curci.—The author shows that rubidium and cæsium, like potassium, increase the pressure of the blood, and have the same characteristic action upon the pulse as potassium. Potassium, rubidium, and cæsium form a definite pharmacological group, all of which at first violently excite the muscular fibres of the blood-vessels, but in larger doses have a paralysing effect. Magnesium and calcium increase the pressure of the blood. Calcium, barium, and strontium have a peculiar effect upon the organs of circulation in cold-blooded animals. After the heart has come to a stop the striped muscles and the nervous system still act for a long time.

MEETINGS FOR THE WEEK.

Wednesday, 19th.—Meteorological, 7.
—— Geological, 8.
Thursday, 20th.—Royal, 4.30.
—— Chemical, 8. Ballot for the Election of Fellows.
Saturday, 22nd.—Physical, 3. "Researches on the Electrical Resistance of Bismuth," by Dr. Edmond Von Aubel.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that The Farbenfabriken vormals Friedrich Bayer and Co., of Elberfeld, in the Empire of Germany, have applied for leave to amend the Specification of Letters Patent No. 9606 of 1884 granted to William Weir Grieve for "Improvements in producing yellow colouring matter suitable for dyeing and printing."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 5th June, 1889.

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 month from the date of the said Journal.

(Signed)
H. READER LACK,
Comptroller-General.

J. H. JOHNSON & CO.,
47, Lincoln's Inn Fields, London, W.C.,
Agents for The Farbenfabriken vormals
Friedrich Bayer and Co.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that The Farbenfabriken vormals Friedrich Bayer and Co., of Elberfeld, in the Empire of Germany, have applied for leave to amend the Specification of Letters Patent No. 9162 of 1884 granted to John Erskine for "Improvements in producing yellow colouring matter suitable for dyeing and printing."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 5th June, 1889.

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Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 5th June, 1889.

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PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that The Farbenfabriken vormals Friedrich Bayer and Co., of Elberfeld, in the Empire of Germany, have applied for leave to amend the Specification of Letters Patent No. 3803 of 1885 granted to Herbert John Haddan for "Colouring matters obtainable by the combination of tetrazo-ditolyl or tetrazo-dixylyl salts with alpha- and beta-naphthylamine or their mono- and disulpho-acids, and process for the manufacture of the same."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 5th June, 1889.

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J. H. JOHNSON & CO.,
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Agents for The Farbenfabriken vormals
Friedrich Bayer and Co.

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PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that The Farbenfabriken vormals Friedrich Bayer and Co., of Elberfeld, in the Empire of Germany, have applied for leave to amend the Specification of Letters Patent No. 9510 of 1885 granted to Herbert John Haddan for "A new manufacture of violet and blue azo dyes."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 5th June, 1889.

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THE CHEMICAL NEWS.
VOL. LIX. No. 1543.

ON THE OCCURRENCE OF SKATOLE IN THE VEGETABLE KINGDOM.*

By WYNDHAM R. DUNSTAN, M.A., F.C.S.,
Professor of Chemistry to and Director of the Research Laboratory of the Pharmaceutical Society of Great Britain.

Celtis reticulosa is the name of a large tree growing in Java, whose wood possesses an intolerable odour. A few pieces of this wood, when distilled with water, yielded a minute quantity of a solid crystalline substance having a fæcal odour, which, after purification, melted at 93·5° C. It afforded a crystalline picrate, by the analysis of which the substance is shown to possess the composition of methylindole (C_9H_9N), and is proved to be identical with the Pr3-methyl-indole or skatole which Brieger isolated in 1877 from human fæces, and Salkowski afterwards obtained from the putrefaction products of various kinds of animal proteid. Nencki has observed the formation of the same substance when potash is fused with albumen, and it has also been prepared synthetically. Skatole from *Celtis reticulosa* corresponds in all its properties with synthetical skatole from propylidene-phenylhydrazide.

The occurrence of skatole in a plant has not hitherto been observed.

Indole is associated with skatole in human fæces, but no indole could be detected in the wood of *Celtis reticulosa*.

ON THIOCAMF—A NEW DISINFECTANT MATERIAL.†

By J. EMERSON REYNOLDS, M.D., F.R.S.

EVERY practical physician is asked from time to time "How can I most easily disinfect that room?" after infectious illness or death has occurred in a household: and the answer is by no means simple. The difficulty is to recommend anything sufficiently easy of application in which confidence can be placed.

Chloride of lime, Condy's fluid, carbolic acid, &c., are all more or less good if they can be brought into direct contact with the things to be disinfected; but that is just the difficulty in the case of a room, for mere exposure of the above-named substances in solution or otherwise in a chamber is useless. If carefully *sprayed* they—especially carbolic acid—can do effective work; but thorough spraying involves the presence of the operator in the room, to his discomfort and possible danger, or the use of costly and troublesome apparatus.

It is evident then that apartments can only be disinfected in any real sense by gases or vapours of very volatile substances which are known to possess the requisite power of destroying the vitality of various bacteria. We are therefore practically reduced to chlorine gas, nitrous fumes, or sulphur dioxide gas; but all the common methods for the production of these in sufficient quantity are more or less dangerous, and disinfection by them can only be properly carried out by skilled persons, since there is risk of corrosion by powerful acids, or of setting fire to woodwork, &c.

Since writing the chapter on "Disinfection and Contagion," in the "Manual of Public Health," I have sought some simpler means than is there recommended for disinfection of rooms, so that any intelligent person could attain the end in view without risk of fire, without the use of corrosive materials, or of large quantities of any agents, and without involving the presence of the operator in the room, or the employment of special apparatus.

This search has been successful, and I have now the pleasure of bringing under your notice the singular liquid which fulfils the conditions I have just specified, and to which the name of Thiocamf has been given.

The basis of this novel disinfectant is a very curious liquid which results when sulphur dioxide gas is brought in contact with camphor. At ordinary temperatures the gas alone requires a pressure of more than two atmospheres to liquefy it; but camphor, owing to chemical attraction, can liquefy the sulphur dioxide gas without any pressure whatever. In this liquid are dissolved several known bactericides, therefore Thiocamf is *all* disinfectant; but I am not free to enter into further particulars, as the patent specification has not yet been published.

A quantity of the liquid has been preserved in my laboratory for nearly two years in a corked bottle, and has not undergone sensible alteration during that time.

Thiocamf possesses almost unique properties; for, while it can be preserved *without* pressure in bottles at mean temperature, mere exposure of the liquid in a thin layer to the air determines the steady evolution of relatively enormous volumes of sulphur dioxide gas from it, charged with the vapours of other powerful disinfectants. These gases and vapours diffuse through the whole of the air of a well-closed room, and therefore must reach everything in the room if given reasonable time.

The question then arises whether the sulphur dioxide gas can destroy the bacteria—particularly the infective forms—when it reaches them. The evidence on this point has hitherto been of a rather loose kind, though the results led to the conclusion that sulphur dioxide gas is a powerful bactericide. Happily the truth of this conclusion has now been placed beyond doubt by a critical investigation of the subject, aided by modern methods of bacteriological study. This examination has been carried out in Paris by MM. Dubief and Bruhl, under the direction of Dr. Dujardin-Baumetz, and the results have been recently communicated to the Academy of Sciences. (*Comptes Rendus*, cviii., 324).

Starting with air rich in germs of various kinds, and combining Miquel's method of numbering the bacteria with alkaline culture, Dubief and Bruhl found that the germs were always reduced in number after the action of diluted sulphur dioxide gas; therefore the latter destroyed the vitality of bacteria. It was further found that the number destroyed increased with the duration of the action of the gas, and that this destructive action was accelerated when the humidity of the air was increased.

In all the experiments with the rather dilute sulphur dioxide gas used the *latter proved particularly fatal to micrococci* and allied bacteria, whether diffused through the air of a chamber or attached to its walls. As these are organisms of the class which true disinfectants seek to destroy, this testimony to the value of sulphur dioxide is of exceptional importance.

Lastly, those investigations have shown that sulphur dioxide gas is a true bactericide even in a dry state, though longer time is then required for the production of its full effect,

The bearing of these results on the value of Thiocamf is obvious, for if simple sulphur dioxide gas be the powerful bactericide MM. Dubief and Bruhl have proved, the mixture of sulphur dioxide with vapours of other disinfectants of acknowledged value should be a reliable combination. Moreover, there is no material that I know of, save Thiocamf, which can give off so large a relative volume of sulphur dioxide gas (the contents of a small six ounce bottle can afford over 20,000 c.c.) without any special treatment, save exposure in a very thin layer on

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* Abstract of a Paper read before the Royal Society, June 6, 1889.
† Read before the Royal Dublin Society, May 22nd, 1889.

an old tray or dish to the air of a room to be disinfected. Further, one ounce of Thiocamf shaken up with a quart of water forms a powerful disinfectant for ordinary purposes, such as sprinkling over various matters, purifying drains, &c.; while a still more dilute solution (one ounce to a gallon) can be used for soaking clothes which have been in contact with infected persons. The residue of Thiocamf has a pleasant aromatic odour.

This concentrated disinfectant can now be obtained at a cheap rate, as a company formed for its manufacture, can produce several hundredweight of Thiocamf per week.

NOTES ON BURMESE PETROLEUM.

By the late R. ROMANIS, D.Sc., Rangoon College.

The petroleum wells of Burma are found in two great groups: the Irrawaddy Valley, eastward of the Arracan Yoma, and the Kyauk-Pyn and Borongas group to the westward. The first, or Irrawaddy group, seems to be the longest known, having been worked for at least two centuries. It includes four districts, Yay-nan-chaung, Pagan, Yaw, and Mimbu. The first of these, Yay-nan-chaung, is the centre of the Burmese petroleum industry; at Pagan there is a group of a few wells worked in an indolent fashion; in the Yaw and Mimbu districts there are a few surface springs of petroleum, but no wells—in fact, the Yaw district is not yet opened up by roads, and is hardly known.

The petroleum from Yay-nan-chaung and Pagan is generally a viscous liquid of sp. gr. from 0·850 to 0·900, with a strong green fluorescence, solidifying about 24° C.; but curious variations have been observed even in closely adjacent wells.

The method of working is described in Yule's "Ava" and elsewhere. Shortly, it consists in sinking a well about 4 feet square, roughly lined with timber, through the strata of soft sandstone, shale, and limestone until the gas issuing from the sand stops further progress, generally at a depth of 300 feet, in a bed of shale with thin layers of sand.

The flashing-point of the fresh oil is about 3° or 4° above the melting-point, but, by the time it reaches Rangoon in the oil barges, the flashing-point rises to 35°, or even higher, by evaporation of the volatile portion. It contains a notable proportion of benzene, and 11 per cent of solid paraffin. When refined at Rangoon it yields about 30 per cent of burning-oil (flashing-point = 36), about the same quantity of lubricating and batching oil, and 5 per cent of solid paraffin. It was this substance that was examined by De la Rue and Miller, under the name of Rangoon tar (*Proc. Roy. Soc.*, viii., 21). Their specimen, no doubt, had lost the volatile part by exposure to the air during the long voyage down the Irrawaddy to Rangoon in earthern pots on board native boats. As now obtained, by American drills, from a greater depth than the natives could reach, and brought rapidly to Rangoon in tank barges, it generally contains gas in solution as well as benzene.

The only well in the Irrawaddy Valley, in the province of Lower Burma, at Padoukben, near Thayetmyo, produces petroleum of the same kind as Yay-nan-chaung.

To the westward of the mountains in the province of Arracan a different kind of oil is found. Arracan oil, whether from the Borongas or from Kyauk-Pyn, is a reddish brown limpid liquid, sp. gr. at 32° C. 0·825. It does not solidify. The flashing-point is 40° C. by Abel's test, and it, like the Yay-nan-chaung oil, contains much benzene and hydrocarbons of the aromatic series.

There are two groups of oil wells in Arracan, one in the Borongas islands, and the other near Kyauk-Pyn. A company was floated to work them by American methods, but resulted in failure from some cause or other, although the crude oil yields over 70 per cent of burning oil. There is some trade done by natives yet in this oil, which is used throughout Arracan for burning in lamps, being preferred to all others by the Arracanese.

The following is the result of the fractional distillation of a specimen from an unknown locality in Arracan; I believe from Kyaukpyn:—

Gas was evolved at 30° C. Liquid began to distil at 70° C.

70— 90°	3·1	per cent
90—100°	7·6	,,
100—130°	10·6	,,
130—200°	18·7	,,
200—300°	18·7	,,
Over 300°	12·5	,,
Heavy oil left in retort	8·0	,,
Paraffin crystals	3·1	,,
	82·3	,,
Loss	17·7	,,

The same distilled in a current of steam at—

100°	23·3	per cent
100—110°	33·0	,,
110—130°	29·3	,,
Residue	13·3	= heavy oil.

The strata in which this petroleum is found are much disturbed and full of faults; adjacent wells give very different results; and generally they soon run dry. At Yay-nan-chaung, although the geological features are similar, yet the duration of the wells seems much greater. The present out-turn at Yay-nan-chaung is about 15,000 tons per annum, but could be easily increased if there were a demand for it.

FURTHER NOTES ON THE VOLUMETRIC ESTIMATION OF NICKEL, WITH A NEW METHOD FOR ITS APPLICATION IN PRESENCE OF IRON, &c.

By THOMAS MOORE.

On a previous occasion I gave a description of a method for the volumetric estimation of nickel, by means of which a rapid and tolerably accurate determination of that metal may be arrived at. In following up the experiments it has been found that large quantities of ammonic salts, or the presence of manganese, interferes with the accuracy of the process. The presence of the former may be got rid of by employing the basic acetate method for the iron-nickel separation, instead of repeated precipitation by ammonic hydrate, and titrating the filtrate after the addition of a small quantity of ammonic hydrate with potassic cyanide, and certainly the results so obtained are sufficiently accurate for all practical purposes; nevertheless, there is still the unpleasant fact that the basic precipitation must be repeated at least three times, giving a large filtrate which requires some hours for its concentration before being reduced to a convenient volume, besides containing all the manganese, and, very often, some aluminium. Bearing these difficulties in mind, I endeavoured to find a process by which the presence of these foreign bodies would be rendered immaterial, or, at least, innocuous, with the result that iron, aluminium, zinc, and small quantities of manganese have no deleterious action whatever, and, furthermore, their preliminary separation is rendered quite unnecessary. This object is attained by adding to the slightly acid solution an excess of sodic pyro-phosphate until the precipitate which first formed is re-dissolved, and forms, even in presence of much iron, a practically clear colourless solution; this is then *slightly* acidified with hydrochloric acid, thereafter rendered distinctly alkaline with ammonic hydrate. To this solution the standard potassic cyanide (22 to 25 grms. KCN per litre) is added until the blue colour disappears; now add a measured quantity of cupric ferrocyanide emulsion, and continue the addition of the cyanide until the violet-brown colour is replaced by yellow, the formation of which is most distinctly seen when the titration takes place in an evaporating basin. It will be at once noticed that a great advantage gained by this process is that the necessity for the separation of iron, &c., is done away with. In those cases where zinc is present, the potassic cyanide must be added slowly, and only until the colour of the cupric ferrocyanide disappears, as in this case if titrated until the yellow appears, the results are too high.

In place of an emulsion of cupric ferrocyanide, a solution of the same in ammonic oxalate may be employed, thus dispensing with the necessity of agitating previous to use, and rendering it more uniform.

Subjoined I give a few of the results obtained by this process, compared with those obtained by the usual methods for electro-deposition, which amply testify to its accuracy and utility.

	Electro-deposition. P.c. Ni.	Volumetric. P.c. Ni.
Mineral 1 (containing Ni, Fe, Mg, Al)	6·65	6·62
,, 2 ,, ,,	7·00	7·05
,, 3 ,, ,,	12·45	12·45
,, 4 ,, ,,	13·98	14·04
German silver ,, ,,	11·25	11·31
,,	18·66	18·69

Thio, New Caledonia.

DETERMINATION OF NITRIC NITROGEN BY MEANS OF FERROUS SULPHATE.

By M. BAILHACHE.

Pelouze first applied the reaction of nitric acid with the ferrous salts for the determination of nitrates, making use of ferrous chlorides. This method is defective; Fresenius declared the results variable, and enumerated the chief causes of their want of accuracy. In consequence, all the agricultural stations have adopted the method of Schlœsing with Grandeau's modification. This method has been applied for a long time by the author at the Agricultural Laboratory of Seine-et-Oise. Its tediousness and the frequency of absorptions compelled him to seek for a method equally accurate and more expeditious. Such a method he considers that he has found in a modification of the process of Pelouze. Instead of the chloride he uses ferrous sulphate strongly acidulated with sulphuric acid. He thus avoids the losses of iron by volatilisation against the heated sides of the flask, which often happens when the chloride is used. Further, as the sulphuric solution of ferrous sulphate boils at a higher temperature, the whole of the nitric oxide is more rapidly expelled.

The apparatus consists of a flask marked at 250 c.c., to which is fitted a caoutchouc stopper traversed by two tubes. One of these is from 5 to 6 c.m., and is drawn out at its upper end. The second tube descends to half a c.m. from the bottom of the flask. It is surmounted with a funnel fitted with a tap, having a cylindrical form and a capacity of 35—40 c.c. This funnel serves not only for the introduction of the nitrate to be examined, but also for the gentle influx at the beginning and the end of the operation of a solution of sodium hydrocarbonate, the carbonic acid of which, at the outset, expels the air of the apparatus, and at the end drives out the last traces of nitric oxide.

For titrating the residue of iron not peroxidised, the author uses potassium dichromate, potassium ferricyanide serving as indicator.

The following solutions are needed:—Ferrous sulphate containing per litre 100 grm. actual sulphate, and 75 c.c. of monohydrated sulphuric acid; potassium bichromate containing per litre 17·85 grms. of the pure dry salt; a solution of sodium nitrate containing 50 grms. of the pure dry salt per litre; and a solution of sodium hydrocarbonate saturated in the cold. The chromic solution peroxidises exactly its own volume of the ferrous solution, and both correspond to 10·192 grms. sodium nitrate per litre.

