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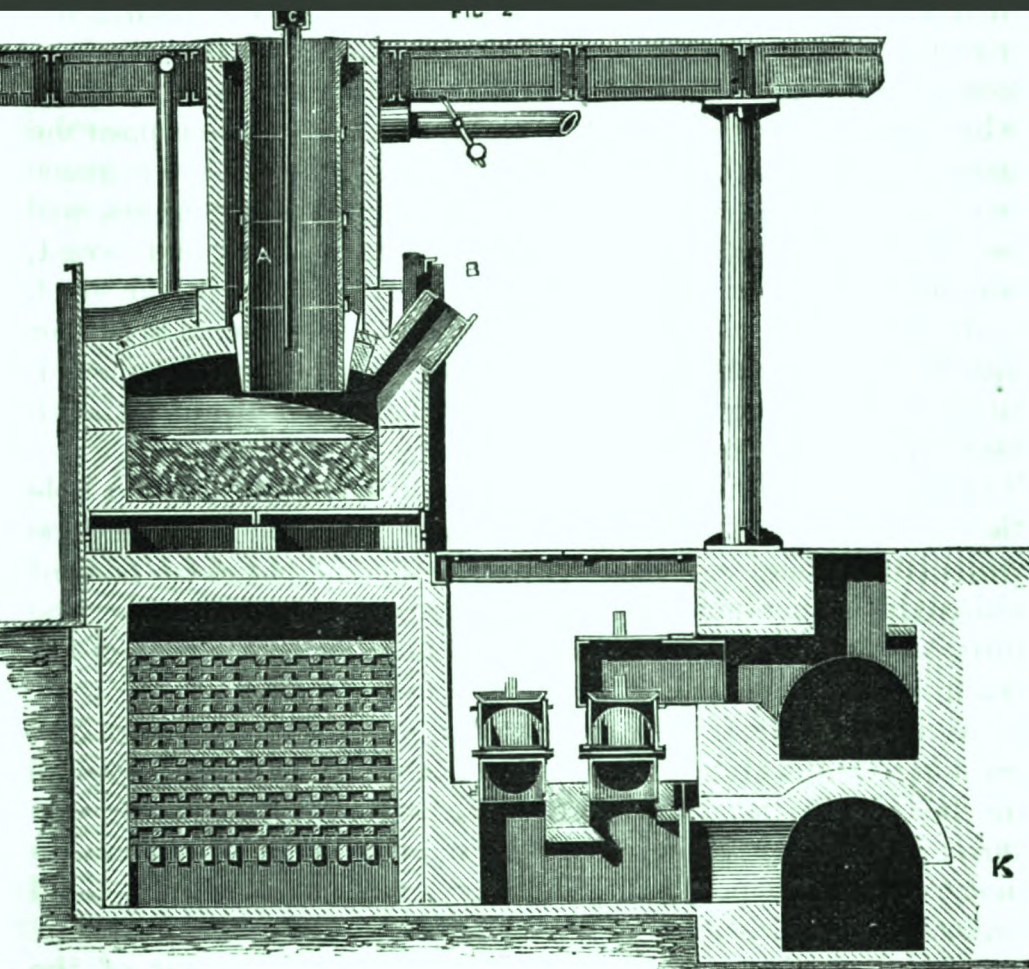
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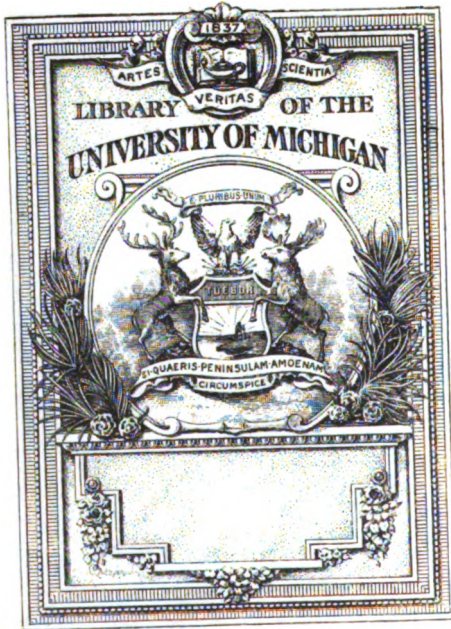
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Editor :

HENRY WATTS, B.A., F.R.S.

NEW SERIES, VOL. VI. (Entire Series, Vol. XXL)

LONDON :  
VAN VOORST, 1, PATERNOSTER ROW.  
1868.

LONDON :

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

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JOURNAL  
OF  
THE CHEMICAL SOCIETY.

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I.—*On the part taken by Oxide of Iron and Alumina in the Absorptive Action of Soils.*

By ROBERT WARINGTON, Junr.