To carry out the process there are introduced into the flask 50 c.c. of the ferrous sulphate solution and 25 c.c. of monohydrated sulphuric acid. The flask is shaken up, and the stopper, with its two tubes, is inserted. The flask is then set on a sand-bath capable, if needful, of holding five or six such flasks. The tap is shut and 25 c.c. of the sodium hydrocarbonate solution are placed in the funnel. The tap is then regulated so that this liquid may flow in drop by drop. The liquid boils, and the ebullition continues as the funnel empties. Before all the liquid has run off there are introduced into the funnel 10 c.c. of the standard solution of sodium nitrate.

At this moment the operator concentrates his attention on the continuity of the ebullition and the regular escape of the nitric oxide, which ought never to become tumultuous and never to stop.

As the liquid escapes from the funnel the contents of the flask become more and more deeply brown. The tap is closed before the funnel is completely empty. When the deep brown colour of the liquid has disappeared, 25 more c.c. of the solution of hydrocarbonate are introduced into the funnel and let flow gently into the flask; the tap is closed and the fire withdrawn. It is then let cool, the volume is made up with distilled water, the flask is shaken, and the residual iron not peroxidised is titrated with the chromic solution.—*Comptes Rendus*, Vol. clviii., No. 21.

OXIDATIONS BY MEANS OF THE ELECTRIC CURRENT.*

By EDGAR F. SMITH.

In using the electric current for the determination and separation of metals, it occurred to me that its oxidising power might be utilised to convert sulphur and other elements into higher oxides, thus bringing them into forms in which they could be readily determined. To test this I undertook the oxidation of the sulphur in chalcopyrite after the following manner: About ten grms. of solid potassium hydroxide were placed in a small nickel crucible, and carefully heated over a Bunsen burner until the water was expelled, when the flame was reduced, so that its heat was just sufficient to retain the alkali in liquid form. The crucible was put in connection with the positive pole of a battery, and the powdered mineral placed upon the alkali. A heavy platinum wire, from the negative pole, extended just under the surface of the fused mass, and, when the current was passed, a lively action ensued, accompanied with considerable spattering. Loss was prevented by placing a perforated watch-crystal over the crucible. When the action had continued for ten minutes the connection was broken, the crucible and its contents allowed to cool, placed in a beaker, covered with water, and warmed upon an iron plate. On filtering off the insoluble oxides the filtrate was blue in colour, due to a little copper. The liquid was acidulated with hydrochloric acid, and care taken to detect any hydrogen sulphide or sulphur dioxide, which are always present, when the oxidation of the sulphur is incomplete. In this particular case all the sulphur was changed to sulphuric acid and removed as barium sulphate. When ignited the

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* Chemical Section of the *Journal of the Franklin Institute*, April, 1889.

latter presented a perfectly white appearance, showing not the slightest trace of iron.

Having succeeded so well with the first portion I weighed off 0·1734 grm. chalcopyrite, subjected it to a like treatment, and obtained 0·4086 grm. $BaSO_4$=0·0561 grm. S or 32·35 per cent S. One of my students oxidised another portion (0·5 grm.) of the same material with nitric acid and potassium chlorate and obtained 32·54 per cent sulphur.

The current used above registered one ampère (10·45 c.c. HO gas) per minute as it passed through the fused alkali. The solution containing the potassium sulphate contained no iron. A little copper was present in it. The residue of oxides (Fe_2O_3, CuO, &c.) should dissolve readily and completely in warm hydrochloric acid. There may, however, be a residual mass, red in colour, but this can be disregarded, as it is only metallic copper. In some of the oxidations the wire attached to the negative pole was coated red by copper, or with a black deposit of metallic iron. The idea suggested itself to me that, as the metal was depositing as such, it might possibly inclose some mineral, as yet unacted upon, and thus withdraw it from the field of oxidation. I therefore invariably, in every determination, reversed the current for a few minutes before its final interruption. This seems to have been unnecessary with chalcopyrite, but was required with some other minerals with which similar experiments were tried.

With a chalcopyrite different from that analysed before the following percentages of sulphur were obtained :—

(1) 29·9 p.c. S—(2) 30·11 p.c. S—(3) 29·7 p.c. S.

The quantity of mineral used was in (1) 0·1528 grm., in (2) 0·1445 grm., and in (3) 0·1082 grm. About 10 grms. of potassium hydroxide were used in each determination. The current was one ampère, acting for a period of ten minutes. In working with a quantity of mineral varying from 0·2 — 0·3 grm. the quantity of alkali should be doubled.

This method affords a rapid oxidation of sulphur to sulphuric acid, so that the inconveniences arising from the slow time-consuming method with nitric acid and potassium chlorate, or that with nitric acid alone, can be avoided, where a current of the strength indicated above can be obtained.

Iron salts also are removed. I have endeavoured to oxidise the sulphur of pyrite by this means, but thus far the experiments have been fruitless. I have not obtained more than half of the sulphur in the form of sulphate. Even when the current acted for thirty minutes the result was no better. The cause of this singular behaviour appears to be due to the presence of the iron. I expect, however, to so modify the experiment in this case that pyrite may yet be as easily oxidised as chalcopyrite.

As time permits this mode of oxidation will be extended to other natural sulphides and to compounds containing sulphur.

My experiments in oxidising with the current really began with chromite. It was treated the same as the chalcopyrite. Twice I obtained a little over fifty-three per cent Cr_2O_3 from a specimen of this mineral, which, by an older method, gave fifty-four per cent Cr_2O_3. At present I am not prepared to say anything more in regard to this mineral. Some difficulties have appeared which require solution before entering into details.

Nickel crucibles, as well as iron, have been used in this work, and with chromite an old platinum vessel was made to do service. The crucibles were one and one-fourth inches in height, and one and three-eighths inches wide; the most convenient form would be that measuring two inches in length and one and one-half inches in width.

In closing I must extend my sincere thanks to Mr. D. L. Wallace, of this laboratory, for his kind assistance, without which it would have been impossible for me to carry out these experiments at this time.

University of Pennsylvania, Philadelphia.

A PLATINIFEROUS NICKEL ORE FROM CANADA.

By F. W. CLARKE and CHARLES CATLETT.

During the autumn of 1888 we received through two different channels, samples of nickel ores taken from the mines of the Canadian Copper Co., at Sudbury, Ont. From one source we obtained two masses of sulphides, to be examined for nickel and copper; from the other source came similar sulphides, together with a series of soil and gravel-like material, seven samples in all. In the latter case an examination for platinum was requested, and in five of the samples it was found, the gravel above mentioned yielding 74·85 ozs. of metals of the platinum group to the ton of 2000 lbs. At the outset of the investigation we were decidedly incredulous as to the existence of platinum in such ores; but the discovery of sperrylite by Mr. Wells in material from the same mines gave our work a wholesome stimulus, and the assays were carefully carried through.

The sulphide ores submitted to us from Sudbury were all of similar character. They consisted of mixed masses, in which a grey readily tarnishing substance was predominant, with some chalcopyrite, possibly some pyrite, and a very little quartz. Two samples were examined in mass; one gave 31·41 per cent of nickel with a little copper, the other gave 35·39 per cent of nickel, and 5·20 of copper. The nickel mineral itself proved to be a sulphide of nickel and iron, and as ores of that composition are not common, it was thought desirable to examine the substance further.

As above stated, the nickel mineral is the predominating constituent of the masses submitted for examination. It is steel-grey, massive, and exceedingly alterable in the air, and its specific gravity, determined by picnometer, is 4·541. An analysis of carefully selected material gave the following results :—

Ni	41·96
Fe	15·57
SiO_2	1·02
Cu	0·62
S	40·80
	99·97

Neither cobalt nor arsenic could be detected.

The foregoing figures work out sharply into the ratio R : S : : 4 : 5; and approximately into the formula Ni_3FeS_5. If we deduct silica, together with the copper reckoned as admixed chalcopyrite, and re-calculate the remainder of the analysis to one hundred per cent we have the following figures :—

	As found	Calc. as Ni_3FeS_5.
Ni	43·18	44·6
Fe	15·47	14·4
S	41·35	41·0
	100·00	100·0

In short, the mineral has the composition Ni_4S_5, with *about* one-fourth of the nickel replaced by iron. The only known species with which this agrees is Laspeyres's polydymite, of which the Sudbury mineral is evidently a ferriferous variety. What relations it may bear toward beyrichite, pyrrhotite, &c., is as yet a matter of considerable uncertainty. Probably in most cases the niccoliferous constituent of pyrrhotite is millerite, but other sulphides, like the polydymite, may perhaps occur also.

The polydymite which was selected for the above analysis came from the mass in which, in average, 35·39 Ni and 5·20 Cu had previously been found. The mass weighed several kilogrms., and was remarkably free from quartz. The same mass, with two smaller pieces resembling it, were also examined for platinum, by the following method:—One assay ton of the finely ground ore was treated with nitric acid until all or practically all of the sulphides had been dissolved. The dried residue was then assayed in the usual manner; except that, to facilitate cupellation, a little pure silver was introduced into the lead button. From the final bead the silver was dissolved out by sulphuric acid, leaving the platinum in a finely-divided grey powder. The latter dissolved easily in aqua regia, and gave all the reactions needful to identify it thoroughly. The results were as follows, "A" representing the large mass in which the polydymite was determined.

A	2·55 ozs. Pt to the ton, or	0·0087	per cent
B	1·8 „	„ 0·0060	„
C	7·0 „	„ 0·024	„

That the metal weighed was nearly all platinum is certain; but it may have contained small amounts of other metals of the same group. The material separated was not sufficient to warrant a search for the rarer associates of platinum. Probably the platinum exists in the ore as sperrylite, although this point was not proved. The amount of platinum in the mass most thoroughly examined would require to form sperrylite only about 0·007 per cent of arsenic, which is too small a quantity for detection by ordinary analysis. That platinum should exist in appreciable quantities in an ore of such character is something quite extraordinary. Whether it could be profitably extracted is an open question.—*American Journal of Science*, Vol. xxxvii., May, 1889.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 4th, 1889.

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

Professor Mendeleeff's Faraday lecture on the Periodic Law of the Chemical Elements, owing to the enforced absence of the lecturer, was read by the Secretary.

At the conclusion of the lecture, a vote of thanks to Professor Mendeleeff was moved by Professor Frankland and seconded by Sir F. A. Abel.

The Faraday medal was then presented by the President to Mr. Anderson, by whom it was received on behalf of Professor Mendeleeff.

June 6th, 1889.

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

Messrs. Alfred Edward Sibson, M. Carleton Williams, C. W. Priestley, A. L. Stern, T. E. J. Cridland, and B. Brauner were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frank Thornton Addyman, Queenwood College, Hants; Charles Frederick Baker, B.Sc., 27, London Road, N.W.; John Simpson Ford, 11, Abbotsford Park, Edinburgh; J. T. Norman, 2, Mornington Road, Regent's Park, N.W.; Sydney Steel, Fairlawn, Blackheath; John Bishop Tingle, Jäger Strasse, F/iv., Munich.

The President drew attention to the large number of interesting papers to be brought before the Society that evening, and expressed the hope that the authors present would endeavour to give an account of the essentially important points in their communications without entering into details which could not be appreciated by listeners. He was of opinion that communications made at the meetings should almost invariably be of a different character to the published papers, and should be divested of details; and he ventured to express the hope that authors generally would accept this suggestion.

The following papers were read:—

52. "*Experimental Researches on the Periodic Law. Part I., Tellurium.*" By B. Brauner, Ph.D.

The author gives a detailed account of his attempts to determine the atomic weight of tellurium by as many different methods as possible; in all 11 were adopted, but each gave a different result, varying from 125—140. He eventually succeeded, but with great difficulty, in preparing what appeared to be pure tellurium tetrabromide, and on most carefully analysing this obtained the value Te = 127·64 (O = 16). This number, however, is incompatible with the position of tellurium in the periodic system, and having satisfied himself that there were no experimental errors which could account for the discrepancy, the author was forced to conclude that what had hitherto been regarded as pure tellurium contained foreign elements. By submitting tellurium solutions to a systematic fractional precipitation, he has, in fact, succeeded in obtaining a variety of substances, some of which are undoubtedly novel elements. One of these it is proposed to call *Austriacum* (*Austrium*). In all probability this is the *Dvi-tellurium* (212), the probable existence of which was pointed out for the first time by Mendeleeff in his recent Faraday lecture. From analyses made with material, the uniformity of which is not yet quite established, the author is satisfied that the atomic weight of the element in question approaches very closely to that indicated by Mendeleeff. In addition, there is at least one other novel constituent, and this appears to be more or less closely allied to arsenic and antimony. It follows that true tellurium has yet to be discovered, and that its atomic weight and properties remain to be determined.

Discussion.

Mr. J. Newlands remarked that he had always placed tellurium below iodine; he had no doubt that the exceptional atomic weight would ultimately be rectified, and that true tellurium, when isolated, would be found to have an atomic weight near 125.

53. "*The Amylodextrin of W. Nägeli and its Relation to Soluble Starch.*" By Horace T. Brown and G. Harris Morris, Ph.D.

Amylodextrin, described by W. Nägeli in 1874, is prepared by the long-continued action of cold dilute acids on intact starch-granules; when purified by dissolution in water and precipitation with alcohol, it forms crystalline spherules, closely resembling the well-known spherules of inulin. Amylodextrin is coloured a reddish brown by iodine. The values obtained on analysis of the purified substance were—

$[\alpha]_j$ .. 3·86 206·25° κ .. 3·86 9·07°

which correspond to a percentage composition of—

Maltose	..	14·87	which requires	$[\alpha]_j$ ..	3·86	205·4°
Dextrin	..	85·13		κ	3·86	9·07
		100·00				

The substance is shown to be a definite compound: (*a*) by its absolute unfermentability by ordinary top fermentation yeast; (*b*) by the impossibility of differentiating it by fractional precipitation or partial dissolution; (*c*) by its passing through a dialyser in an unaltered form; and (*d*) by its distinct crystalline form.

The authors consider amylodextrin to be analogous in composition to the malto-dextrin previously described by them (*Trans.* xlvii., 528), and assign to it the formula $C_{12}H_{22}O_{11}\cdot(C_{12}H_{20}O_{10})_6$; *i.e.*, it may be regarded as constituted of one *amylon* or maltose group in combination with six *amylin* or dextrin groups.

A determination of the molecular weight by Raoult's method gave the following numbers :—

	Calculated for $\left\{\begin{matrix}C_{12}H_{22}O_{11}\\(C_{12}H_{20}O_{10})_6\end{matrix}\right.$.	Found (mean).
A	0·0096	0·0086
M	1962·0	2220·0

Amylodextrin, like malto-dextrin, is rapidly and completely converted into *maltose* by the action of diastase.

The authors point out that amylodextrin has been confused by former workers with soluble starch on the one hand, and with the so-called starch-cellulose on the other hand. From these substances it is differentiated by its solubility, its iodine colouration, and its behaviour with diastase and with acids. When acted on by diastase, soluble starch yields a mixture of maltose and dextrin corresponding to the No. 8 equation of the authors' previous papers, whilst amylodextrin is completely converted into maltose by the same treatment. The authors also show that soluble starch is the first product of the action of cold dilute acids on starch, and that this is slowly hydrolysed to amylodextrin, a portion of the starch substance at the same time going into solution as dextrose.

54. "*The Determination of the Molecular Weights of the Carbohydrates.*" Part II. By Horace T. Brown and G. Harris Morris, Ph.D.

After referring to their former paper on this subject (*Trans.*, 1888, 610), and stating that the results there given have been since confirmed by Tollens and Mayer (*Ber.*, 1888, 1566, and 3508), and by de Vries (*Compt. Rend.*, cvi., 751), the authors give the results of the determination by Raoult's method of the molecular weights of the following carbohydrates :—

Galactose.

	Calculated for $C_6H_{12}O_6$.	Found (mean).
A	0·106	0·1073
M	180·0	177·0

Inulin.

	Calculated for $2(C_{36}H_{62}O_{31})$	Found (mean).
A	0·0096	0·0087
M	1980·0	2176·0

Kiliani has assigned the formula $C_{36}H_{62}O_{31}$ to inulin, but the authors' results point to the correct value being double this. They have already shown the great similarity between amylodextrin and inulin as regards their physical properties (see preceding Abstract), and they are inclined to regard the two substances as closely analogous in composition, thus :—

$$\left\{\begin{matrix}(C_{12}H_{22}O_{11})_2\\(C_{12}H_{20}O_{10})_4\end{matrix}\right.; \qquad \left\{\begin{matrix}C_{12}H_{22}O_{11}\\(C_{12}H_{20}O_{10})_6\end{matrix}\right.;$$

Inulin; M=1980. Amylodextrin; M=2286.

although the amylin and amylon groups in each possess very different optical and other properties, and the products of hydrolysis with dilute acid are very different.

Malto-dextrin.

	Calculated for $\left\{\begin{matrix}C_{12}H_{22}O_{11}\\(C_{12}H_{20}O_{10})_2\end{matrix}\right.$.	Found (mean).
A	0·0191	0·0197
M	990·0	965·0

Starch.— It was found impossible to apply Raoult's method to starch-paste; solutions of soluble starch produced so slight a depression that no reliable results could be obtained: a number of fairly concordant results, however, pointed to a molecular weight of 20,000 to 30,000. In order to ascertain whether the failure in this case was due to a high molecular weight, and not to the fact that the method was inapplicable to colloid substances, an arabinic acid, having a rotatory $[\alpha]_j = +61·16°$, was examined; this gave A=0·0265, M=717·0, thus rendering it probable that the small influence exercised by soluble starch was due to its high molecular weight.

Indirect evidence was then sought for by an examination of the dextrins. The authors have previously shown that when starch is broken down by diastase, a resting stage in the reaction is reached when the amount of dextrin produced corresponds to *one-fifth* by weight of the starch taken, and that *the molecule of this stable dextrin is one-fifth of the size of the starch-molecule from which it has been derived.* Determinations made with several specimens of this low dextrin gave the following mean values :—

	Mean values.	Calculated for. $20C_{12}H_{20}O_{10}$.
A..	0·0030	0·0029
M	6221·0	6480·0

and consequently the formula of soluble starch would be $5(C_{12}H_{20}O_{10})_{20}$, and its molecular weight 32,400. The endeavour was also made to apply Raoult's method to the determination of the question whether the dextrins are a series of polymers, or whether they are simply metameric. For this purpose a number of the higher dextrins were prepared from starch-transformations which had been stopped at an early stage of hydrolysis. All the numbers obtained show that the freezing method affords no evidence of there being any difference in molecular weight between the high and low dextrins, the numbers being, in fact, almost identical.

From a consideration of the results obtained with soluble starch and with dextrins of varying position in the series, the authors conclude that the evidence points to the conclusion that the dextrins are metameric and not polymeric compounds. They therefore abandon their former working hypothesis of the hydrolysis of starch, and now suppose the starch-molecule to consist of four complex amylin-groups, arranged round a fifth similar group, constituting a molecular nucleus. When hydrolysis takes place this complex is broken up, four amylin-groups being liberated, which in turn are capable of undergoing complete hydrolysis into malto-dextrins, and ultimately into maltose, whilst the fifth amylin group which constituted the nucleus of the original molecule, resists the action of hydrolysing agents and forms the stable dextrin of the No. 8 equation.

Each amylin group of the five has the formula—

$$(C_{12}H_{20}O_{10})_{20},$$

corresponding to a molecular weight of 6480; the molecule of soluble starch being represented by $5(C_{12}H_{20}O_{10})_{20}$, corresponding to a molecular weight of 32,400.

Discussion.

Dr. Gladstone remarked that the observations made by Mr. Hibbert and himself on the molecular weights of colloid substances completely confirmed those now brought forward by the authors. He believed Raoult's method to be capable of distinguishing polymers, as satisfactory results had been obtained on examining polymeric C_5H_8 compounds.

Dr. Armstrong remarked that as both the universal applicability of Raoult's method and the molecular weights of colloids were in question, neither was at present a safe standard. He was not satisfied with the conclusion arrived at in the case of the dextrins.

55. "*Researches on Silicon Compounds. Part V.*" By J. Emerson Reynolds.

The author has already shown that silicon tetrabromide unites with some amidic compounds, especially thiocarbamide, allyl-, phenyl-, and diphenyl-thiocarbamides, without loss of halogen, and produces compounds of the type $(CSN_2H_4)_8SiBr_4$. In this part a detailed account is given of the products of interaction of silicon haloids with excess of aniline, orthotoluidine, and paratoluidine, and the three following bodies are described which result from the complete substitution of halogen by NHR-groups derived from the amido-compounds.

Silicotetraphenylamide, $Si(NHC_6H_5)_4$, a beautiful crystalline body, is obtained from its carbon disulphide solution in fine monoclinic forms which have been subjected to a determined crystallographic examination by Professor Sollas.

Silicoparatolylamide, $Si(pNHC_7H_7)_4$, is obtained from its benzene solution in botryoidal masses of fine needles; it is but slightly soluble in ligroin, and therefore is precipitated by it from a benzene solution.

Silico-orthotolylamide, $Si(oNHC_7H_7)_4$. This differs from the para-compound in being soluble in ligroin. When the mixed benzene and ligroin solution is distilled a very thick syrupy liquid remains which, after long exposure in a vacuum, gradually affords a quantity of minute needles which do not exhibit any tendency to form aggregations.

56. "*The Isomerism of the Alkyl-derivatives of mixed Diazoamido-compounds.*" By R. Meldola, F.R.S., and F. W. Streatfeild.

The authors first describe a detailed series of experiments undertaken with the object of testing the chemical individuality of the mixed diazoamide—

$$(p)NO_2\cdot C_6H_4\cdot N_3H\cdot C_6H_4\cdot NO_2(m),$$

and its alkyl-derivatives. A critical study of the compound has served to confirm the former result that this compound and its alkyl-derivatives are perfectly definite, and that they cannot be formed by crystallising together the corresponding symmetrical compounds. Mixtures of $(p)NO_2\cdot C_6H_4\cdot N_3H\cdot C_6H_4\cdot NO_2(p)$ and—

$$(m)NO_2\cdot C_6H_4\cdot N_3H\cdot C_6H_4\cdot NO_2(m)$$

can be easily separated into their constituents by crystallisation from alcohol. The same holds good for the corresponding ethyl-derivatives, which are equally capable of being separated whether formed separately and afterwards mixed or whether a mixture of the unalkylated compounds is first prepared and then afterwards ethylated by the authors' method. A more extended study of the mixed diazoamides containing a halogenised radicle has served to convince the authors that the mixed diazoamides are most difficult to prepare in a state of purity, owing to the tendency to the formation of the corresponding normal (symmetrical) compounds at the same time. It is pointed out as a result of this experience that all the mixed diazoamides prepared by Continental investigators have been of very doubtful purity, and that in nearly all cases a nitrogen determination only has been considered sufficient to establish the composition. It is shown that the presence of one or the other of the normal compounds might thus escape detection, as a considerable percentage of such an impurity would not affect the percentage of nitrogen beyond the ordinary limits of experimental error. Criticising their own former work in the light of this experience, the authors have come to the conclusion that the diazoamides from para- and meta-nitraniline are not so well adapted for ascertaining when a pure product is obtained as those mixed compounds which form the subject of the present paper, and which contain a halogenised radicle on one side of the N_3H-group. The mixed compound derived from the two nitranilines might obviously contain some of the dipara- or dimeta-compound without affecting the analytical numbers, since both sides of the N_3H-group have the same composition. Many new preparations have, therefore, been made and studied, and the melting-points revised with the following results:—

$(p)NO_2\cdot C_6H_4\cdot N_3H\cdot C_6H_4\cdot NO_2(m)$	212—213° (instead of 211).
$(p)NO_2\cdot C_6H_4\cdot N_3(C_2H_5)\cdot C_6H_4\cdot NO_2(m)$	151—155° (instead of 148).

This vagueness of melting-point has been found to be a very general character of all the alkyl-derivatives of mixed diazoamides prepared by direct alkylation, and is attributed to the circumstance that the melting-point is also the point of decomposition, this instability being especially observable in the case of the compounds containing strongly acid radicles. The authors re-state their original proposition, viz., that every pair of amines, $X\cdot NH_2$ and $Y\cdot NH_2$, can give rise to *three* isomeric alkyl-derivatives:—

1. By the action of diazotised $X\cdot NH_2$ on $Y\cdot NHR'$.
2. By the action of diazotised $Y\cdot NH_2$ on $X\cdot NHR'$.
3. By the direct alkylation of $X\cdot N_3H\cdot Y$.

A large number of triplets have been prepared, all of which conform to this proposition. Their formulæ and melting-points are:—

I.	$(p)NO_2\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot Br(p)$	151—151·5°
	$(p)Br\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot NO_2(p)$	163—164
	$(p)NO_2\cdot C_6H_4\cdot N_3(CH_3)\cdot C_6H_4\cdot Br(p)$	150·5—151·5°
II.	$(p)NO_2\cdot C_6H_4\cdot N_2\cdot N(C_2H_5)\cdot C_6H_4\cdot Br(p)$	139—140°
	$(p)Br\cdot C_6H_4\cdot N_2\cdot N(C_2H_5)\cdot C_6H_4\cdot NO_2(p)$	124—125
	$(p)NO_2\cdot C_6H_4\cdot N_3(C_2H_5)\cdot C_6H_4\cdot Br(p)$	115—116
III.	$(m)NO_2\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot Br(p)$	144°
	$(p)Br\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot NO_2(m)$	160·5—161°
	$(p)Br\cdot C_6H_4\cdot N_3(CH_3)\cdot C_6H_4\cdot NO_2(m)$	125—137·5 (much decomposition
IV.	$(m)NO_2\cdot C_6H_4\cdot N_2\cdot N(C_2H_5)\cdot C_6H_4\cdot Br(p)$	111°
	$(p)Br\cdot C_6H_4\cdot N_2\cdot N(C_2H_5)\cdot C_6H_4\cdot NO_2(m)$	135—136°
	$(p)Br\cdot C_6H_4\cdot N_3(C_2H_5)\cdot C_6H_4\cdot NO_2(m)$	96—117 (much decomposition
V.	$(p)Br\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot CH_3(p)$	113—114°
	$(p)CH_3\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot Br(p)$	99—99·5°
	$(p)CH_3\cdot C_6H_4\cdot N_3(CH_3)\cdot C_6H_4\cdot Br(p)$	97—97·5
VI.	$(p)Cl\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot CH_3(p)$	99·5—100°
	$(p)CH_3\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot Cl(p)$	91—92
	$(p)CH_3\cdot C_6H_4\cdot N_3(CH_3)\cdot C_6H_4\cdot Cl(p)$	80—82

The isomerism of these triplets is shown not only by their melting-points, but also by their products of decomposition by cold hydrochloric acid. These products have, in all cases, been examined quantitatively, and the general results are shown by the equations—

1. $X\cdot N_2\cdot NR'\cdot Y + HCl = X\cdot N_2\cdot Cl + Y\cdot NHR'$.
2. $Y\cdot N_2\cdot NR'\cdot X + HCl = Y\cdot N_2\cdot Cl + X\cdot NHR'$.
3. $2X\cdot N_3R'\cdot Y + 2HCl = X\cdot N_2\cdot Cl + Y\cdot N_2\cdot Cl + X\cdot NHR' + Y\cdot NH\cdot R'$

From this it appears that the alkyl-derivatives of the mixed diazoamides always split up, like the unalkylated products, into a mixture of the two diazochlorides and two alkylamines. The most feasible interpretation of these facts is that the *mixed* diazoamides have double the molecular weight usually assigned to them, and in support of this conclusion the authors have discovered that the mixed alkyl-diazoamides can be synthesised by simply boiling the alcoholic solutions of the other two isomerides of the triplet, thus:—

$$X\cdot N_2\cdot NR'\cdot Y + Y\cdot N_2\cdot NR'\cdot X = (X\cdot N_3R'\cdot Y)_2.$$

This observation must necessarily lead to a considerable modification in the existing views respecting the constitution of the diazoamides generally, and experiments in the direction indicated are being carried on both by means of Raoult's method of determining molecular weights as well as by purely chemical methods.

57. "*The Atomic Weight of Zinc.*" By J. H. Gladstone, Ph.D., F.R.S., and Walter Hibbert.

The authors have observed that when amalgamated zinc is used as anode in a zinc sulphate voltameter, the metal dissolved appears to be free from impurity. This they attribute to the electro-chemical relations between zinc and its ordinary impurities, the latter being less readily attacked than the more electro-positive metal. Results obtained in different voltameters with the same current showed a very close agreement, and the authors therefore determined the atomic weight of zinc by applying Faraday's law of electrolysis.

For this purpose a series of copper, silver, and zinc voltameters were arranged in a simple circuit, and the quantity of zinc dissolved was compared with the weights of deposited silver and copper.

The results of five experiments are given, but as two zinc voltameters were employed in each, the data afford ten comparisons of the equivalents of silver and zinc, and eight comparisons of those of zinc and copper. The mean ratio of the equivalents of silver and zinc is 3·298 ± 0·00008. Taking the atomic weight of silver as 107·93, this ratio gives 65·44 as the atomic weight of zinc. If silver is taken as 107·66, zinc = 65·29.

The copper sulphate voltameter is not so accurate as the silver one, owing to the solvent action of the solution on copper. But by keeping the density of the current within certain limits, this action can be made extremely small. Still the ratio *Zn* : Cu given by the experiments (1·0322) is probably rather higher than it ought to be. There is also uncertainty as to the atomic weight of copper, but the authors have used W. N. Shaw's value, 63·33. This gives 63·33 × 1·0322 = 65·37 as the atomic weight of zinc.

The two comparisons indicate 65·3 as being very near the true value. This is higher than the results obtained in recent years by Marignac, Baubigny, Morse, and Burton, but lower than that given by Reynolds and Ramsay.

58. "*The Amount of Nitric Acid in the Rain-water at Rothamsted, with Notes on the Analysis of Rain-water.*" By R. Warington, F.R.S.

Determinations of chlorine and sulphuric acid have been made in the Rothamsted rain-water for several years, and new determinations of ammonia for five years (*Trans.*, 1887, 501); new determinations of nitric acid are now communicated.

The first method employed involved the concentration of 10 lbs. of rain-water with a little magnesia, filtering, and determining the nitric acid as nitric oxide gas by Schloesing's method. This plan gave low results with the stronger rain-waters; the loss apparently took place during the last stage of the concentration, being due to a reduction of a portion of the nitrates by the agency of the organic matter and lead which the water contained.

The method finally adopted involves the reduction of the nitric acid to ammonia by means of the copper-zinc couple. 1 litre of the water is boiled in a retort with magnesia till 250 c.c. have distilled; in the distillate the ammonia present in the water is determined; the residue is diluted to 800 c.c., copper-zinc couple added, and the whole allowed to stand three days at 20—24°; the ammonia present is then determined by distillation and Nesslerising, and its equivalent in nitric acid calculated.

The rain of twenty months, analysed by the copper-zinc method, contained an average of 0·138 of nitrogen as nitric acid per million of water; this is a little higher than that found by Way in 1855—56, namely, 0·12 per million, but is almost identical with that found by Frankland as a mean of his analyses of Rothamsted rain in 1869—70. In a whole year, 1888—89, with a rain-fall of 29·27 inches, the quantity of nitric nitrogen in the rain was 0·917 lb. per acre, and the nitrogen as ammonia 2·823 lbs., or a total of 3·74 lbs. These quantities are compared with those found by other experimenters.

A brief account of the methods employed at Rothamsted in determining the ammonia, chlorine, and sulphuric acid in rain is then given.

59. "*The Product of the Action of Sulbhur on Resin.*" By G. Harris Morris, Ph.D.

Pelletier and Walter, in 1838, described a solid hydrocarbon which they separated from the products of the distillation of resin; later observers obtained a similar product by distilling resin with sulphur. The author has examined this latter substance.

The hydrocarbon separates from its solutions in alcohol, benzene, &c., in pale yellow crystalline scales, which melt at 84—85° C.; it boils without decomposition slightly above the boiling-point of mercury. Its composition is expressed by the formula $(C_5H_6)_n$; the density, determined by Victor Meyer's method, using the vapour of sulphur, was 160·07, whilst $(C_5H_6)_5$ requires 165.

From the examination of a number of its derivatives the author concludes that Kelbe is wrong in regarding the substance obtained by the action of sulphur on resin as identical with retene.

60. "*The Vapour-pressures and Specific Volumes of Similar Compounds of Elements in Relation to the Position of those Elements in the Periodic System.*" Part I. By Sydney Young, D.Sc.

Determinations have been made of the vapour-pressures and specific volumes of the four haloid derivatives of benzene, and also of benzene itself, within very wide limits of temperature; benzene, fluobenzene, and chlorobenzene having been heated to their critical points, 288·5°, 286·55°, and 360·8° respectively.

It is shown that if the four haloid derivatives are compared at such temperatures that their vapour pressures are equal, the (absolute) temperatures and also the specific volumes bear a constant ratio to each other, whatever the common pressure.

But on comparing benzene with one of its haloid-derivatives it is found that these simple relations do not hold. The ratios of the absolute temperatures of benzene and fluobenzene corresponding to equal pressures are very exactly expressed by the equation $R' = R + ct$, where R' is the ratio at a pressure for which the corresponding centigrade temperature of fluobenzene is t, $R = 0{\cdot}0838$, and $c = 0{\cdot}0000313$.

If the specific volumes of benzene and fluobenzene are compared at temperatures corresponding to pressures which are in all cases proportional to the critical pressures of the two liquids, the ratios of the volumes are found to be very nearly constant. If, again, the specific volumes are compared at absolute temperatures which are in all cases proportional to the absolute critical temperatures, the ratios of the volumes are again nearly constant. But the two methods of comparison are not equivalent—though that is stated to be the case by Van der Waals—and they cannot both be correct, for it cannot be taken as even approximately true that the absolute temperatures corresponding to pressures which are always proportional to the critical pressures are themselves proportional to the absolute critical temperatures. Moreover, the values obtained by the two methods of comparison are not quite the same, and for two liquids which are chemically dissimilar, the values may differ considerably. It is impossible at present to say with certainty which method of comparison gives the better results, but the author is inclined to think that the comparison at "proportional" or "corresponding" pressures is most likely to be correct.

The relations of Van der Waals as regards "corresponding" temperatures, pressures, and specific volumes of liquid hold good accurately in the case of the haloid-derivatives of benzene, but the critical pressures of the haloid-derivatives are *equal* and the comparisons must therefore be made at *equal* pressures.

Fluorine, chlorine, bromine, and iodine belong to the same group in the periodic table; the effect of substituting one of these elements for another in the compounds of the type C_6H_5R, as regards the relations between vapour-pressure, temperature, and specific volume, is extremely simple, but if hydrogen be substituted for one of the halogens, the changes produced are much greater.

61. "*The Vapour-pressures of Quinoline.*" By Sydney Young, D.Sc.

Four years ago Dr. Ramsay and the author, in describing their method of obtaining constant temperatures (*Trans. Chem. Soc.*, 1885, 640, and 1886, 37), gave tables of the vapour-pressures of various pure liquids from 0° to 360° C. One of these, methyl salicylate, gives less satisfactory results than the others, and it is proposed to substitute quinoline for it. Determinations of the vapour-pressures of quinoline are described, and a table is given for each degree between 180° and 240°.

PHYSICAL SOCIETY.

June 8, 1889.

Prof. Ayrton, F.R.S., Vice-President, in the Chair.

Dr. Bond and Mr. Britton were elected Members.

The following communications were made:—

A "*Photograph of Lightning Flashes*" was exhibited and described by Dr. Hoffert.

The photograph was obtained during the storm on the 6th inst., whilst the camera was being waved about in the hands, and shows three similar and parallel flashes, thus proving that successive sparks in multiple flashes may traverse the same path and may be separated by appreciable intervals of time. The supposed primary spark is intersected by numerous tributary ones spreading out on both sides, the second spark shows one tributary, and the third none. Faint bands of light pass across the plate parallel to the direction of motion, and these prove that some residual illumination exists during the intervals between the successive flashes. Evidence of a dark flash is also presented by the plate.

Prof. Herschel, who had taken photographs during the same storm, referred to the fluttering appearance of the flashes and on their long duration; in many cases the time was sufficient to allow him to direct the camera towards the flash and make a successful exposure. He had also observed multiple flashes with the unaided eye, and on waving his hand about he had sometimes noticed about a dozen distinct images of it during one discharge.