SOME time ago I laid before the Society the results of some experiments upon the solubility of phosphate of calcium under various conditions.\* Two of these experiments were upon the behaviour of hydrated ferric oxide and hydrated alumina when placed in contact with a solution of tricalcic phosphate in carbonic water; the result obtained was of a very decided character. In both cases the phosphoric acid was almost entirely abstracted from the solution, while the calcium remained dissolved in the form of carbonate.† This reaction suggested the idea that the power possessed by soils of removing phosphoric acid from its solutions was probably owing to the presence in soils of ferric oxide and alumina; that indeed the absorptive action of soil towards phosphoric acid was nothing more than an ordinary case of chemical affinity, the oxide of iron and alumina of the soil uniting with the phosphoric acid to form insoluble phosphates of iron and aluminium. To ascertain the correctness of this conclusion was the object of the first experiments; it was sought to discover whether the oxide of iron and alumina that occur in soil had the same action towards phosphoric acid as the precipitated ferric oxide and alumina previously employed.

\* Jour. Chem. Soc. [2], iv, 296.

† The ferric oxide absorbed 95·7 per cent. of the phosphoric acid present, the whole of the calcium remained in solution. The alumina absorbed 96·8 per cent. of the phosphoric acid, and 95·6 per cent. of the calcium remained dissolved.

I. *Absorption of Phosphoric Acid by Soil.*—The plan of the experiment was to take a soil and place it in contact with a solution of phosphate of calcium in carbonic water—to treat it in fact precisely as the precipitated ferric hydrate had been treated—to observe if absorption of phosphoric acid took place, and if so, whether this absorption were accompanied by a *decomposition* of the phosphate of calcium.

The conditions of the experiment required that the soils used should be as nearly as possible free from lime; since if lime were present it would dissolve in the carbonic water, and render valueless any determination of the proportion of calcium to phosphoric acid in the liquid after the action of the soil. Two soils were made use of. In the state in which they were employed they had the following composition. :—

	Soil A.	Soil B.
Moisture .....	1·54	6·57
Organic and volatile matter.....	3·69	17·03
Silica and insoluble silicates.....	87·31	55·29
Oxide of iron and alumina .....	6·82	19·31
Phosphoric acid .....	·05	·34
Lime .....	·11	·28
Magnesia.....	·14	·63
Potash.....	·16	} ·55
Carbonic acid, traces of other substances, and loss .....	·18	
	<hr/> 100·00	<hr/> 100·00

It will be remarked that soil B contained much more oxide of iron and alumina than soil A.

In the first experiments the attempt was made to free the soils entirely from soluble calcium salts before subjecting them to the action of the phosphate. To this end the soils were treated with water, and a stream of carbonic acid made to pass through the mixture, the water being removed by decantation every two or three days and fresh water substituted. As however after a long treatment of this nature fresh carbonic water still continued to remove traces of lime, the soils were further treated with dilute acetic acid, and then thoroughly washed with water.



*Experiment 1.*—600 grs. of soil A were freed from lime as above described, and then treated with 8000 grs. of a solution of tricalcic phosphate in carbonic water: carbonic acid was passed through the mixture from time to time. After 18 days the liquid was filtered from the soil, and the latter washed two or three times with carbonic water. The liquid yielded to analysis 1.09 grs.  $\text{CaCO}_3$ , and .63 gr.  $\text{Mg}_2\text{P}_2\text{O}_7$ .

*Experiment 2.*—600 grs. of soil B treated exactly as soil A. After 17 days the liquid was removed: it yielded .74 gr.  $\text{CaCO}_3$ , and .05 gr.  $\text{Mg}_2\text{P}_2\text{O}_7$ .

*Experiment 3.*—8000 grs. of the solution of tricalcic phosphate in carbonic water used in experiments 1 and 2, gave 1.92 grs.  $\text{CaCO}_3$ , and 1.28 grs.  $\text{Mg}_2\text{P}_2\text{O}_7$ .\*

From these data we find that soil A had absorbed 50.8 per cent. of the phosphoric acid originally present, and 43.2 per cent. of the lime. Soil B had under the same circumstances absorbed 96.1 per cent. of the phosphoric acid, and 61.5 per cent. of the lime.

It is to be remarked in the first place, that soil B (the one containing the large amount of iron) had absorbed a much greater quantity of phosphoric acid than soil A. Next, that in neither case had the absorption of phosphoric acid and lime been equal, as it would have been had the tricalcic phosphate been absorbed without chemical change, but that each soil had removed more of phosphoric acid than lime from the solution, this being especially the case with soil B. Notwithstanding, the soils have not comported themselves entirely as the pure ferric oxide and alumina of the former experiments, for these while absorbing phosphoric acid, left, practically speaking, the whole of the lime in the solution, whereas the soils have each removed lime to a considerable extent. This removal of lime as well as phosphoric acid from the solution might of course be urged as evidence that the absorption of phosphoric acid by the soils could be only partially attributed to chemical affinity; that, in fact, phosphate of calcium had been withdrawn as such from the solution by mere physical attraction.