Mr. Gregory said that he watched the storm along with two others, and they could seldom agree as to the shape of the flashes, or on their simple or multiple character. The want of agreement as to multiplicity he thought might be caused by their eyes being directed towards different parts of the sky when a multiple flash occurred; the one who happened to be looking towards the flash might be conscious of only one impression, whereas the others, in directing their eyes, would receive the flashes on different parts of the retina. In some cases as many as three distinct flashes (occurring at intervals of about ten seconds) traversed the same path, and a number of the discharges presented a beaded or striated appearance. The beads seemed to remain after the main flash had faded, and this might account for the bands shown in Dr. Hoffert's photograph.

Mr. C. V. Boys, in referring to multiple flashes, said that although his statements made in the discussion of Mr. Whipple's paper on April 13th were not readily accepted, yet no one who watched the recent storm could doubt their existence.

Prof. S. P. Thompson thought the order of the flashes on the photograph may have been the reverse of that supposed, for he observed that the bands of light extended on both sides of the (so-called) primary flash, whereas the outside of the third flash was quite dark.

Mr. E. W. Smith noticed many cases of "sympathetic discharge," in which a flash in the north seemed to precipitate another in the N.W. within a few seconds, and in this he was corroborated by Mr. Gregory, who viewed the storm from a different locality.

Mr. C. V. Burton thought the heating of the air by the first spark of a multiple flash might give rise to the tributary sparks in subsequent ones.

Mr. A. W. Ward mentioned a long flash observed at Cambridge, which passed from the zenith and struck some farm buildings at a distance, and he was particularly impressed by the considerable time occupied in its progress.

"*On the Methods of Suppressing Sparking in Electro-Magnets.*" By Prof. S. P. Thompson, D.Sc.

The object of this paper is to classify the methods which have been suggested, and to draw attention to a novel method of some importance. The classification is as follows:—(1) *Mechanical Devices:* (*a*) simple snap switch; (*b*) break in magnetic field; (*c*) break under liquid; (*d*) wiping breaks (asbestos, &c., brushes); (*e*) blow-out. *Electrical Devices:* (A) use of condensers, (*a*) placed across gap, and (*b*) across terminals of magnet; (B) mutual induction protectors, (*a*) copper sheath around core and (*b*) layers of foil between winding; (C) short-circuit working; (D) differential winding; (E) high resistance shunt (non-inductive); (F) voltameter or liquid resistance across gap; (G) multiple wire arrangement of Mr. Langdon Davies; (H) electro-magnet with two bobbins in series or parallel.

The merits and demerits of the different methods are indicated. The multiple-wire arrangement used by Mr. Langdon Davies in his harmonic telegraph consists in winding each layer separately and uniting all in parallel. The effect of this is to make the time constants of the layers different, and on breaking the circuit the energy is spent in mutual discharges.

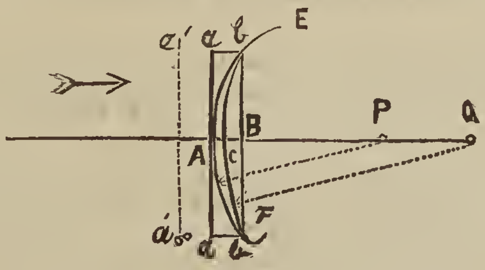
"*A Shunt Transformer.*" By Mr. E. W. Smith.

Two conductors, A and B, of equal impedance, are placed in series between alternate current mains, and the same mains are connected through two incandescent lamps in series. The conductor A has great resistance and B has large self-induction, and when their junction is joined to that of the two lamps both lamps become brighter, and the main current is reduced. These phenomena were shown before the Society. Since A may consist of lamps and B may be a choking coil the arrangement will serve to increase the P.D. between the terminals of the lamps without wasting much energy.

Experiments of a similar nature have been made on a Mordey transformer wound with three equal coils. One coil was used as primary and the other two as separate secondaries, their respective circuits consisting of lamps and an alternate current motor. Under these conditions the arithmetical sum of the mean secondary currents exceeded the primary current by 14 per cent; the secondary volts were 8 per cent less than the primary. All these experiments strikingly illustrate the effects of acceleration and lag in alternate current circuits, and (as was pointed out by the author) show that meters registering "ampère-hours" merely may give readings differing greatly from the numbers representing the energy used.

"*Notes on Geometrical Optics:* (1) *On the Deduction of the Elementary Theory of Mirrors and Lenses from Wave Principles;* (2) *On a Diopteric Spherometer;* (3) *On the Formula of the Lenticular Mirror.*" By Prof. S. P. Thompson.

Instead of deducing the formulæ for lenses and mirrors by means of "rays" and the relations between angles of incidence, reflection, and refraction, the author considers it better to derive them from the curvatures impressed on waves at the bounding surfaces of the different media. Indices of refraction are replaced by their reciprocals, which express the relative velocities of light, and curvature is measured by the camber at the middle of chords of equal (but small) length. An example will assist in



making the method of treatment clear. Suppose a', a'; a, a; two successive positions of a plane wave front in air, which impinges on a curved surface E A F at A, and let the curvature at A be R and the velocity constant of the substance h. Then, whilst the part a travels in air to b, the part in the denser medium reaches C where $\text{A C} = h \,.\, a\, b$ and a curvature, F, represented by B C, is impressed on the wave, which thus converges to at point, Q. Since $\text{A C} = h \,.\, a\, b = h \,.\, \text{A B}$ and—

$$\frac{\text{B C}}{\text{A B}} = \frac{\text{A B} - \text{A C}}{\text{A B}} \therefore \frac{\text{B C}}{\text{A B}} = 1 - h,$$

and the relation between the impressed curvature and that of the surface becomes $\text{F} = \text{R}\,(1 - h)$.

By successive application of the above methods all the ordinary lens problems may be treated, and the resulting expressions are simplified by being expressed in curvatures. The ordinary mirror formula, $f = \frac{r}{2}$ becomes $\text{F} = 2\text{R}$, and that for the lenticular mirror $\text{F}' = 2\text{R} + \text{F}$. The method readily lends itself to the determination of the changes in the shape of wave-fronts entering or emerging from surfaces of irregular outline.

The diopteric spherometer has its outer feet situated on a circle of 44·71 m.m. radius, and is provided with a screw of 1 m.m. pitch. The instrument so constructed reads off directly in "diopteries," *i.e.*, curvatures expressed on a scale in which that of a sphere of one metre radius is taken as unity.

"*On the Use of the Biquartz.*" By Mr. A. W. Ward.

This is a mathematical investigation into the causes of the varying degrees of accuracy obtained by different observers who have used the biquartz in rotation measurements. Assuming that elliptically polarised light passes through the biquartz, the equation which must be satisfied to give equality of tint on the two halves is shown to be $\cos 2\psi \,.\, \sin 2\phi \,.\, \sin 2\,\overline{\omega - \theta} = 0$, where $\tan \psi =$ ratio of axes of ellipse, $\phi =$ rotation produced by quartz for wave-length λ, $\theta =$ angle between plane of vibrations of analyser and that of $x\,z$, the axis of z being parallel to the direction of transmission, and $\omega =$ angle between one axis of the ellipse and that of x. The equation is satisfied by either $\cos 2\psi = 0$, or $\sin 2\phi = 0$ or $\sin 2\,\overline{\omega - \theta} = 0$. The first solution relates to circularly polarised light and need not be considered; the second can only hold for one particular wave-length, depending on the thickness of the quartz, and in interpreting the third solution it is shown that a satisfactory result is only obtained when the light is plane polarised. The deductions are in accordance with experiment, for the biquartz has been used with considerable accuracy when experimenting on isotropic media, but with doubly refracting substances, where the light is liable to become elliptically polarised, the results are very discordant.

NOTICES OF BOOKS.

The Uses of Plants: A Manual of Economic Botany, with Special Reference to Vegetable Products Introduced during the last Fifty Years. By G. S. Boulger, F.L.S., F.G.S. London: Roper and Drowley.

This interesting work opens with a historical introduction. Here we learn that in 1838 it was actually proposed to abolish the Kew Botanical Gardens. The author omits, however, to give us the names of the persons responsible for so disgraceful a proposal. He considers that the increased variety of raw vegetable products now imported is due in part to "free trade" and in part to the "International" Exhibitions. We should suspect that the Imperial Exhibition of 1886 would do much more for the introduction of new materials than any of the "International" displays. Nor does he notice the fact that products from the tropical regions, even those forming part of the British Empire, are introduced into continental regions sooner than into this country. Mr. Boulger points out that as so much has been done in economic botany without the aid of science much more may be hoped for from the systematic application of the principles of research. The mention of the nutritive value of the banana reminds us of the difficulty always experienced in introducing any new article of food to the British public. Thus, the yam could be sold here at a lower price than the potato, but, as the author tells us, "it is not appreciated." We believe that it was more frequently used in the last century than it is now.

In speaking of sugars the author omits to state that bees are perfectly able to distinguish beet-sugar from cane-sugar and prefer the latter, and that they repudiate Fahlberg's "saccharine" altogether.

Solanum maglia, from Chili, may, the author hopes, prove capable of general cultivation in Britain as a disease-proof substitute for the potato.

The flavour of pears, it is said, "may be due to isoamylic acetate,"—a very judicious reservation. If we may judge from their physiological action, the so-called artificial fruit-essences are not identical with the natural flavours of fruits. There is no mention of the billberry, a much more pleasant fruit than the unsweetenable cranberry, rich in gallic acid.

Mr. Boulger deplores with good right the increasing sale of absinthe in Britain. It always seems to us strange that none of our temperance reformers propose the prohibition of its importation and sale.

The artificial vanilla does not seem to have greatly interfered with the cultivation of the natural product. Mention is made of a novel fraud in coffee, its adulteration with or substitution by bad figs, roasted and powdered.

It must not be supposed that this book is of interest merely to botanists. For manufacturers on the look-out for new raw materials it will prove a valuable handy book of reference.

An Elementary Text-Book of Chemistry. By William G. Mixter, Professor of Chemistry in the Sheffield Scientific School of Yale University. Second and Revised Edition. London: Macmillan and Co.

This book, which, though published in London, is evidently and admittedly printed in the United States, presents, at any rate, one feature of distinction from the almost endless array of chemical manuals—it is based upon the periodic classification. Strangely enough we can find in it no mention of the originator of this system, Mr. Newlands! It is scarcely necessary to say that no errors are to be detected in the descriptions of the elements, their compounds, and their reactions.

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. cviii., No. 21, May 27, 1889.

Exact Determination of the Quantity of Water contained in the Blood.—MM. Gréhant and Quinquaud.—In a dog the blood in the femoral vein contains 77·09 per cent of water, whilst that of the femoral artery contains 78·01 per cent. The plentiful introduction of water into the stomach raises the proportion slightly.

Determination of Urea in the Blood and in the Muscles.—MM. Gréhant and Quinquaud.—In 100 grms. of the blood of a rabbit the authors found 35·1 m.grms. of urea, and in the same weight of the muscles 37·8 m.grms. In another experiment the respective proportions were 98·2 and 107·3 m.grms. Hence they conclude that the urea is formed in the muscles.

The Expansion of Metals at High Temperatures.—H. Le Chatelier.—For all the metals the coefficient of expansion increases with the temperature. The law of increase is generally regular, anomalies having been observed only with some alloys of silver and with all varieties of iron.

Researches on Rotatory Magnetic Polarisation in Iceland Spar.—H. Chauvin.—Iceland spar possesses a rotatory magnetic power not merely along the axis, but also in directions inclined to the axis. Along the axis the magnetic action is a simple rotation of the incident vibration. In directions forming angles with the axis the action of the field generally produces at once a rotation and a transformation of the incident rectilinear vibration into an elliptical vibration. The rotation changes its direction periodically, becoming null for a series of particular directions. These phenomena are identical with those occurring in quartz crystals.

The Electro-conductivity of Saline Solutions. Reciprocal Displacements of Acids.—P. Chroutschoff.—The author's conclusions are that acetic acid is entirely displaced by hydrochloric acid. Sulphuric acid displaces almost entirely tartaric acid in combination with soda, though there are indications of a slight sharing. A sharing takes place between acetic and tartaric acids. But in very dilute solutions the former acid is entirely displaced. In a mixture of sodium acetate and oxalic acid there is a division of the base.

The Electric Resistance of Bismuth.—E. Van Aubel.—Bismuth cannot be obtained pure by chemical processes of precipitation. A determination of the electric conductivity is the most convenient and accurate method of ascertaining the purity of bismuth, and especially the absence of lead. Prof. Classen electrolyses a solution of impure bismuth, when pure metal is deposited at the negative pole and the lead, as peroxide, at the positive pole.

The Combustion-heat of Some Organic Compounds.—J. Ossipoff.—The substances examined in this thermo-chemical paper are racemic acid, hydrated and anhydrous, methyl racemate, and methyl dextro-tartrate.

Some Methods of Producing Mercury-Ammonium Chlorides.—G. André.—The action of dilute ammonia upon a solution of mercuric chloride gives rise either to mercury chloramidide or dimercuriammonium chloride or to a mixture of both compounds. The reaction is different if, along with the mercuric chloride, there is added an equivalent quantity of potash, thus forming yellow mercuric oxide, upon which a solution of ammonium chloride is then poured, or if a portion only of the mercuric chloride is decomposed by potash and ammonia is poured upon the mixture of chloride and oxide. In these cases there is produced, in part at least, tetra-mercuriammonium chloride.

On Certain Metallic Sulphides.—Armand Gautier and L. Hallopeau.—The authors, after referring to a former paper (*Comptes Rendus*, 1889, April 15th) describe the action of carbon disulphide upon nickel, chrome, and lead. In each case a sulphide is obtained. The nickel compound Ni_2S has a metallic appearance and a yellowish lustre. It is absolutely non-magnetic. It does not decompose water, either hot or cold. It is but very slowly attacked by hydrochloric or sulphuric acid. Arfvedson's sulphide, Ni_2S, must have contained metallic nickel. The action of carbon disulphide upon chrome produces the well-known sesquisulphide. The vapours of carbon disulphide convert lead into galena, mixed, at times, with lead sulphocarbonate.

The Presence of Sodium Sulphate in the Atmosphere.—F. Parmentier.—The author traces this fact to the wide distribution of this salt in the soil and to its tendency to crystallise on the surface of porous bodies, whence it is carried away by the wind. An interesting fact mentioned is that if sodium sulphate is allowed to crystallise between plates of unglazed porcelain in the open air, and if the crystallisation is reproduced two or three times by sprinkling with water, the plates fall into powder. The same phenomenon is observed with very hard stones. This crystallisation may be a cause of the comminution of rocks which resist water.

On Cyanacetophenone, Ortho-methyl-cyanacetophenone, and Ortho-toluyl-acetic Ether. General Method of the Synthesis of β-Acetonic Ethers of the Aromatic Series.—A. Haller.—This paper does dot admit of useful condensation.

Action of Potassium upon Triphenylmethane.—M. Hanriot and O. Saint-Pierre.—The authors inquire if the phenyl group, C_6H_5, the presence of which rapidly decreases basicity in the phenylamines, does not suffice to impress acid properties on an adjacent atom of hydrogen.

Determination of Nitric Nitrogen by Means of Ferrous Sulphate.—M. Bailhache.—(See p. 293).

Journal fur Praktische Chemie.
Vol. xxxix., No. 4, 1889.

On Benzyl Acetate and Similar Bodies, Particularly their Behaviour with Chlorine and Bromine.—E. Seelig.—In this memoir the author discusses the substitution of the fatty halogen by acid groups, the action of chlorine upon benzyl acetate, as also that of bromine upon benzyl acetate and parabenzylacetate; the behaviour of chlorine with ethyl benzoate, ethyl acetate, and phenyl acetate; the action of bromine upon phenyl acetate; the behaviour of the esters with hydrochloric acid; and the reaction of chlorine and bromine with toluol.

On Some Di-molecular and Tri-molecular Nitriles.—E. von Meyer.—This paper does not admit of useful abstraction.

On Ortho-nitro-ethyl-aniline and Some of its Derivatives.—A. Hempel.—A preliminary communication.

MISCELLANEOUS.

The London Hospital.—H.R.H. the Duke of Cambridge, K.G., has kindly consented to present to Sir Andrew Clark, Bart., F.R.S., the Senior Consulting Physician of the London Hospital, on July 15, his portrait by the late Frank Holl, which was exhibited at the Royal Academy's Exhibition last year, and subscribed for by the medical and surgical staff and friends of the Hospital. A replica of the painting will, at the same time, be presented to the College. H.R.H. will afterwards distribute the prizes to the Students and the Nursing Probationers.

The Use of Potassium Manganate in Analysis.—Ad. Jolles (*Repertorium der Anal. Chemie*).—An alkaline solution of manganate has the property of forming, in contact with certain metallic oxides, insoluble compounds of constant composition. Upon this reaction the author has founded a method for the volumetric determination of manganese and of cobalt. For determining manganese he adds to a measured quantity of a slightly alkaline solution of potassium manganate the manganous salt in question, constantly shaking the vessel until the supernatant liquid becomes colourless. There is thus produced manganese peroxide free from manganous oxide, which readily subsides, so that the completion of the reaction is distinct. The determination of cobalt is effected in a corresponding manner.

MEETINGS FOR THE WEEK.

Wednesday, 26th.—Society of Arts, 4. (Anniversary).
Thursday, 27th.—Royal Socitty Club, 6.30. (Anniversary).
Friday, 28th.—Quekett Club, 8.

MESSRS. BELL'S PUBLICATIONS.

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London: GEORGE BELL AND SONS,
4, York Street, Covent Garden, W.C.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that The Actien Gesellschaft für Anilin Fabrikation (Assignees), have applied for leave to amend the Specification of Letters Patent No. 4415 of 1884 granted to Gerard Wenzeslaus von Nawrocki for "Improvements in the manufacture of colouring matters."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 12th June, 1889.

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 month from the date of the said Journal.

(Signed),
H. READER LACK,
Comptroller-General.

ABEL AND IMRAY,
Agents for the Applicants,
28, Southampton Buildings, London, W.C.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that The Actien Gesellschaft für Anilin Fabrikation (Assignees), have applied for leave to amend the Specification of Letters Patent No. 3724 of 1882 granted to Frank Wirth for "An improved manufacture of certain sulpho-acids and of colouring matters therefrom."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 12th June, 1889.

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 month from the date of the said Journal.

(Signed),
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THE CONDITIONS OF THE REACTIONS BETWEEN COPPER AND NITRIC ACID.[*]

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

Introduction.

About fifty years ago De La Rive[†] observed that pure metallic zinc but slowly enters into reaction with dilute sulphuric acid; shortly afterwards Faraday[‡] confirmed this observation in the case of amalgamated zinc. In the course of some investigations on the equivalent of this metal, Ramsay and Reynolds[§] failed to obtain any hydrogen from sulphuric acid and samples of zinc which they had purified by every possible precaution. Thus the evolution of hydrogen from zinc and sulphuric acid depends initially upon the presence of some third substance, be it an impurity of the acid or of the metal.

Similarly Russell[||] has also observed that metallic silver is slowly attacked by nitric acid freed from any considerable quantity of nitrous acid, and that the rate with which the change proceeds depends upon the proportion of nitrous acid present.

Reactions between Copper and Nitric Acid.

The changes which take place when metallic copper is dissolved in nitric acid have attracted the attention of a number of investigators; the complexity of these changes and their almost infinite variety produced by slight variations of the conditions, are evidenced by the elaborate researches of Deville,[¶] Armstrong,[**] with Acworth and Divers.[††] In the present communication I have the honour of laying before the Royal Society a short and preliminary account of some experiments on the conditions necessary for a reaction to take place between metallic copper and nitric acid.

The Methods of Experiment.

By means of a mechanical device, described fully in another paper before the Chemical Society, spheres of the purest electrotype copper procurable were placed on a small glass dish which was kept continually revolved in dilute nitric acid; a fairly uniform current of carbonic acid was also passed through the liquid to ensure its perfect agitation, and thus to remove the products of the reaction from the immediate vicinity of the metal.

The nitric acid was made up in considerable quantity at a time by diluting acid of sp. gr. 1·41 with a suitable proportion of water; the specific gravity of the diluted acid was taken by means of a very delicate picnometer of the form devised by Sprengel, and the amount of free acid determined in the same portion by the ordinary process of acidimetry. The weight of the copper sphere, as also its diameter, was determined before and after each experiment, which lasted for one hour; from the diameters the mean area of metallic surface exposed was calculated; thus the amount dissolved off per unit area could be directly determined.

In some earlier experiments made with a view of ascertaining this amount, it was noticed that when the sphere of copper was introduced into the acid the evolution of gas did not commence at once, but if, other conditions remaining the same, the sphere was introduced into the acid containing in small quantities the products of the reaction of a former experiment, the evolution of gas commenced immediately. Further, the amount of copper dissolved per unit area was less in the first than in the succeeding experiments, after that the products of the change had been allowed to accumulate in the acid. This will be rendered more evident by the figures given in the table below, the first two columns of which contain the weights of two copper spheres, A and B (placed alternately in the acid), before and after each experiment, the third the differences between these two numbers, the fourth the mean area in square m.m., and the fifth the amounts dissolved off per unit area expressed as decimilligrms. per square m.m. surface, written for the sake of brevity M/A. In this and all succeeding experiments a long-range thermometer was used.

Table I.

Sp. gr. of acid at 19° compared with water at the same Temperature = 1·1699. Percentage of free nitric acid = 27·53. Temperature 25°.

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of M/A.
4·4153 (A)	4·0768	0·3385	291·95	11·60
4·5823 (B)	4·2049	0·3774	300·05	12·38
4·0768 (A)	3·7378	0·338	275·83	12·25
4·2049 (B)	3·8465	0·3584	283·16	12·65
3·7378 (A)	3·4166	0·3125	261·23	12·37
3·8465 (B)	3·5268	0·3197	266·78	12·10
3·4166 (A)	3·1188	0·2975	246·52	12·07

It will be seen from the above table that the amount dissolved off per unit area in the first experiment is less than that in the succeeding experiments, when the products of the change were present in the acid.

In another series of experiments the nitric acid used in the first operation was rejected, and another portion of the same sample was taken for the second operation; but for those succeeding this latter was used again. It was observed that in the first two experiments the evolution of gas did not commence immediately after the introduction of the sphere into the acid, whereas in all the succeeding experiments this was the case.

Table II.

Sp. gr. of acid at 19° = 1·1643. Percentage of free nitric acid = 27·02. Temperature 20° C.

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of M/A.
4·762	4·6519	0·1102	313·16	3·52
4·6519	4·5451	0·1068	307·29	3·48
4·5451	4·3823	0·1628	300·41	5·42
4·3823	4·2303	0·1520	293·23	5·20
4·2303	4·0838	0·1475	286·77	5·29
4·0838	3·9456	0·1383	280·15	5·05

It will be manifest from the above table that the values for the amount dissolved off per unit area on the first two experiments are concordant among themselves, as also are those of the succeeding experiments, but that those of the former are lower than those of the latter.

When copper is dissolved in nitric acid, the substance more immediately evident to the senses is cupric or cuprous nitrate or nitrite, or possibly a mixture of some of them; at first I was inclined to the belief that the copper salt was the third substance which induced the reaction between the metal and the nitric acid to start at once. Indeed, at a meeting of the Chemical Society I expressed this opinion in the course of a debate.

It was found subsequently that the dilute nitric acid used in the above experiments contained a small trace of nitrous acid. Accordingly a sample of nitric acid of sp. gr. 1·41 was freed from nitrous acid by passing a rapid stream of air through it at a temperature not ex-

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[*] A Paper read before the Royal Society, June 6, 1889.

[†] *Annales de Chimie*, vol. xliii., 1830, p. 425.

[‡] "Experimental Researches," Series VII., p. 863.

[§] *Chem. Soc. Journ.*, 1887 (*Trans.*), p. 854.

[||] *Chem. Soc. Journ.*, 1874, p. 3.

[¶] *Compt. Rend.*, lxx., pp. 20 and 550.

[**] *Chem. Soc. Journ.*, 1877, p. 54.

[††] *Chem. Soc. Journ.*, 1883, p. 443.

ceeding 35° C.; during the process the acid was protected from direct sunlight. If the temperature rose to 40° C., or the acid was not properly sheltered, nitrous acid was formed by the decomposition of the nitric acid at a rate faster than that at which it was oxidised by the air current. The acid was subsequently diluted with the required quantity of water and preserved in a dark cupboard. When 3—4 c.c. of this diluted acid were mixed with about 100 c.c. of water, no blue colour was produced on addition of starch and potassium iodide solutions, and the faintest possible orange tinge imparted to an aqueous solution of meta-phenylene-diamine-hydrochloride. The acid was thus free from any considerable trace of nitrous acid. Experiments similar to the above were repeated, but the current of carbonic acid omitted, in order to more precisely fix the conditions.

After introduction of a copper sphere there was no evolution of gas for three minutes, and five minutes after that the reaction had set in a considerable quantity of nitrous acid was shown to be present. As regards the production of nitrous from nitric acid under these conditions, Professor Armstrong writes, in a note appended to a paper by Dr. Divers:* "With reference to the formation of N_2O_4 during the dissolution of metals, &c., I some time ago satisfied myself by experiment that it is produced . . . . and there is, I believe, no doubt that, whatever the nature of the reducing agent, be it hydrogen or metal, ... the primary product of the reduction of nitric acid is nitrous acid." This observation, made some time ago, is amply confirmed by the above and succeeding experiments. I would, therefore, merely wish to call attention to the short interval of time which elapses between the commencement of the reaction and the formation in considerable quantities of nitrous acid. Again, when the copper sphere was introduced into the acid containing the copper salt and the nitrous acid, the evolution of gas commenced at once.

In another experiment, in which the copper sphere was previously heated and then allowed to cool in a current of hydrogen to remove any superficial coating of cupric or cuprous oxide, no gas was evolved for 1 min. 50 secs. after the introduction of the sphere into the acid, and 4 min. 30 secs. after the reaction had set in an abundance of nitrous acid was shown to be present.

At this point, Mr. Harcourt, from a recollection of some experiments by the late Sir Benjamin Brodie, suggested to me to place into the acid a substance which should remove the nitrous acid as fast as it might be formed; urea fulfils this requirement, in that it reacts immediately with nitrous acid to form nitrogen and carbonic acid, according to the equation—

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O.$$

Accordingly 1 grm. of urea, dissolved in 1 c.c. of water, was added to a litre of nitric acid (sp. gr. $\frac{19}{19}$ = 1·1662, percentage of nitric acid = 27·25), into which was also placed 0·9445 grm. of copper nitrate (prepared by dissolving a few of the discarded copper spheres in dilute nitric acid, evaporating the solution over the water-bath, and twice re-crystallising from water). At a temperature of 25° C. no gas was evolved for two minutes after insertion of the copper sphere; it was then taken out, the liquid agitated mechanically, and the sphere again introduced; no gas was evolved for 2 mins. 50 secs. A further quantity of 2 grms. urea, dissolved in 2 c.c. water, was introduced and the experiment repeated; no gas was evolved for 7 min. 30 secs. These experiments show that even in the presence of a small quantity of copper nitrate the addition of comparatively small proportions of urea will temporarily prevent the solution of the copper. It also appeared that when once the reaction had set in it could not be stopped, even though there were present in the acid more than sufficient urea to destroy the nitrous acid which might have been formed. For after agitation of the liquid the copper was again unattacked by the acid. If, then, the apparently purely local formation of nitrous acid could be prevented, it might be possible to prevent also any reaction between the copper and nitric acid from taking place.

To test this point, 1 grm. of urea dissolved in 1 c.c. of water was added to a litre of nitric acid taken from the same sample as that used in the preceding experiments. The little glass dish was more quickly rotated by means of the machine, and a very rapid current of carbonic acid passed in, so that the whole liquid was kept in violent agitation. The copper sphere was introduced, the acid being heated to 25° C. During an interval of *one hour* no gas was evolved, no blue colour imparted to the acid, no alteration of the metallic surface apparent, and the loss in weight experienced was only 0·0025 grm. Whereas, if all other conditions had remained the same, except that the nitrous acid had been initially present and had been allowed to accumulate, the loss of weight from a sphere exposing a surface of 256·85 m.m. would have been about 0·3 grm. (calculated from the results given in Table I., the conditions of the experiments in the two cases being practically identical). This experiment might doubtless have been allowed to proceed for a longer time with the same result.

It shows, I believe, that *pure copper will not dissolve in pure dilute nitric acid*, for though the proportion of nitric acid to that of urea present was, under these conditions, 272·5 : 1, yet the small quantity of the latter was sufficient to completely stop the reaction. It also appears that the dissolution of copper in nitric acid is dependent solely upon the local production of nitrous acid, effected probably by local electric circuits due to traces of impurities in the copper; the proportion of nitrous acid initially produced is possibly also increased by a local rise of temperature. As regards this point Dr. Russell writes (*loc. cit.*):—"The nitrous acid attacks the silver, forming silver nitrite, nitric oxide, and water, the nitric oxide thus formed reducing hydric nitrate, and forming more nitrous acid. Thus the action gets quicker and quicker. The point still remaining to be explained is, then, how the first trace of nitrous acid is formed." My experiments, *mutatis mutandis*, are quite in accord with these observations. To test the matter further, the temperature of the same sample of acid was raised to 30° C., other experiments having shown that the amount of copper dissolved off per unit area is doubled for every 4° C. No gas was evolved for four minutes after the introduction of the copper sphere; it was then taken out, and again introduced, and again no gas was evolved for four minutes. The loss in weight after the eight minutes insertion was only 0·0025 grm., whereas it was calculated that the amount dissolved off during the interval of time, supposing the urea to have been absent, would have been 0·11 grm.

Into the same liquid a further quantity of 2 grms. urea dissolved in 2 c.c. of water was added; the acid was heated to 28—28·2° C., no gas was evolved for eighteen minutes; then, as the supply of carbonic acid accidentally failed, the evolution of gas from the copper started; the loss of weight observed was 0·0015 grm., a quantity which might well have been dissolved off during the interval of time which elapsed between the commencement of the reaction and the removal of the sphere from the acid. During the experiment it was interesting to observe from time to time the formation of a bubble of gas on the metallic surface, which was brushed off by the rotation of the glass dish or the stream of carbonic acid, and consequently any further reaction stopped.

As a further confirmation another sample of acid was made up, containing a slightly greater proportion of free acid, viz., 28·2 per cent, sp. gr. $\frac{19}{19}$ = 1·1723; a larger sphere was taken, presenting an area of 322·38 sq. m.m.

The acid was heated to 27° C., and 2 grms. urea dissolved in 2 c.c. water were added. No gas was evolved for fifty minutes, and the loss of weight observed was only 0·0015 grm.

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* *Chem. Soc. Journ.*, 1883 (*Trans.*), p. 456.

Several other similar experiments have been made with similar results, which, however, it is not considered necessary to quote.

The conclusions which I venture to think may fairly be drawn from the observations herein described are :—

(i.) The view ot Professor Armstrong is corroborated that the primary product of the reduction of nitric acid by copper is nitrous acid; the latter is formed immediately after any chemical change has taken place.

(ii.) If this initial formation of nitrous acid be prevented by suitable means *copper by itself will not dissolve in dilute nitric acid by itself.*

It would follow that the production of nitric acid and nitrous oxides with nitrogen, in proportions varying according to the conditions, is due to subsequent changes occurring between nitrous acid and cupric or cuprous nitrate or nitrite in presence of nitric acid.

I propose to continue these researches, substituting other metals for copper, especially those which are supposed to yield primarily nitrous acid.

In conclusion, I would express my thanks to Mr. Vernon Harcourt for the suggestion which proved of so much value, and to the authorities of the University for affording me facilities for this investigation.

Postscript.—Since the above was written experiments have been made in which the reaction between the copper and dilute nitric acid (sp. gr. = 1·1723), heated to 27° C., was successfully prevented for some time, even in absence of urea, by substituting a current of air for that of carbonic acid.

NOTES OF RECENT AND FUTURE RESEARCH THE SYNTHESIS OF CAFFEINE.

By SAMUEL E. PHILLIPS, F.C.S.

Uric acid, so-called, is no acid at all, and the supposed salts are metal and other replacements in the amide or ureide. It is the strict analogue of xanthine, sarcine, guanine, carnine, and other animal ultimates; and it is interesting to note that we have their close analogues in the vegetable kingdom, in theobromine and caffeine; the former being dimethyl xanthine. All of which proclaim their amide or ureide characters by forming chlorides, sulphates, acetates, &c., &c., of their ammonium forms.

Some time ago Adolph Strecker obtained a silver xanthine with Ag_2 replacing H_2, and by a familiar reaction with methyl iodide, 2AgI were eliminated and the nascent Me_2 assimilated, when the product was proved to be identical with theobromine. On another occasion he obtained a mono-silver theobromine, and treating this with methyl iodide the product was found to be identical with caffeine, thus proving it to be a trimethyl xanthine.

Chemists are familiar with a dimethyl-malonyl-urea,—

$$\left.\begin{matrix} 6\ 1\ 4 \\ 2\ 3\ \ \ \\ 2\ 3\ \ \ \end{matrix}\right\} = (10\ 5\ 4),$$

therefore, $(CO)_2C_{10}H_5O_4,H_3N_2$; and this + urea − 4HO would give the elements of theobromine, thus—

$$\begin{aligned} (CO)_2\ 10\ 5\ 4, H_3N_2 + (CO)_2H_4N_2 &= (CO)_4C_{10}H_5O_4, H_7N_4 (a) \\ -2HO &= (CO)_2Cy\ 10\ 5\ 4, H_5N_3 (b) \\ -2HO &= \quad Cy_2\ 10\ 5\ 4, H_3N_2 (c) \end{aligned}$$

(*a*) the normal di-ureide; (*b*) the pseudo-uric acid analogue; (*c*) the elements of theobromine.

Now it is an easy problem with chemists to obtain a trimethyl-malonyl-urea ($C_{12}H_7O_4$); and this + urea − 4HO = the elements of caffeine, thus—

$$\begin{aligned} (CO)_2\ 12\ 7\ 4\ H_3N_2 + (CO)_2H_4N_2 &= (CO)_4\ C_{12}H_7O_4H_7N_4 (a) \\ -2HO &= (CO)_2Cy\ 12\ 7\ 4\ H_5N_3 (b) \\ -2HO &= \quad Cy_2\ 12\ 7\ 4\ H_3N_2 (c) \end{aligned}$$

a) the normal diureide; (*b*) the pseudo-uric acid analogue; *c*) the elements of caffeine.

The only point of novelty or originality in this contention is the fact of ureas or carbonyl bodies—2HO—giving cyanogen; but this is so abundantly elucidated in the papers referred to under uric acid that it ought to be accepted.

Another fact of much interest which is wholly obscured by the skittle-playing types of modern theory is the unimpaired radical persistence through all the complex changes of M. Grimaux's numerous ureides. In some cases 2, 3, or 4 atoms of acid are combined with 2, 3, or 4 atoms of urea, and every item of these empirical syntheses strictly corresponds with the views we are seeking to enforce.

In conclusion we cite two of the simplest cases. M. Grimaux has synthesised allantoin and pyruvil, and has the penetration to see that both should have similar constitutions. We find them both one stage short of the ultimate and therefore pseudo-uric acid analogues—

Allantoin is from glyoxalic acid + urea, thus—

$$\begin{aligned} (C_4H_1O_4)O.HO + (CO)_2H_4N_2 - 2HO &= (CO)_2 4\ 1\ 4\ H_3N_2 (a) \\ (a) + (CO)\ H_4N_2 &= \quad (CO)_4 4\ 1\ 4\ H_7N_4 (b) \\ -2HO &= \quad \underline{(CO)_2Cv\ 4\ 1\ 4\ H_5N_3} (c) \\ -2HO &= \quad Cy_2 4\ 1\ 4\ H_3N_2 (d) \end{aligned}$$

(*a*) Glyoxal urea, miscalled allanturic acid; (*b*) the normal diureide; (*c*) allantoin; and (*d*) the ultimate amide or cyanamide, miscalled mycomelic acid.

That (*c*) really is a cyanamide is proved by the fact that it may be produced by the direct union of glyoxal urea (*a*) with cyanamid.