It is well known that lime, in common with other bases, comes within the influence of soil absorption; it seemed therefore not

\* The solutions of phosphate of calcium used throughout these experiments were never saturated with the salt, lest any should be deposited in the soil by mere change of temperature or pressure.

unlikely that the soils in these experiments, impoverished in lime as they actually were, had absorbed it by virtue simply of their affinity for itself: that in fact, the decomposition of the phosphate of calcium might have been *complete* so far as the absorption of phosphoric acid was concerned, and a portion of the carbonate of calcium produced have been subsequently removed from the solution by a distinct action of the soil. If therefore it could be shown that the soils used in the experiments absorbed carbonate of calcium from a carbonic solution, the force of the objection would cease, and the results obtained would become consistent with the idea, that the oxide of iron and alumina were the *only* agents in the absorption of the phosphoric acid.

The next experiment was planned with a view to determine the question. The trial was made with soil B, the soil which had given the greatest absorption both of lime and phosphoric acid.

*Experiment 4.*—400 grs. of soil B were treated with 5816 grs. of a solution of carbonate of calcium in carbonic water, gas being passed through the mixture from time to time. After three days, 5255 grs. of the solution were removed; they yielded 3·15 grs.  $\text{CaSO}_4$ .

*Experiment 5.*—2371 grs. of the solution of carbonate of calcium used above gave 1·96 grs.  $\text{CaSO}_4$ .

From these figures it appears that the solution in contact with the soil had contained 3·53 grs. of carbonate of calcium, of which ·97 gr. was removed by the 400 grs. of soil.\* This experiment leaves no doubt that the soil really possessed the property of removing lime from its solution in carbonic acid.

It was thought that by employing a soil less exhausted of lime than in the previous experiments, the quantity of lime absorbed by it from the solution might be reduced, and the decomposition of the phosphate of calcium made more evident; in the next experiment the treatment of the soil with acetic acid was therefore omitted.

*Experiment 6.*—400 grs. of soil B, well washed with carbonic water, were treated with 8000 grs. of a solution of tricalcic phosphate; gas passed each day. After six days the liquid was removed; it yielded 1·32 grs.  $\text{CaCO}_3$ , and ·12 gr.  $\text{Mg}_2\text{P}_2\text{O}_7$ .

\* That the same soil should give up lime to a solution of carbonic acid, and yet absorb lime from a carbonic solution when offered to it in larger quantity, is quite agreeable to the laws of soil absorption.

*Experiment 7.*—8000 grs. of the solution of tricalcic phosphate used above yielded 2·59 grs.  $\text{CaCO}_3$ , and 1·94 gr.  $\text{Mg}_2\text{P}_2\text{O}_7$ .

It appears that the soil had here absorbed 93·8 per cent. of the phosphoric acid contained in the tricalcic phosphate, and only 49·0 per cent. of the lime. The decomposition of the phosphate during the absorption is more evident than in the former experiments, owing to the smaller appetite of the soil for lime.

I think it will now be allowed that the two soils operated on have shown a power of decomposing phosphate of calcium, a power quite similar to that possessed by hydrated ferric oxide and alumina: that, in addition to this, the soils had the property of absorbing carbonate of calcium from its solution in carbonic acid. These points have been established, not indeed so fully as they might have been by a more extended research, but yet sufficiently to show that the ferric oxide and alumina of a natural soil, have the same power of removing phosphoric acid from solution and combining with it which is possessed by the precipitated hydrates. Such being the case it follows that in all soils containing a sufficient amount of oxide of iron or alumina, the phosphoric acid will be found in combination with these bases, and not as an alkaline or alkaline-earthly phosphate. It is evident also that in such soils phosphate of iron or aluminium must be the ultimate state of all phosphoric acid applied in manure. When we recollect the small amount of phosphoric acid that occurs in soil, and the universal and generally abundant presence of ferric oxide, it appears that the exceptions to this rule must be very rare.

It is too much however to say that a soil in every case removes phosphoric acid from solution solely by virtue of the oxide of iron and alumina which it contains. Dr. Voelcker has shown that when a solution of superphosphate of lime is brought in contact with various soils, it is the soil which contains most calcium that generally removes the greatest quantity of phosphoric acid. Way has also told us that soils have the property of removing carbonic acid from its solution in water, so that a saturated solution of phosphate of calcium in carbonic water would deposit on contact with soil.