Pyruvil is from pyruvic acid + 2 urea, thus—

$$\begin{aligned} 6\ 3\ 4,O.HO + (CO)_2H_4N_2 - 2HO &= (CO)_2\ \ C_6H_3O_4H_3N_2 (a) \\ (a) + (CO)_2H_4N_2 &= \quad (CO)_4\ \ 6\ 3\ 4\ H_7N_4 (b) \\ -2HO &= \quad \underline{(CO)_2Cy\ 6\ 3\ 4\ H_5N_3} (c) \\ -2HO &= \quad Cy_2 6\ 3\ 4\ H_3N_2 (d) \end{aligned}$$

(*a*) Pyruvic urea, probably not yet obtained (M. Grimaux's pyruvil urea is acid + urea − 4HO, which must be a cyanamide, Cy 6 3 4 HN); (*b*) the diureide; (*c*) pyruvil; and (*d*) the ultimate not yet obtained.

Wokingham Road, Reading,
May 25, 1889.

ON DIACETYL AND SOME OF ITS DERIVATIVES.[*]

By HARRY F. KELLER.

With a view to a synthetic formation of citric acid, Fittig and Daimler[†] subjected ethyl oxalate to the action of ethyl monochloracetate and zinc. The reaction did not take place in the desired manner, but they found among the products the ether of a dibasic diketonic acid, which they termed ketipic (diketoadipic) acid. From the reactions of this ether it appeared highly probable that the structure of the acid must be expressed by one of the two formulæ:

$$\begin{matrix} CO,CH_2COOH \\ CO,CH_2COOH \end{matrix} \qquad \begin{matrix} CO,CH_2,COOH \\ CH_2,CO,COOOH \end{matrix}$$

It was observed that upon heating the acid was decomposed into carbonic dioxide and a yellow volatile liquid. At the suggestion of Professor Fittig I undertook the study of this reaction in the hope of arriving at a definite conclusion in regard to the structure of ketipic acid. The former of the two formulæ given above proved to be correct; ketipic acid is readily split up into diacetyl and carbonic anhydride according to the equation—

$$\begin{matrix} CO,CH_2,COOH \\ CO,CH_2,COOH \end{matrix} = \begin{matrix} CO,CH_3 \\ CO,CH_3 \end{matrix} + 2CO_2$$

---

[*] From the "Inaugural Dissertation for the Degree of Doctor of Philosophy," Strassburg, 1888. Chemical Section of the *Journal of the Franklin Institute*, April, 1888.

[†] *Ber.*, xx., 202.

Diacetyl is the simplest orthodiketone of the fat series, a class of compounds for the production of which a great many fruitless attempts have been made. Since the discovery of its formation from ketipic acid, diacetyl has been obtained by two other reactions, viz.: (1) By V. Pechmann,* on treating isonitrosomethylacetone successively with acid sulphites of the alkalies and dilute sulphuric acid, and (2) by L. Wolff,† who found that it was formed by boiling β-dibrom-lævulinic acid with water.

The constitution of diacetyl is deduced from the following facts:—

(1). Its empirical formula is $C_4H_6O_2$.

(2). It combines readily with two molecules of phenylhydrazine, of hydroxylamine, and of hydrocyanic acid. It must, therefore, contain twice the carbonyl group.

(3). As the dicyanhydrin yields dimethylracemic acid, the two carbonyl groups must be directly united.

Preparation.—In order to obtain a sufficient quantity of diacetyl for investigation, it was necessary to prepare large quantities of ketipic ether. In the beginning the method described by Daimler‡ was strictly adhered to, while later it was found more convenient to prepare it according to W. Wislicenus's§ reaction from ethyl acetate, ethyl oxalate, and metallic sodium. The ether was converted into the free acid by treating it in the cold with hydrochloric acid saturated at 0°; small quantities of it that had escaped saponification were removed by boiling the dry powdered product with chloroform, in which the acid is insoluble.

From this acid diacetyl can be obtained either by destructive distillation or by boiling with dilute sulphuric acid.

In decomposing ketipic acid in the dry way it was found necessary, for obtaining a satisfactory yield of the diketone, to distil *small* quantities, not exceeding five grms. at a time and to heat rapidly. The escaping vapours and gases were passed through a U-tube, provided below with a collecting bulb, and at the farther limb with an inverted condenser. The U-tube and bulb were placed in ice. The heating is continued until white fumes cease to come off. In the receiver there collects a liquid which consists of two layers: the upper one, which is of an oily appearance, is almost pure diacetyl, and the lower one, an aqueous solution of it. They were separated by means of a tap funnel, and sodium chloride added to the watery solution. Diacetyl and very little water passed over first on distillation. The oily layers were then united, dried with neutral chloride of calcium, and fractioned. The by far greater portion distilled over between 85° to 89°, and but a small reddish brown residue of empyreumatic odour remained in the bulb. The distillate showed a much lighter colour than the original product; it was again treated with chloride of calcium, and then distilled over completely between 87·5° and 88°.

The decomposition of ketipic acid is also readily effected by heating with dilute sulphuric acid (1 : 10). A violent evolution of carbonic anhydride is observed when the liquid is heated to near its boiling-point, and great care must be exercised in regulating the temperature in order to avoid serious losses. The aqueous distillate is treated as described above.

The yield never exceeds fifty per cent of the theory; it is about the same for both methods.

All attempts to obtain the monocarboxylic acid of diacetyl by splitting off only one molecule of carbonic acid were unsuccessful.

Diacetyl is a mobile liquid of an intensely yellow colour and characteristic odour. It boils without decomposition between 87·5° and 88°; the vapour is greenish yellow, resembling chlorine. Its specific gravity is ·9734 at 22°. It is soluble in four parts of water at ordinary temperature, and is miscible with alcohol and ether in all proportions.

I. 0·2563 grm. gave 0·5207 grm. CO_2 and 0·1632 grm. H_2O.

II. 0·2150 grm. gave 0·4390 grm. CO_2 and 0·1386 grm. H_2O.

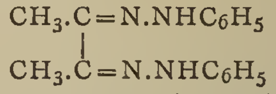
	Calculated for $C_4H_6O_2$.	Found. I.	Found. II.
C	55·81	55·40	55·68
H	6·98	7·07	7·16

Diacetyl prepared by the reactions of V. Pechmann and of L. Wolff was found, on comparison, to be identical in every respect with that from ketipic acid.

Diacetyl shows all the reactions which are peculiar to the ketones. It combines with the acid sulphites of the alkalies with the evolution of heat. The compound formed was not isolated, as it did not crystallise out of the solution upon standing.

When sulphurous anhydride is passed into an aqueous solution of diacetyl, its smell and colour rapidly disappear; nothing can be extracted from the solution by shaking with ether. No sulphuric acid is produced by the reaction, and on evaporating the liquid over sulphuric acid *in vacuo*, diacetyl is regenerated. It is probable that a loose combination of the diketone with SO_2 exists which breaks up as soon as the excess of the latter is removed.

Osazone of Diacetyl.—



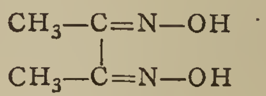
$$\begin{array}{l} CH_3.C=N.NHC_6H_5 \\ \quad\;\; | \\ CH_3.C=N.NHC_6H_5 \end{array}$$

On adding two mols. of phenylhydrazine to the ethereal solution of one mol. of diacetyl, the osazone separates out on standing in the form of beautiful yellowish needles. This compound is insoluble in most of the ordinary solvents, soluble with difficulty in $CHCl_3$, somewhat more readily in acetone, and in boiling benzol. It was obtained pure by re-crystallisation from the latter as a light yellowish powder, melting at 239°, with decomposition.

I. 0·3017 grm. gave 0·8009 grm. CO_2 and 0·1882 H_2O.
II. 0·2213 „ „ 0·5870 „ „ 0·1401 „
I. 0·2579 „ „ 46·5 c.c. N at 17·5° and 751 m.m.
II. 0·2133 „ „ 39·2 „ „ 18° „ 750 „

	Calculated for $C_{16}H_{18}N_2$.	Found. I.	Found. II.
C	72·18	72·38	72·32
H	6·76	6·93	7·03
N	21·06	21·02	21·38

Dioxim.—



$$\begin{array}{l} CH_3—C=N—OH \\ \qquad\;\; | \\ CH_3—C=N—OH \end{array}$$

This compound is formed by mixing aqueous solutions of diacetyl and of hydroxylamine hydrochloride, which has previously been neutralised with carbonate of sodium. It is precipitated white in the form of microscopic needles. It is insoluble in water, readily soluble in alcohol and ether, and melts with partial sublimation at 234·5°. By boiling it with dilute sulphuric acid, diacetyl is again produced.

0·2380 grm. gave 0·3606 CO_2 and 0·1525 grm. H_2O.
0·2278 „ „ 45·7 c.c. N at 8° and 759 m.m.

	Calculated for $C_4H_8H_2O$.	Found.
C	41·38	41·32
H	6·90	7·11
N	24·14	24·48

A compound prepared by Schramm* in the laboratory of V. Meyer several years ago, was found to be identical

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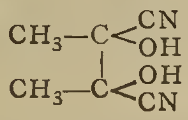
* *Ber.*, xx., 3, 162.
† Private communication.
‡ "Inaug. Diss.," Strassburg, 1886.
§ *Ber.*, xx., 590.

* Schramm, *Ber.*, xvi., 179.

with this dioxim after a re-determination of the melting-point.* It had not been analysed.

Dicyanhydrin.—



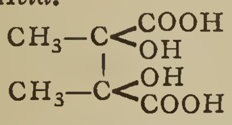
$$\begin{array}{l} CH_3-C<^{CN}_{OH} \\ \qquad | \\ CH_3-C<^{OH}_{CN} \end{array}$$

This is obtained by adding diacetyl to an excess of prussic acid in aqueous solution. The mixture is gently warmed for some time and then extracted with ether. On evaporation of the latter, the nitrile remains in the form of colourless needles or prisms, united to peculiar dendritic shapes. It is soluble in water, alcohol, and ether, insoluble in all other solvents. It is very hygroscopic, and decomposes when heated with water. It melts at about 110°.

0·3189 grm. dried in the desiccator gave 57·9 c.c. N at 19° and 734 m.m.

	Calculated for $C_6H_8N_2O_3$.	Found.
N	20·00	20·58.

Dimethylracemic Acid.—



$$\begin{array}{l} CH_3-C<^{COOH}_{OH} \\ \qquad | \\ CH_3-C<^{OH}_{COOH} \end{array}$$

Strecker† has observed that racemic acid is formed upon boiling glyoxal, prussic acid, and dilute hydrochloric acid. It was, therefore, to be expected that diacetyl, under similar conditions, would give dimethylracemic acid.

An acid of the composition $C_6O_6H_{10}+H_2O$, and whose properties closely resemble those of racemic acid, was obtained by slightly modifying Strecker's method. It was prepared in the following manner:—The finely powdered crystals of the hydrocyanide were placed in a small flask, and covered with concentrated hydrochloric acid; it passed slowly into solution, but on standing, colourless crystals were observed to separate; they probably represent the acid amide. No attempt was made to determine their character, but the mixture was first heated and then the hydrochloric acid evaporated on the water-bath; the residue was dissolved in water, and the solution divided into two equal parts. Of these one was exactly neutralised with K_2CO_3, and boiled; the other portion was then added. Upon cooling, the acid potassium salt, which—like that of tartaric acid—is difficultly soluble, crystallised out. This was re-crystallised, then converted into the neutral salt, and the solution of this precipitated with acetate of lead. The lead salt was washed with water, dried, pulverised, and then suspended in water and decomposed with hydrogen sulphide. On evaporating the filtrate the new acid crystallised out in large shining prisms and plates. These have the habitus of crystals of racemic acid. They contain one mol. of H_2O, but do not effloresce in the air. The acid is readily soluble in water and in alcohol, insoluble in ether.

0·2494 grm. of air-dry acid gave 0·0227 grm. loss, and 0·3361 CO_2, and 0·1177 CO_2.

	Required for $C_6H_{10}O_6+H_2O$.	Found.
C	36·73	36·75
H	5·10	5·24
H_2O	9·18	9·10

The anhydrous acid melts at 180°; it is decomposed at this temperature. Heated on platinum foil, it is decomposed and completely volatilised without leaving a trace of carbon.

Böttinger‡ has described, as dimethyltartaric acid, an acid which he obtained as a side product by the action of zinc upon an alcoholic solution of pyruvic acid. It showed no tendency to crystallise, undoubtedly because it was impure; its salts are certainly identical with some of those described below.

Potassium Salts.—The neutral salt is obtained from the acid one by exact neutralisation with potassium carbonate. It is quite soluble in water, and crystallises in needles.

The acid salt, $C_6H_9O_6K$, the preparation of which has been described above, is readily soluble in hot water, sparingly in the cold. It crystallises in crusts or little plates. It contains no water of crystallisation.

0·2526 grm. gave 0·1008 grm. K_2SO_4.

	Required for $C_6H_9O_6K$.	Found.
K	18·05	17·92

Calcium Salts.—$C_6H_8O_6Ca+1\frac{1}{2}HO$.* Chloride of calcium throws down from solutions of the neutral salts of the alkalies a white crystalline precipitate, insoluble in water and acetic acid.

0·2653 grm. lost on heating to 215—220° 0·0282 grm. H_2O, and gave 0·1483 grm. $CaSO_4$.

	Calculated for $C_6H_8O_6Ca+1\frac{1}{2}H_2O$.	Found.
H_2O	11·11	10·64
Ca..	16·46	16·43

Barium Salt.—$C_6H_8O_6Ba+H_2O$. Although quite as insoluble as the calcium salt, this is not precipitated immediately by barium chloride or acetate; it separates out completely after some time in the form of small needles, which are generally grouped around a common centre. It contains two mols. of water, which are driven off at 160°.

0·2046 grm. gave 0·0211° loss and 0·1364 grm. $BaSO_4$.

	Required for $C_6H_8O_6Ba+2H_2O$.	Found.
Ba	39·25	39·19
H_2O	10·32	10·31

The lead salt is precipitated in the form of a voluminous precipitate on adding lead acetate to the neutral potassium salt solution. It is likewise insoluble in water and in acetic acid. From acid solutions it is obtained in small needles.

In addition to the reactions described, the solution of potassium dimethylracemate gives the following:—$ZnSO_4$ produces a white amorphous precipitate, insoluble in water and dilute acetic acid. $AgNO_3$ in concentrated solutions gives a white curdy precipitate. With ammoniacal silver solutions a metallic mirror is formed, especially on warming.

$HgCl_2$ throws down a white precipitate.

$CuSO_4$ is coloured deep blue by the solution; the liquid remains clear on adding alkalies.

Ferric chloride produces a voluminous yellowish brown precipitate.

Halogen Derivatives of Diacetyl.—Bromine acts upon diacetyl but slowly in the cold; on warming, two atoms of hydrogen are replaced. Dibromdiacetyl is best prepared by adding bromine dissolved in CS_2 or $CHCl_3$ to a similar solution of the diketone until the red colour no longer disappears on heating in the water-bath. The solvent is then distilled off and the residue repeatedly crystallised from carbon disulphide and from petroleum ether. Thus obtained, it forms yellow leaflets of a waxy lustre, melting at 117°. It is soluble in ether, carbon disulphide, chloroform, and petroleum ether.

I. 0·2 grm. gave, after treating with Na amalgam, 3·3083 grm. AgBr.

II. 0·2 grm. gave, after boiling with Na_2CO_3 solution, 0·3079 grm. AgBr.

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[*] Private communication of Professor Meyer to Professor Fittig.

[†] *Zeitschrift fur Chem.*, 1868, 216.

[‡] *Annalen*, clxxxviii., 315.

[*] Both the Ba and Ca salt were dried in the desiccator before they were analysed; for this reason the Ba salt was found to contain less H_2O than Böttinger determined.

	Calculated for $C_2H_4Br_2O_2$.	Found.	
		I.	II.
Br	65·57	65·59	65·51

It is probable that the two atoms of bromine are attached to two *different* carbon atoms, as the action of Br does not seem to proceed any further even when a large excess is added.

Monochlordiacetyl.—By the action of chlorine upon diacetyl in the sunlight, a thick oily liquid, possessing the colour of diacetyl and a pungent smell, was obtained; it did not crystallise at −12°. Its boiling-point is about 150°. Sodium carbonate solution decomposes it, especially on heating.

0·5656 grm. gave, after treating with Na_2CO_3, 0·6566 grm. AgCl.

	Required for $C_2H_5O_2Cl$.	Found.
Cl	29·46	28·72

The further study of the halogen derivatives of diacetyl is being proceeded with.

Metallic Compounds.—When diacetyl is added to a solution of silver nitrate with just enough ammonia to hold the oxide of silver in solution, metallic silver is precipitated, sometimes as a mirror upon the glass; if, on the other hand, a large excess of ammonia be used, a voluminous white precipitate is formed, even in extremely dilute solutions of the diketone. A similar precipitate forms in ammoniacal solutions of cuprous chloride.

After drying them at 100° these substances were analysed with the following results:—

Ag Compound—

I. 0·234 grm. gave 0·2874 CO_2, and 0·892 H_2O, and 0·1153 Ag.
II. 0·2368 grm. gave 0·2898 CO_2, and 0·0923 H_2O.
III. 0·294 grm. gave 0·1442 Ag.

	Required for $C_6H_9N_2Ag$.	Found.		
		I.	II.	III.
C	33·18	33·46	33·37	—
H	4·14	4·23	4·33	—
Ag	49·77	49·28	—	49·04

Copper Compound—

I. 0·2123 grm. gave 0·3216 CO_2 and 0·1030 H_2O.
II. 0·4335 grm. gave 58·6 c.c. N at 15·5° and 755 m.m.
III. 0·2008 grm. gave 0·091 CuO.

	Required for $C_6H_9N_2Ag$.	Found.		
		I.	II.	III.
C	41·86	41·39	—	—
H	5·23	5·35	—	—
N	16·27	—	16·32	—
Cu	36·62	—	—	36·14

These compounds are quite stable; at high temperatures they are decomposed with formation of acetamide.

They are evidently salts of the trimethylglyoxaline, discovered by v. Pechmann.* This was proved also by preparing the hydrochloride of the base, by decomposing the salts with hydrochloric acid, and evaporating the filtrate. The residue was re-crystallised from alcohol-ether.

0·2275 grm. gave 0·2219 AgCl.