There are thus several ways in which phosphate of calcium may be thrown out of solution on contact with soil; but though the oxide of iron takes no part in these comparatively sudden

actions, it must in every case *finally* convert the phosphate of calcium into phosphate of iron.

The property belonging to ferric oxide, alumina, and soil, of readily decomposing phosphate of calcium, had not I think been previously ascertained; several writers have however ascribed to the ferric oxide and alumina of soil the power of combining with phosphoric acid. The only research on the subject I have met with is a recent one of Dr. Peters.\* He tried to discover the condition in which phosphoric acid exists in soil by acting upon soils with a variety of solvents. The conclusion he draws from an extended research is, that by far the greater part of the phosphoric acid contained in soils is combined with iron and aluminium. The view thus confirmed is strikingly opposed to that idea of the absorptive power of soils advocated by Liebig, who tells us that the power of absorption depends on a surface attraction enjoyed by all the component parts of a fertile soil, in which the attracted particles enter into no chemical combination; and that the arable soil will withdraw phosphoric acid without any chemical interchange with the constituents of the earth taking place.\*

We pass now to another part of the subject. What is the action of the oxide of iron and alumina of a soil towards potash, ammonia, and other bases, which soils are known readily to remove from solution? In the hope of affording some answer to this question, the behaviour of pure hydrated ferric oxide and alumina towards solutions of potassium and ammonium salts was made the subject of the next experiments. The series will be found in many points incomplete, but being at present unable to pursue it further, I must be content to speak with doubt on points where further research might clear the subject.

II. *Absorption of Carbonate of Potassium by Ferric Oxide.*—The ferric oxide was prepared by precipitating a dilute solution of ferric chloride by ammonia; the precipitate was washed by decantation till no trace of chlorine was found in the washings. The ferric oxide was next transferred to a large filter, and the excess of water removed by pressure between blotting paper. The amount of water present was determined in a portion of

\* Ueber das Verhalten der Phosphorsäure in Erdboden. (Annalen der Landwirtschaft, January 1867, p. 31.)

† Liebig's Natural Laws of Husbandry, pp. 67-9.

the mass by ignition, and the remainder taken for the absorption experiment.

Of course all hygroscopic water would diffuse into the salt-solution, while the water of hydration would remain with the ferric oxide. As the absorption of salt was ascertained only by the weakening of the solution, it was essential to know exactly the amount of water diffused into it from the moist hydrate; the state of hydration of the ferric oxide had thus to be determined. This was done in two instances, and being found constant, the result was adopted for all the experiments.

Hydrated ferric oxide prepared as above, and dried over oil of vitriol, gave in one case 15.66 per cent.; in another, 15.45 per cent. of water. According to Wittstein, the hydrate when freshly precipitated contains 25.71 per cent. of water ( $\text{Fe}_2\text{H}_6\text{O}_6$ ), but after keeping for some time under water contains but 14.75 per cent. ( $\text{Fe}_4\text{H}_6\text{O}_9$ ). It is seen that the hydrate prepared as above had not quite reached this last stage.

Two solutions of carbonate of potassium were employed; solution A contained .9905 per cent.; solution B .9993 per cent.  $\text{K}_2\text{CO}_3$ . In all the experiments with carbonate of potassium, the salt was determined in the form of nitrate.

*Experiment 1.*—234 grs. of hydrate containing 80 per cent. of water, and 4420 grs. of solution A; the mixture shaken from time to time. After two days the liquid was filtered. 510 grs. of the solution gave 6.62 grs.  $\text{KNO}_3$ , or .8872 per cent.  $\text{K}_2\text{CO}_3$ . The oxide of iron had here removed 2.99 grs.  $\text{K}_2\text{CO}_3$ , or 6.38 for 100 of the anhydrous oxide present.

*Experiment 2.*—188 grs. of moist hydrate containing 80 per cent. water, and 4420 grs. of solution A, saturated with carbonic acid before addition of the iron. After five days, 510 grs. of solution gave 6.59 grs.  $\text{KNO}_3$ , or .883 per cent.  $\text{K}_2\text{CO}_3$ . The ferric oxide had here absorbed 3.48 grs.  $\text{K}_2\text{CO}_3$ , or 8.72 per cent. of the anhydrous oxide present.

*Experiment 3.*—409 grs. of hydrate containing 84.4 per cent. water, with 2090 grs. solution B. After two days, 652.7 grs. of solution gave 5.55 grs.  $\text{KNO}_3$ , or .5812 per cent.  $\text{K}_2\text{CO}_3$ . The hydrate had here absorbed 6.80 grs.  $\text{K}_2\text{CO}_3$ , or 10.67 per cent. of the anhydrous oxide present.