	Calculated for $C_6H_{10}N_2HCl$.	Found.
Cl	24·38	24·13

The free base was liberated with sodium carbonate and extracted with ether. Re-crystallised from a mixture of ether and ligroin, it forms small white needles, which have a bitter taste and melt at 130 or 131°.

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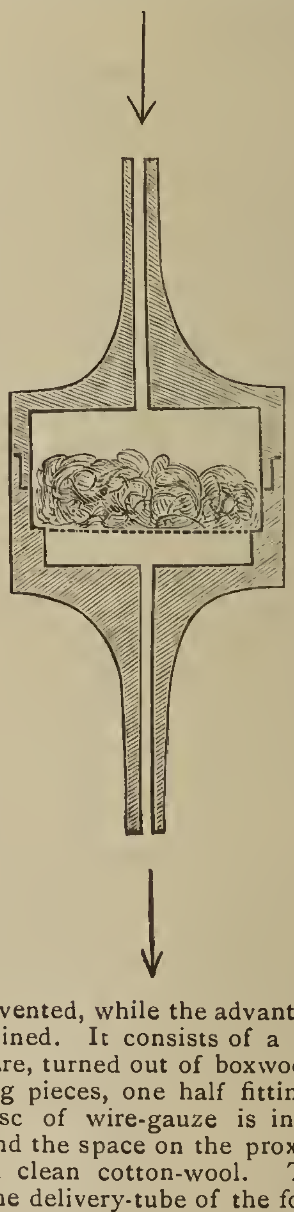
* *Ber.*, xxi., 1411.

AN IMPROVED APPARATUS FOR USE IN DRYING COMBUSTION-TUBES.

By AUGUSTUS E. DIXON, M.D., F.C.S.,
Assistant Lecturer in Chemistry, Trinity College, University of Dublin.

The ordinary method of drying tubes for use in combustion analysis, by heating in a gas or other oven, and withdrawing the contained air at intervals, is tedious and open to the objection that dust is very apt to be introduced. The method of passing the tube backwards and forwards through a large gas-flame, while a current of air is maintained through the former by means of a footblower, though rapid and otherwise efficient, is still more open to the objection stated; for the footblower is necessarily placed upon the floor, whence it readily picks up the lighter particles of solid matter which are near the valve.

I enclose a rough sketch of a simple piece of apparatus by which the entrance of dust into the combustion-tube is completely prevented, while the advantage of using the footblower is retained. It consists of a box of the form shown in the figure, turned out of boxwood, and made in two corresponding pieces, one half fitting air-tight into the other. A disc of wire-gauze is inserted near the distal opening, and the space on the proximal side of the disc packed with clean cotton-wool. The inlet tube is connected with the delivery-tube of the footblower, while the exit-tube is attached to a clean piece of rubber tubing about six feet long. The latter, in turn, is connected with the long narrow glass tube which is used in blowing out the moisture from the heated combustion-tube. These three—filter, rubber tube, and glass tube—are kept exclusively for the purpose alluded to, and are ready for use at a moment's notice.



I have had the apparatus for some time in use, and find that it works very satisfactorily.

THE REDUCTION OF BARIUM SULPHATE TO BARIUM SULPHIDE ON IGNITION WITH FILTER-PAPER.

By CHARLES W. MARSH.

In reading on the subject of some barium salts, while looking over the preparation of barium sulphide by means of igniting the mineral barite with coal and extracting the barium sulphide with water, my attention was again called to the reduction of barium sulphate precipitates by the carbon of the filter-paper on ignition in the regular method for estimation of sulphur. I have noticed in some text-books on quantitative analysis the direction to separate the precipitate of barium sulphate from the filter, ignite the filter, and burn to ash, moisten the mass with sulphuric acid to transform any barium sulphide formed by reduction of the carbon of the filter to sulphate, drive off excess of acid, and ignite again. The precipitate previously separated is now added, and the whole ignited and weighed. I could find no literature on the reduction of barium sulphate by ignition with the filter in the determination of sulphur, and have therefore made the experiments herein described.

Two series of experiments were conducted.

In the first case the method of procedure was as follows:—25 c.c. concentrated sulphuric acid were diluted to 500 c.c. and it was with this acid that all the experiments were made. The diluted sulphuric acid was taken instead of a soluble salt to avoid as much as possible liability of error from incomplete washing. For the first ten determinations various amounts of the acid were further diluted with distilled water, heated to boiling, and barium chloride solution added, and allowed to stand several hours or over night. The precipitates of barium sulphate were repeatedly washed with water by decantation and on the filter until the filtrates gave no reaction for hydrochloric acid. After drying the precipitates the filters were folded over, enveloping them, and cautiously ignited in a platinum crucible with the lid on until the escaping gases were ignited, when the burner was removed. When the flame went out the burner was again applied and the crucible brought to a red heat. The cover was removed, the crucible placed in a horizontal position, and heated until the filter was burned to an ash, cooled, and weighed.

A little water was then added to the contents of the crucible and the whole well stirred, and allowed to settle and the liquid decanted on a filter. In many cases hydrogen sulphide was detected after the addition of water by its odour, and by turning lead acetate paper brown. After having extracted two or three times with water, 2 c.c. of dilute hydrochloric acid were added in small portions with addition of water, whereupon, in most cases, the evolution of hydrogen sulphide was still more pronounced. The precipitate was further treated with water. If there was an odour of hydrogen sulphide in the filtrate a few drops of bromine water were added, and the solution boiled to expel the excess of bromine. A little of the diluted sulphuric acid was added, allowed to stand several hours, and the precipitate of barium sulphate collected on a filter, washed, dried, ignited, moistened with concentrated sulphuric acid, and the barium sulphate ignited and weighed.

This precipitate was derived from the barium sulphide formed by reduction of the barium sulphate by the carbon of the filter-paper during ignition, and was dissolved by the water and dilute hydrochloric acid added, and reprecipitated by sulphuric acid.

The total washings varied between 15 and 20 c.c.

The following table shows the results obtained by working in the manner described:—

	A.	B.	C.	D.	E.
1.	0·9844	0·0068	0·0048	0·9864	0·67
2.	1·0291	0·0073	0·0053	1·0311	0·70
3.	0·9926†	0·0377	0·0273	1·003	3·75
4.	1·0287†	0·025	0·0181	1·0356	2·41
5.	0·9634*	0·0071	0·0051	0·9654	0·73
6.	1·1462†	0·0915	0·0663	1·1714	7·81
7.	1·532†	0·0483	0·0350	1·5453	3·12
8.	1·9413†	0·0679	0·0492	1·96	3·46
9.	1·788*	0·0127	0·0092	1·7915	7·08
10.	1·9247	0·1503	0·109	1·966	7·64
11.	0·2166	0·0021	0·0015	0·2172	0·96
12.	0·1526	0·0012	0·0008	0·153	0·78
13.	0·076†	0·0147	0·0106	0·0801	18·32
14.	0·1621†	0·0039	0·0028	0·1632	2·38
15.	0·0919†	0·006	0·0043	0·0936	6·41

Explanation:—

A = weight of $BaSO_4$ and BaS after ignition in the crucible.

B = weight of $BaSO_4$ obtained by dissolving out BaS and precipitating the barium as sulphate.

C = the weight of $BaSO_4$ found in B, calculated to BaS, from which it was obtained.

D = the weight of A if it were all $BaSO_4$, obtained by subtracting the weight calculated in C from the weight of A, and adding to the remainder the weight given at B.

E = percentage of $BaSO_4$ reduced, found by dividing B by D and multiplying by 100.

Schleicher and Schüll's ashless filter-paper, number 590, was used.

In the first ten experiments the diameter of the filter was 9 c.m., and in the last five 5½ c.m.

The barium sulphate used on the last five experiments as well as in the second series was prepared in one beaker and carefully washed. This saved the individual washings for several precipitates, at the same time giving a precipitate identical in all cases.

The next set of experiments was made in similar manner with this change in manipulation. The ignition of the precipitate was performed without the lid on the crucible, thus giving complete access of air, and more nearly approaching the ignition of barium sulphate as carried out in the determination of sulphur. The results are as follows:—

	A.	B.	C.	D.	E.
16.	0·1389	not reduced			
17.	0·0631	,, ,,			
18.	0·061	,, ,,			
19.	0·0547†	0·0015	0·0010	0·0552	2·71
20.	0·0513†	0·0024	0·0017	0·0520	4·61
21.	0·0654	0·0003	0·002	0·0655	4·59
22.	0·0514	0·0006	0·004	0·0516	1·12
23.	0·0545†	0·0011	0·0008	0·0548	2·00
24.	0·0585†	0·0012	0·0008	0·0589	2·04
25.	0·0598*	0·0057	0·0041	0·0614	9·28
26.	0·7423†	0·0069	0·005	0·7442	0·92
27.	0·7437†	0·0059	0·0042	0·7454	0·79
28.	0·6776†	0·0122	0·0088	0·681	1·79
29.	0·5042†	0·0142	0·0103	0·5081	2·79
30.	0·77†	0·0143	0·0103	0·774	1·84

In the above experiments a filter of 5½ c.m. diameter was used in each case but the last five, where one of 9 c.m. diameter was used. The average reduction in the first table was 4·41 per cent of the barium sulphate originally present, and in the second 2·29 per cent, a trifle more than one half of that in the first case.

A blank experiment was made on 0·8582 grm. barium sulphate with the same amount of hydrochloric acid and water, and but three-tenths of a m.grm. of barium sulphate were obtained. I have not included this in connection with the above table as it is so small.

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* Odour of hydrogen sulphide when acid was added.

† Odour of hydrogen sulphide on addition of water, with more evolution on addition of acid.

The before mentioned experiments prove conclusively that there is quite an appreciable amount of barium sulphate reduced by the filter-paper in ignition, and that the reduction is about twice as much when the ignition is made with the cover on the crucible as when made without it.

The moistening of the ignited precipitate of barium sulphate with sulphuric acid and again treating should not be omitted in determination of sulphur as already proved.—*Journal of Analytical Chemistry*, Vol. iii., Part 2, April, 1889.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month ending May 31st, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S.,
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 7th, 1889.

Sir,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from 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 189 samples examined, the whole were found to be clear, bright, and well filtered.

The character of the metropolitan water supply during the month of May did not present any noteworthy variation from that recorded now for several months past as being entirely satisfactory; but what variation did present itself for notice was in the direction of an increased degree of uniformity of composition among the different samples examined, of an increased degree of freedom from organic matter, and of an increased degree of freedom from colour-tint. For it is to be noticed that the water supply, although, save on rare exceptional occasions, practically colourless, is yet found, when examined quantitatively by the calorimeter, to approximate more closely to entire freedom from colour at some seasons than at others. Thus taking, for convenience of comparison, the water furnished by the five companies taking their supply from the Thames, whereas the mean ratio of brown to pure blue tint in April was as 17 : 20, in the past month it was as 14 : 20 only. Similarly the mean proportion of organic carbon in the same water, which in the first three months of the year amounted to 0·164 part, and had become 0·154 part in April, was found to be further diminished to 1·144 part, in 100,000 parts of the water, in May; with a maximum amount of organic carbon in any one sample examined in May of 0·155 part, as against a maximum of 0·164 part in any one sample examined in April.

The mean composition of the supplies of Thames water delivered by the different companies was practically identical. As usual, the mean proportion of organic carbon in the East London Company's supply derived from the Lea was somewhat below even the small proportion present in the water derived from the Thames; while the mean proportion present in the New River Company's supply of mixed Lea and spring water was appreciably lower still.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

THE ESTIMATION OF THE TOTAL ORGANIC NITROGEN IN WATER BY THE KJELDAHL PROCESS.

By HENRY LEFFMANN and WILLIAM BEAM.

Chemists will note with much satisfaction, through the recent communication of Messrs. Drown and Martin,* the successful application of the Kjeldahl method to the determination of the total organic nitrogen existing in waters. The so-called albumenoid ammonia process has never been more than a relative determination, and the estimation by the usual combustion method does not seem to be susceptible of general employment in this field. For the benefit of those unfamiliar with the article in question, we present the following abstract:—

Five hundred c.c. of the water are poured into a round-bottomed flask of about 900 c.c. capacity, and boiled until 200 c.c. have been distilled off. The free ammonia which is thus expelled may, if desired, be determined by connecting the flask with a condenser. To the remaining water in the flask, after cooling, is added 10 c.c. pure concentrated sulphuric acid. After shaking, the flask is placed in an inclined position on wire gauze, and boiled cautiously in a good drawing hood until the water is driven off and the concentrated sulphuric acid is white or a very pale yellow. The flask is then removed from the flame, and a little powdered potassium permanganate added until, on shaking, the liquid acquires a green colour. If the colour is purple instead of green, it shows that the water has not been all driven off. After cooling, 200 c.c. of water free from ammonia are added, the neck of the flask being washed free from acid, and then 100 c.c. of sodium hydroxide (200 grms. per litre). The flask is connected with a condenser, shaken to mix the contents, and distilled. The first 50 c.c. are condensed in very dilute hydrochloric acid free from ammonia. The total distillate is made up to 250 c.c., mixed, and 50 c.c. taken and Nesslerised. A correction for the nitrogen in the chemicals used is made by means of a blank experiment. From the experiments made, Drown and Martin conclude that the nitrates and nitrites do not interfere with the accurate determination of the organic nitrogen, the error which might otherwise be caused disappearing under the conditions of great dilution which exist in natural waters.

Numerous observations have established the fact that the organic matter of water is susceptible of decomposition or volatilisation by simple boiling, often in such a manner that a notable proportion of the nitrogen is lost. It appeared, therefore, in experimenting on this process, that it would be advantageous to add the acid at once, and thus obtain the nitrogen existing as organic matter and also in ammonium compounds, estimating that existing in the latter in a separate sample by direct Nesslerising without distillation; the calcium and magnesium, which would otherwise interfere with the colour reaction, being removed by the addition of sodium carbonate and hydroxide, according to the suggestion of

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* *Technology Quarterly*, ii., 3.

Morgan. The same principle can be extended to the determination of the ammonium formed by the sulphuric acid. Instead of distilling the liquid after rendering it alkaline, a little sodium carbonate may be added, allowed to stand, filtered, and the filter Nesslerised. In this way the troublesome distillation is avoided. The procedure is as follows:—

Reagents Required.—Concentrated sulphuric acid as free as possible from nitrogen; that which we used was of the same make (Baker and Adamson) recommended by Drown and Martin, and contained a similar proportion of nitrogen (0·05 m.grm. in 10 c.c.).

Sodium Hydroxide free from Ammonium.—100 grms. of caustic soda are dissolved in about a litre of water, boiled down to about half its bulk in an open vessel, then diluted to one litre with water free from ammonium.

Sodium Carbonate free from Ammonium.—200 grms. pure sodium carbonate are dissolved in a litre of water, and the solution boiled briskly until several hundred c.c. have been evaporated.

Determination of Nitrogen Existing as Ammonium.—200 c.c. of the water are placed in a stoppered bottle, 2 c.c. each of the solutions of sodium carbonate and sodium hydroxide added, the stopper inserted, the solutions mixed, and allowed to stand for an hour or two. A filter is prepared by inserting a rather large plug of cotton in a funnel. This should be washed several times with the ammonia-free water. The clear portion of the sample is drawn off with a pipette and run through the filter, the first portions being rejected, since it is diluted by the water retained in the cotton. The filtration is rapid, and when 100 c.c. of the liquid has passed through it is Nesslerised. If the ammonium present is very small in quantity a rather long and narrow tube should be used for observing the colour.

Estimation of Total Organic and Ammoniacal Nitrogen.—500 c.c. of the water are placed in the round-bottomed flask, 10 c.c. of concentrated sulphuric acid added, and the mixture boiled down until the water is driven off and the acid is colourless or pale yellow. The potassium permanganate is then added as above, but after the green colour is obtained the flask is re-heated until the liquid becomes colourless; this requires but a few minutes. After cooling, 50 c.c. of water are added, and then a slight excess of the sodium hydroxide solution; about 150 c.c. will be required. 2 c.c. of sodium carbonate solution are then added to make sure of the precipitation of the calcium and magnesium, though this is perhaps not necessary, since the caustic soda usually contains more than sufficient carbonate for this purpose. The liquid is cooled by immersing the flask in cold water, made up to 250 c.c., transferred to a stoppered bottle, and allowed to stand for about an hour, or until the greater portion of the precipitate has subsided. The clearer portion of the liquid is then drawn off with a pipette and run through the cotton-plug filter described above. The filtrate is perfectly clear and colourless. An aliquot portion is taken and Nesslerised. We prefer to use 100 c.c. and dilute to 200 c.c., using rather larger glasses than are commonly employed. Drown and Martin have noted that the addition of potassium permanganate to the concentrated acid is not essential, and merely employ it as a precautionary measure. With the method detailed above, however, it will be found that unless it is used, the Nesslerised liquid has a yellowish instead of brown colour, and is more difficult to match. A blank experiment is to be made with the reagents used, to determine the amount of the nitrogenous impurity.

We have made trials of the method with various nitrogeneous bodies of known composition, and have invariably obtained the theoretical quantity of nitrogen. As an illustration of the trustworthiness of the method the following is given:—A sample represented to be pure metadiamidobenzene was purified by re-crystallisation, and a solution containing one m.grm.—equivalent to 0·000259 nitrogen—added to 500 c.c. water and treated as above. Only 0·000155 nitrogen was obtained. The experiment was repeated four times with some slight modifications of the process, but with almost precisely the same result. On examination it was found that the material used was in reality metadiamidobenzene dihydrochloride, and contained therefore 0·000154 nitrogen.

The following are a few of the results obtained with natural waters, and a comparison with the results by the distillation method:—

PARTS PER MILLION.

Modified Process.

	Nitrogen.		
	In NH_4.	Organic.	Total.
Water, already impure, to which decomposing urine was added ..	0·97	2·34	3·31
Pump-well in densely populated district..	0·24	0·56	0·80
Cellar water—impure	0·17	0·56	0·73

Drown and Martin's Process.

	Nitrogen.			
	In free ammonia.	Organic.	Total.	Lost by boiling.
Water, already impure, to which decomposing urine was added	1·25	1·82	3·07	0·31
Pump-well in densely populated district	0·33	0·38	0·71	0·09
Cellar water—impure ..	0·23	0·41	0·64	0·09

In uncontaminated waters much less difference, and sometimes none, was noticed between the results by the original and the modified process.