*Experiment 4.*—880 grs. of hydrate kept under water five months, containing 88 per cent. of water, with 3383 grs. solution B. After three days, 561.6 grs. of solution gave 5.46 grs.

$\text{KNO}_3$ , or .6644 per cent.  $\text{K}_2\text{CO}_3$ . The ferric oxide had here removed 6.31 grs.  $\text{K}_2\text{CO}_3$ , or 6.00 per cent. of the anhydrous oxide present.

In all these experiments we have a considerable absorption of potassium. Experiments 3 and 4 were the first two made; in these, and especially in 3, the mixture of the pasty hydrate with the potassium solution was less perfect than was afterwards obtained; the absorption is possibly therefore below the normal amount. The smallest absorption is in experiment 6, where the ferric hydrate had been kept several months before use. Leaving out this result, we have a mean absorption of 8.39  $\text{K}_2\text{CO}_3$ , or 5.72  $\text{K}_2\text{O}$ , for 100 anhydrous ferric oxide.

It appears from experiment 4, that the presence of carbonic acid is no hindrance to the absorption.

With a view of throwing some light, if possible, on the precise nature of the absorptive action which took place in the above experiments, the amount of carbonic acid removed by the ferric oxide from the carbonate of potassium solution, was determined in three cases. The determination of carbonic acid was effected by means of an ammoniacal solution of chloride of barium.

It appeared that in every case more potassium had been taken from the solution than carbonic acid. In experiment 1, for 10 equivalents of potassium absorbed, 3.6 equivalents of carbonic acid were absorbed. In experiment 3, for 10 equivalents of potassium, 4.5 equivalents of carbonic acid were absorbed. In experiment 4, the proportion was for 10 of potassium, 7.9 of carbonic acid.

The proportions here are very various, much more so than can be accounted for by ordinary experimental error. The variation is certainly connected with the difference in the *amount* of the absorption; the smaller the extent of the absorption, the larger is the proportion of potassium removed. This is at once evident on comparing the figures already quoted.

	Potassium absorbed for 100 originally present.	Equivalents of car- bonic acid absorbed, for 10 of potassium.
Experiment 1 . . . . .	6.84	3.6
Experiment 3 . . . . .	18.67	4.5
Experiment 4 . . . . .	32.57	7.9

The reason of this behaviour is readily perceived. The

ferric oxide commences by absorbing potash, almost to the exclusion of carbonic acid; by so doing, the proportion of carbonic acid in the liquid is increased, but this accumulation of carbonic acid in the liquid now acts as a check on the further decomposition of the potassium salt, which consequently takes place to a less and less extent as the absorption progresses. The experiments are too few, and differ too much in their conditions to give a precise account of this action, they only point to its existence.

III. *Absorption of Nitrate of Potassium by Ferric Oxide.*—The nitrate of potassium solution used contained 1.049 per cent.  $\text{KNO}_3$ .

Three experiments were made with ferric oxide;\* in the first no absorption took place, in the second the absorption amounted to .45 per cent. of the anhydrous oxide, in the third experiment the absorption was .46 per cent. of the anhydrous oxide present. Rejecting the first trial, which is open to the same objection as experiment 3 in the last section, we have a mean absorption of .455  $\text{KNO}_3$ , or .211  $\text{K}_2\text{O}$ , for 100 of anhydrous ferric oxide.

It is a well known fact that soils absorb but little from many salts of potassium and ammonium, unless carbonate of calcium be at the same time present; and that when absorption has taken place under these circumstances, the acid of the salt is found remaining in the solution in combination with calcium. That is to say, soils can absorb but little potassium and ammonium from certain salts; but if these salts be decomposed by carbonate of calcium, then absorption takes place. With these facts in view experiments were made to see if the presence of carbonate of calcium would increase the amount of potassium removed by the ferric oxide.

The residue from the third experiment was taken: to it were added some more nitrate of potassium solution, and 33 grs. of dried, precipitated, carbonate of calcium. After seven days there had been a further absorption of .14 gr.  $\text{KNO}_3$ ; or .10 for 100 of anhydrous oxide.

The absorption being so small, the residue from the above was further treated with 50 grs. carbonate of calcium, and carbonic acid gas passed for eight hours through the mixture.

\* The details of these and of the subsequent experiments were given in the original paper, they are here omitted for want of space.

After two days it was found that no additional absorption had taken place.

It appears then that the addition of carbonate of calcium only very slightly increased the absorption of the potassium salt, and that saturation of the liquid with carbonic acid produced no greater effect.

IV. *Absorption of Sulphate of Potassium by Ferric Oxide.*—The sulphate of potassium solution employed contained 1·077 per cent. of sulphate of potassium.

In the experiment with hydrated ferric oxide the absorption amounted to 2·27  $K_2SO_4$ , or 1·23  $K_2O$ , for 100 of anhydrous oxide. The addition of 50 grs. carbonate of calcium gave no further absorption in three days.

V. *Absorption of Chloride of Potassium by Ferric Oxide.*—The chloride of potassium solution contained 1,053 per cent. of chloride of potassium.

In the absorption experiment the ferric oxide was found to have taken up ·42 KCl, or ·27  $K_2O$ , for 100 of the oxide present.

VI. *Absorption of Carbonate of Potassium by Alumina.*—The experiments with alumina were performed exactly as those with oxide of iron, the same salt-solutions were employed. The alumina was prepared by precipitating a solution of alum with ammonia, and except in the earlier experiments, the precipitate was, after some washing, re-dissolved in hydrochloric acid, and again thrown down by ammonia; washing by decantation being then continued, till no chlorine could be detected in the washings.

The water of hydration was determined in a specimen thus prepared:—Dried over oil of vitriol, it lost on ignition 33·14 per cent.; the formula  $Al_2H_6O_6$  requires 34·50 per cent. As the water of hydrated alumina has not been observed to alter in amount with the age of the hydrate, the theoretical percentage was adopted in all the calculations.

Two absorption experiments were made with the carbonate of potassium solution; in the first the salt absorbed was 2·24 per cent. of the alumina present; in the second it amounted to 2·31 per cent. The mean is 2·275  $K_2CO_3$ , or 1·55  $K_2O$ , for 100 of alumina. In the first experiment the alumina was several months old; the amount of absorption is, however, very slightly below that shown by freshly prepared alumina.



One experiment was made to determine whether any absorption of carbonic acid had taken place; the result showed that no carbonic acid had been absorbed. I made no further experiments on the decomposition of carbonate of potassium by alumina; but it is evident that alumina, like ferric oxide, possesses the power of decomposing the salt.

VII. *Absorption of Nitrate of Potassium by Alumina.*—One experiment was made; the absorption was  $\cdot 42$   $\text{KNO}_3$ , or  $\cdot 195$   $\text{K}_2\text{O}$ , for 100 of alumina.

The residue from the experiment was treated with carbonate of calcium, and the liquid saturated with carbonic acid; a further absorption of  $\cdot 04$  per cent.  $\text{KNO}_3$  took place: this amount is so small as to be quite within the errors of experiment.

VIII. *Absorption of Sulphate of Potassium by Alumina.*—The absorption in one experiment amounted to  $\cdot 84$  per cent. of the alumina present, or to  $\cdot 45$  per cent. reckoned as  $\text{K}_2\text{O}$ . The solution at the end of the experiment was observed to be slightly alkaline.

IX. *Absorption of Carbonate of Ammonium by Ferric Oxide.*—The carbonate of ammonium employed was the sesquicarbonate of commerce; the opaque coating of each fragment was, however, removed; the analyses made showed that the salt was nearly two-thirds monocarbonate.

Two solutions of carbonate of ammonium were employed. One contained  $\cdot 3222$  per cent.  $\text{NH}_3$ ; the other  $\cdot 3363$  per cent.  $\text{NH}_3$ . The determinations were all made by titration.

Three absorption experiments were made. In the first, 100 of ferric oxide absorbed  $2\cdot 08$   $\text{NH}_3$ ; in the second the ferric oxide had been preserved for several months, the absorption was here  $1\cdot 58$  per cent.; in the third experiment the absorption was  $2\cdot 39$  per cent. Taking the mean of the two trials with freshly-prepared hydrate, we have an absorption of  $2\cdot 235$   $\text{NH}_3$  for 100 of ferric oxide, or  $6\cdot 31$  per cent. reckoned as  $2(\text{NH}_4)\text{CO}_3$ . The hydrated oxide which had been kept long under water showed, as in the previous instance, a lower absorptive power.

Carbonic acid determinations were made in the carbonate of ammonium solution, and in the solution after absorption in the second experiment. The result showed that for 10 equivalents of ammonia  $10\cdot 12$  equivalents of carbonic acid had been taken up by the ferric oxide in that experiment; the ammonia had thus been absorbed as mono-carbonate. It appears then that ferric hydrate is capable of decomposing the supercarbonates of

ammonium; more than this can hardly be concluded from a single experiment.

X. *Absorption of Sulphate of Ammonium by Ferric Oxide.*—The solution of sulphate of ammonium employed contained .356 per cent.  $\text{NH}_3$ , or 1.382 per cent. of sulphate of ammonium. In this and all the other experiments with salts of ammonium, excepting those with the carbonate, the ammonia was determined by distillation with caustic potash and titration.