The figures show conclusively, we think, even if there were no other observations on the point, that it is not safe to estimate the ammonium in the water by distillation, nor to boil the water previous to the estimation of the organic nitrogen.—*American Chemical Journal*, Vol. xi., No. 4.

NOTICES OF BOOKS.

A Treatise on the Principles of Chemistry. By M. M. Pattison Muir, M.A., F.R.S.E., Fellow and Prælector in Chemistry of Gonville and Caius College, Cambridge. Second Edition. Cambridge: The University Press.

The present edition of this work is by no means a mere reprint of its predecessor. The first book has been enriched with the results of researches completed in the meantime; the sections on physical methods have been re-written, the arrangement of several parts has been modified, and chapters which have become of less relative consequence have been shortened. The second book, which has been entirely re-written, discusses the questions of dissociation, chemical change and equilibrium, affinity and the relations between chemical action and distribution of the energy of the changing system. The subject matter of the two books the author summarises respectively as chemical statics and chemical kinetics. Some minds perhaps may better grasp these two phases of the science if they are presented as chemical morphology or the doctrine of structure or composition, and chemical physiology the doctrine of function.

In the first book the author treats of atoms and molecules, of nascent actions, of the dualistic and unitary hypotheses, the equivalence of atoms, of allotropy and isomerism, of molecular compounds, and of the periodic law. A separate section deals with miscellaneous physical methods applicable to questions of chemical statics. It seems to us that the author is now somewhat too ready to accept the chemical elements as ultimate facts about whose nature and origin it is useless or perhaps unnecessary to enquire. This reminds us of the old school in biology, who quietly accepted every animal and every plant as a *datum* into which it was vain to pry. Now, if we consider the views formerly expressed by Mr. Muir, *e.g.*, in a valuable memoir which he contributed to the *Journal of Science* (1876, p. 30), entitled "Recent Chemical Researches," we should naturally expect from him a thorough and an impartial summary of the evidences for and against the absolute and independent character of our received elements. But this expectation is not gratified. We find, indeed, a full and a fair exposition of the periodic law, but no hint is given as to any light it may throw upon the point at issue. The researches of Mr. Norman Lockyer, in as far as they relate to the decomposition of our conventional simple bodies, are not discussed, nor do the conclusions of the late Sir B. Brodie meet with any appreciation. Assuredly the time is past when the genesis of the elements can be ignored in a work treating on the "Principles of Chemistry." Assuredly, too, there lives no man better able to do justice to this delicate and difficult subject than Mr. Muir.

The second book—"Chemical Kinetics," or, as we should prefer to call it, "Chemical Physiology" (were the term not liable to misunderstanding)—deals with the law of mass-action, with chemical dynamics—a term which some writers use as equivalent to Mr. Muir's "chemical kinetics"—and which includes the velocity of chemical change, chemical equilibrium, the applicability of thermo-dynamical methods to chemical equilibrium (Berthelot's thermo-chemistry), the corresponding application of molecular methods, and dissociation. Then follows the consideration of chemical affinity, including the specific affinity coefficients of acids and bases, the connection between the affinity coefficients, and the constitution of acids. Lastly, the author takes up the subject of chemical change. He concludes with the words:—"Much work has yet to be done before a general theory of chemical change can be hoped for; a theory which shall represent every process of change as a function of the atomic weight of the elements and the affinities of the reacting substances concerned in the operation. When such a theory is attained will chemistry be complete? I hope not; for what's come to perfection perishes."

There is little fear; we must first know what the elements are. Meantime, a thorough study of the work before us will contribute no little to put the advanced student in a position for aiding in perfecting the science.

CORRESPONDENCE.

ALKARSIN.

To the Editor of the Chemical News.

Sir,—The following are equations concerning the alkarsin (arsenide of acetyl) that I discovered. The first has reference to its formation, the second to its decomposition by water, if that take place, and the third to the formation of the alkarsin, acetate of arsenic, if arsenide of acetyl combine with oxygen to form it, which seems highly probable:—

(α). $6C_2H_3OCl + Zn_3As_2 = 2As(C_2H_3O)_3 + 3ZnCl_2$.

(β). $As(C_2H_3O)_3 + 3H_2O = AsH_3 + 3C_2H_4O_2$.

(γ). $As(C_2H_3O)_3 + 3O = As(C_2H_3O_2)_3$.

—I am, &c.,

G. W. Blythe, M.P.S.

The Petroleum Association.—Mr. William Fox has been appointed Chemist and Secretary to the Petroleum Association in place of Mr. Boverton Redwood, resigned.

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. cviii., No. 22, June 3, 1889.

Combustion-heat of Carbon in its Different Conditions as Diamond, Graphite, and Amorphous Carbon.—MM. Berthelot and Petit.—For amorphous carbon the authors obtain the result C_2+O_4 : +97·65 calories. Pure crystalline graphite gave for C_2+O_4 : + 94·81 cals., whilst the diamond gave 94·31 calories. These values differ from those hitherto accepted based upon the experiments of Favre and Silbermann.

Apparatus for Determining the Melting-point under Ordinary Conditions and at Variable Pressures.—B. C. Damien.—The author's method is chiefly applicable to fatty bodies. The apparatus is a box of 6 c.m. long, 4 c.m. broad, and 3·5 c.m. deep, divided into two distinct compartments, and closed with a lid of gilt brass. Beneath this lid, and touching its side, are two thermometers showing the temperature of the two compartments. The fatty matter, spread out in a thin layer, covers the lid. By means of taps a current of hot water at a temperature a little higher than the approximate melting-point is let pass into the entire box. When the substance is melted cold water is passed into one of the compartments by means of a tube which traverses the apparatus from side to side. At a certain moment the fatty matter is solidified on one side and remains liquid on the other. The observation is easy on account of the different transparency of fats when solid and when melted. The mean of the readings of the two thermometers is the melting-point sought. It is easy to operate at different pressures by substituting two concentric cylinders for the two compartments of the box above described.

The Electric Conductivity of Saline Solutions applied to Chemical Questions. Double Decompositions.—P. Chroustchoff.—The author gives a table of the determinations of the electric conductivity of neutral salts (one equivalent = one litre) capable of undergoing a reaction of double decomposition.

The Electric Conductivity of Saline Solutions containing Mixtures of Neutral Salts.—P. Chroustchoff and V. Pachkoff.—The authors give their results in a tabular form. Their chief object is to furnish experimental evidence in support of the hypothesis that the partial formation of double salts in solutions is a very general phenomenon.

Certain Methods of Producing Mercury-ammonium Chlorides.—G. André.—The author has studied the action of ammonia upon a mixture of mercury chloride and oxide, that of mercury chloride upon a mixture of potassa and ammonia, and that of potassa in excess upon mercury chloramidide in the cold.

The Combinations of Meta-tungstic Acid with the Alkaline and Alkaline-earthy Bases and on the Resulting Thermic Phenomena.—E. Pechard.—The action of an excess of baryta upon metatungstic acid is composed of the following phases:—Formation of barium metatungstate, transformation of the metatungstate into gelatinous neutral tungstate, and transformation of the gelatinous tungstate into a crystalline tungstate, which is the final term of the reaction. This transformation of the metatungstates into the neutral tungstates has been already observed by taking phenolphthalein as indicator, the red colour disappearing as the transformation is effected. This observation, applied to barium, renders it possible to titrate a solution of metatungstic acid. To the acid solution we add a few drops of phenolphthalein and run in baryta-water as long as the red colour disappears. The baryta-water must then be added, cautiously stirring the liquid and keeping up a gentle heat to promote the formation of the crystalline tungstate. When the last drop has given a permanent red colour four equivalents of baryta have been added for each equivalent of metatungstic acid.

Certain Compounds derived from Ethyl Cyanide by Polymerisation.—M. Hanriot and L. Bouveault.—This paper is not adapted for abstraction.

On the Enrichment of Phosphatic Chalk and on the Origin of the Rich Phosphate of Beauval.—A. Nantier.—By lixiviation a phosphatic mineral can be obtained containing as much as 55 to 60 per cent of actual phosphate. The author supposes that the Beauval mineral, containing 80·9 per cent of pure phosphate, owes its origin to the removal of the calcium carbonate by the action of waters saturated with carbonic acid.

Bulletin de la Société Chimique de Paris.
Vol. i., (Ser. 3), No. 8. April 20, 1889.

The Acetic and Ethylic Ethers of Campho-nitrophenol.—P. Cazeneuve.—An account of campho-nitrophenol acetine and of the ethylic ether of campho-nitrophenol.

The Phosphoric Ether of Campho-nitrophenol.—P. Cazeneuve.—This compound is obtained by boiling campho-nitrophenol for some hours with phosphorus trichloride. It is an amorphous yellowish body, insoluble in water, alcohol, benzene, and most solvents. It is infusible, but it is decomposed by heat and burns with a white flame.

On the Benzoic and Phthalic Ethers of Campho-nitrophenol.— P. Cazeneuve.—The former of these bodies forms small white crystals, insoluble in water, but very soluble in boiling alcohol, ether, and benzene. The phthalic ether forms white crystals, insoluble in water, very slightly soluble in boiling alcohol, insoluble in ether, but more soluble in chloroform and benzene. The crystals melt at 275° with decolouration and slight decomposition.

Researches on the Cadmium Phosphates and Arseniates.—In this paper the author gives an account of the neutral orthophosphate, the mono-cadmium phosphate, the chloro- and bromo-cadmium apatites, the anhydrous cadmium pyrophosphate, and the corresponding arsenical compounds.

The Production of the Neutral Crystalline Lithium Phosphate and of the Corresponding Arseniate.—A. de Schulten.—If lithium chloride is fused with tri-lithium phosphate the latter dissolves easily in the phosphoric acid, its solubility increasing with the temperature. The crystals obtained have the composition Li_3PO_4. They are free from chlorine and form rhomboidal tabular crystals, easily soluble in dilute acids. The corresponding arsenical compound may be obtained in a similar manner.

A Difference of Reaction in Organic Chemistry between the Sulphuric and Selenic Acids. — Prof. Istrati.—Strong sulphuric acid reacts easily upon benzene, its homologues, and their haloid derivatives, yielding a sulphonic derivative, a sulpho-benzide, and a franceine. If selenic is allowed to react upon benzene, neither a franceine nor a selenobenzide is produced.

Transformation of Sulphonic Derivatives under the Influence of Heat in Presence of Sulphuric Acid.—Prof. Istrati.

New Data Concerning the Franceines. — Prof. Istrati.—In one and the same reaction there may be obtained two franceines varying completely in their proportion of chlorine.

On the Franceine derived from $C_6H_3Cl_3$.—Prof. Istrati.—The production of the franceine is directly as the high temperature employed and inversely as the quantity of the sulphonic derivative obtained.

On the Introduction of Acid Radicles into the Molecules of the Acetones.—Dr. L. Claissen.—These two extensive papers do not admit of useful abstraction.

No. 9, May 5, 1889.

Action of Sodium upon Ethyl Cyanide.—M. Hanriot and L. Bouveault.—The autnors reject the formulæ proposed by Herr von Meyer in the *Journal für Praktische Chemie.*

Resistance to Light of Colouring-matters when fixed on Tissues.—Jules Joffre.—The author examines the part in the action of light which may be due to oxygen. Chrevreul found, in 1837, that dyed tissues are not discharged if exposed to the action of light in a vacuum, turmeric and prussian blue forming exceptions. The author, in resuming these experiments, placed the dyed swatches, not in a vacuum, but in pure nitrogen gas. Under these a great number of colouring-matters remained unaffected. Among these rank the shades dyed with cyanine which disappear in a few hours' exposure to the sun in the air, but retain all their intensity in the absence of oxygen. The shades obtained with picric acid turn to an orange in nitrogen gas just as in air. The action of atmospheric oxygen may be eliminated by coating the dyed swatches with paraffin or with gum-arabic.

On a Method of Detecting the Presence of Carbon Monoxide in Air.—M. Raceine.—The apparatus which the author has devised is based upon the power of platinum black to absorb carbon monoxide, during which process heat is liberated and an electric current is generated, which rings a bell placed in the circuit.

Transformation of Nitrocamphor into Nitrosocamphor.—P. Cazeneuve.—The author effects this transformation by direct reductive action, heating chloronitrous camphor in dilute alcohol with copper precipitated by zinc.

The Crystallisation of Anhydrous Iodic Acid.—H. Lescœur.—The products obtained on heating nitric and iodic acids together vary with the strength of former acid. With the nitric acid of commerce and with stronger kinds there are obtained flattened crystals formed of trapezoidal plates, which at 170° lose 0·8 per cent of their weight but retain their lustre.

No. 10, May 20, 1889.

Determination of Aniline and of Monomethylaniline.—F. Reverdin and Ch. de la Harpe.—The authors weigh out 7 to 8 grms. of the mixture in question and dissolve it in 28 to 32 c.c. of HCl and the quantity of water necessary to make up a total volume of 100 c.c. On the other hand they make up a solution of the "salt R" (a standard solution of the sodium salt of β-naphthol-disulphonic acid) containing, per litre, the quantity corresponding to 10 grms. naphthol. They then measure out 10 c.c. of the solution of the bases and dilute it with a little water and ice and introduce a quantity of sodium nitrite capable of completely diazotising the mixture if it contained nothing but aniline. The product of the reaction is then poured into a measured quantity of the solution of the salt R, to which an excess of sodium carbonate has been added, and proceeding by approximations until, the colouring-matter having been precipitated by sodium chloride, the filtrate no longer gives a red colour on the addition either of the salt R or of diazobenzene chloride. The proportion of aniline contained in the mixture is found from the quantity of the salt R consumed in arriving at this result.

Preparation of Amyl Chloride by Means of Amylic Alcohol.—H. Malbot.—The author saturates the amylic alcohol with hydrochloric acid and heats it in a closed vessel with a considerable proportion of strong hydrochloric acid.

Journal fur Praktische Chemie.
Vol. xxxix., Parts 5 and 6, 1889.

Behaviour of the Mercurous Salts with Ammonia.—C. Barfoed (conclusion).—The author's principal results are:—The ammoniacal precipitates of the mercurous compounds, if exposed to air and placed in circumstances where no chemical decomposition can be assumed, give off about half their mercury in a free gaseous condition, and lose their dark colour. They contain originally equal quantities of free and of combined mercury, but on standing a part of the free mercury enters into combination. The white or pale compounds which remain after the free mercury has evaporated agree with the ammoniacal precipitates of the mercuric salts. The dark precipitates, therefore, are not, as it has been hitherto assumed, ammonium-mercurous compounds, but are mixtures of mercury and ammonium-mercuric compounds. The black precipitate which Kane obtained by an incomplete precipitation of the nitrate with ammonia, and which he regarded as a definite compound, is also a mixture containing mercury. The so-called ammonium mercurous chloride of Rose, obtained from anhydrous ingredients, agrees otherwise with the precipitate of the chloride, but contains also ammonium chloride.

Contributions to the Knowledge of the Polymerisation of the Nitriles (communicated by E. von Meyer).—These contributions include memoirs by R. Holtzwart on di-molecular cyan-methyl; by R. Wache on the polymerisation of certain nitriles; and by E. von Meyer on the chemical constitution of kyanethine, with contributions to a knowledge of its derivatives.

Researches from the Laboratory of the University of Freiburg in Breisgau.—These include memoirs by C. Willgerodt and F. Dürr on our knowledge of solid aceton-chloroform and its derivatives; by C. Willgerodt and A. Kornblum, on the iodation of phenoloid bodies in ammoniacal solution; by K. Elbs and H. Förster on triphenyl trichlorethan and its homologues; by A. Claus and H. Decker on γ-brom-chinolin; and by Ad. Claus on a new dioxynaphthaline.

The Action of Alkalies and Ammonia upon Halogen-substituted Quinones.—Fr. Kehrmann.—A preliminary notice.

Part 7, 1889.

The Determination of Sulphuric Acid in Presence of Iron.—P. Jannasch and Th. W. Richards.—The substance of this paper will be given at some length.

Researches from the Laboratory of Prof. Saytzeff, at Kasan.—We have here papers on the oxidation of erucic acid in an alkaline solution by means of potassium permanganate, by L. Urwanzoff; on the oxidation of ricinoleic acid under similar conditions, by W. Dieff; and a comment on the above papers, by Prof. Saytzeff.

On the Oil of Betel.—J. Bertram and E. Gildemeister.—A study of the essential oil contained in the leaves of the betel (*Piper betle*).

Researches from the Laboratory of the University of Freiburg.—These investigations include a paper by A. Claus and W. Fabrion on carvol and carvacrol-sulphonic acid, and a memoir by A. Claus and A. Dreher on metacresol.

On Potassium-Magnesium Bromide.—W. Feit.—This double salt has a composition answering to the formula $KBr,MgBr_2+6H_2O$.

Archives Neerlandaises des Sciences Exactes et Naturelles.
Vol. xxiii., Part ii.

This issue contains no chemical matter.

MISCELLANEOUS.

Elizabeth Thompson Science Fund.—This fund, which has been establised by Mrs. Elizabeth Thompson, of Stamford, Connecticut, "for the advancement and prosecution of scientific research in its broadest sense," now amounts to 25,000 dollars. As accumulated income is again available, the trustees desire to receive applications for appropriations in aid of scientific work. This endowment is not for the benefit of any one department of science, but it is the intention of the trustees to give the preference to those investigations *which cannot otherwise be provided for*, which have for their object the advancement of human knowledge or the benefit of mankind in general, rather than to researches directed to the solution of questions of merely local importance. Applications for assistance from this fund, in order to receive consideration, must be accompanied by full information, especially in regard to the following points:—(1). Precise amount required. Applicants are reminded that one dollar (1·00 or 1 dollar) is approximately equivalent to four English shillings, four German marks, five French francs, or five Italian lire. (2). Exact nature of the investigation proposed. (3). Conditions under which the research is to be prosecuted. (4). Manner in which the aporopriation asked for is to be expended. All applications should be forwarded to the Secretary of the Board of Trustees, Dr. C. S. Minot, Harvard Medical School, Boston, Mass., U.S.A. It is intended to make new grants at the end of 1889. The trustees are disinclined for the present to make any grant exceeding five hundred dollars; preference will be given to applications for smaller amounts.

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END OF VOLUME LIX.