Two absorption experiments were made. In the first the ferric oxide took up 2.40 per cent.; in the second experiment 2.69 per cent. of sulphate of ammonium. The mean absorption was therefore, 2.545  $2(\text{NH}_4)\text{SO}_4$ , or .66  $\text{NH}_3$ , for 100 of ferric oxide. The liquid became very distinctly alkaline during the absorption.

Carbonate of calcium was added to the residue from the second experiment, and the liquid saturated with carbonic acid, but no further absorption was obtained.

XI. *Absorption of Chloride of Ammonium by Ferric Oxide.*—The solution of chloride of ammonium contained .958 per cent. of that salt, or .3044 per cent.  $\text{NH}_3$ .

The ferric oxide absorbed in one experiment .24  $\text{NH}_4\text{Cl}$ , or .08  $\text{NH}_3$ , for 100 of the oxide present. The solution became distinctly alkaline.

On the addition of carbonate of calcium a further absorption took place, amounting to .32  $\text{NH}_4\text{Cl}$  for 100 of ferric oxide.

XII. *Absorption of Nitrate of Ammonium by Ferric Oxide.*—The salt-solution contained 1.552 per cent. nitrate of ammonium, or .3298 per cent.  $\text{NH}_3$ .

In one experiment the absorption of nitrate of ammonium amounted to .41 per cent. of the ferric oxide, or to .09 per cent. reckoned as  $\text{NH}_3$ . The solution, as in the preceding experiments, became distinctly alkaline.

The addition of carbonate of calcium produced a further absorption of .28 per cent.  $\text{NH}_4\text{NO}_3$ .

XIII. *Absorption of Carbonate of Ammonium by Alumina.*—The same salt-solutions were used in the following experiments with alumina, as in the corresponding trials with oxide of iron:—

Two experiments were made. In the first the absorption of ammonia amounted to .76 per cent. of the alumina present; in the second experiment the absorption was 1.45 per cent. of the alumina. The difference between these experiments is very great; it was unfortunately not observed till there was no

longer an opportunity of repeating the experiments. The mean gives an absorption of 1.105 NH<sub>3</sub> for 100 of anhydrous alumina, or 3.12 per cent. reckoned as 2(NH<sub>4</sub>)CO<sub>2</sub>.

No experiment was made as to the proportion of carbonic acid absorbed.

XIV. *Absorption of Sulphate of Ammonium by Alumina.*—In one experiment the absorption of sulphate of ammonium amounted to 1.13 per cent. of the alumina present, or to .29 per cent. reckoned as NH<sub>3</sub>.

The solution at the end of the experiment was found to be decidedly alkaline; the same fact has been already mentioned as having been observed in the experiments with ferric oxide; the reaction is apparently due to a decomposition of the salt, and a greater absorption of its acid than of its base. In the experiment above described, the alkaline reaction was perhaps more marked than in any of the preceding experiments; it was thought, therefore, worth while to determine the absorption of acid which had taken place. The result showed that while 3.09 per cent. of the ammonia present had been absorbed, there had been removed 8.71 per cent. of the sulphuric acid; or for 10 equivalents of ammonia, 28.2 equivalents of sulphuric acid had been taken up.

No experiments were made as to the absorption of chloride or nitrate of ammonium by alumina.

To facilitate the discussion of the results arrived at in the before-mentioned experiments, the proportion of each salt absorbed by the ferric oxide and alumina is given in the following table:—

*Absorption of Salts of Potassium by Hydrated Ferric Oxide and Hydrated Alumina.*

Salt employed.	Strength of Solution.		Amount absorbed by 100 anhydrous ferric oxide.		Amount absorbed by 100 anhydrous alumina.	
	Per cent. of salt.	Per cent. of K <sub>2</sub> O.	Amount of salt.	Amount of K <sub>2</sub> O.	Amount of salt.	Amount of K <sub>2</sub> O.
Carbonate of potassium.....	.995*	.678*	8.89	5.72	2.27	1.55
Sulphate of potassium	1.077	.582	2.27	1.28	.84	.45
Chloride of potassium	1.053	.664	.42	.27	no experiment	
Nitrate of potassium	1.049	.488	.45	.21	.42	.19

\* Two solutions of the salt were employed; their strength differed but little.

*Absorption of Salts of Ammonium by Hydrated Ferric Oxide and Hydrated Alumina.*

Salts employed.	Strength of solution.		Amount absorbed by 100 anhydrous ferric oxide.		Amount absorbed by 100 anhydrous alumina.	
	Per cent. of salt.	Per cent. of NH <sub>3</sub> .	Amount of salt.	Amount of NH <sub>3</sub> .	Amount of salt.	Amount of NH <sub>3</sub> .
Carbonate of ammonium† .....	·930*	·829*	6·31	2·23	3·12	1·10
Sulphate of ammonium .....	1·382	·856	2·54	·66	1·13	·29
Chloride of ammonium .....	·958	·804	·24	·08	no experiment	
Nitrate of ammonium .....	1·552	·830	·41	·09	no experiment	

It is probable that if stronger solutions had been employed, the absorption by the oxide of iron and alumina would have been greater, and, on the other hand, that if weaker solutions had been used, the absorption would have been less. This rule has been well ascertained in the case of soil absorption. It follows, of course, that the figures quoted above expressing the amount of absorption can refer only to those particular conditions under which the experiments were made. The potassium solutions all contained about 1 per cent. of salt. With the ammonium solutions a better plan was adopted; each solution contained nearly the same amount of ammonia—about ·33 per cent.

On looking at the results collected in the table, it is at once evident that the absorptive power of alumina is not nearly so great as that possessed by ferric oxide. Of carbonate and sulphate of potassium the ferric oxide absorbs about three times as much as the alumina; with the corresponding ammonium salts it takes up about twice as much as the alumina. This was an unexpected fact, as from the lower equivalent of alumina it was presumed that it would exhibit a greater power of absorption than ferric oxide.

\* Two solutions of the salt were employed; their strength differed but little.

† The carbonate of ammonium is here reckoned as  $(2\text{NH}_4)_2\text{CO}_3$ ; for the actual composition of the carbonate used, see back.

The other prominent fact exhibited by the table is the very different absorption of the different salts. Both with potassium and ammonium salts the carbonate is absorbed to a considerable extent, the sulphate to a small extent, while of the chloride and nitrate only traces are taken up. The order of absorption appears to be the same for alumina as for ferric oxide, as far as the experiments allow us to judge.

Such seem to be the principal facts regarding the amount of absorption; it may be next asked, what is the real nature of the action here observed? There is a considerable amount of evidence that the absorption is due to a weak chemical affinity. First, it is found that a decided preference is shown for the salts of certain acids. It is also observed, that in these cases of ready absorption, the salt is nearly always decomposed to a considerable extent. Ferric oxide and alumina in absorbing carbonate of potassium take up much more potassium than carbonic acid; sesquicarbonate of ammonium is decomposed by ferric oxide in a similar manner. Sulphate of potassium and sulphate of ammonium are decomposed by alumina, and, especially in the case of the latter salt, much more sulphuric acid is taken up than base. Ferric oxide also decomposes sulphate of ammonium, and to a less extent the chloride and nitrate of ammonium. The absorption of sulphate of potassium by ferric oxide is the only instance of a notable absorption, apparently unattended with decomposition. It appears then, that chemical affinity was engaged in the process of absorption. That to the action of such affinity the absorption should be referred in every case is very probable, but hardly permits of being established by evidence.

The compound of the metallic hydrate and the alkaline salt is decomposed by water, but not without some difficulty. The action of water was tried on ferric hydrate saturated with carbonate of potassium. After two washings, with thorough agitation, each washing remaining in contact one day, the iron was found to have lost two-thirds of its potassium. The washing was sufficient to have reduced a perfectly soluble salt to  $\frac{1}{14}$ th its original quantity.

The amount of ammonia present in the ferric hydrate prepared for use in the absorption experiments was determined. The ferric hydrate, precipitated by ammonia from ferric chloride, was of course originally saturated with ammonia; to render it free

of chlorides, it received in the instance selected 14 washings. By calculation only  $\frac{1}{500000}$ th of the salt originally present would remain with the hydrate at the end of the operation. On distilling a portion of it with caustic potash it yielded ammonia equal to .042 per cent. of the anhydrous oxide present. A trace of ammonia was thus pertinaciously held by the ferric oxide, notwithstanding the abundant washing it had undergone.

Such is the character, as far as the present investigation goes, of the absorptive action of hydrated oxide of iron and alumina. Do the properties here recognized agree with those actually possessed by soils? may we in short conclude, that the absorptive power exhibited by soil towards potash and ammonia is in any way connected with the presence in soil of the hydrates of ferric oxide and alumina?

It is well known that soils usually contain a considerable proportion of ferric oxide in a more or less hydrated condition; they appear also to contain small quantities of uncombined alumina. Unless there be some preventing cause, the absorptive powers belonging to these bodies must therefore certainly be possessed by ordinary soil.

In entering on this subject, it must not be forgotten, however, that other ingredients of soil, the humus,\* and especially the hydrated silicates, have been shown to possess absorbent powers. We do not therefore expect to find that the comparative absorptive power of different soils is exactly in the proportion of the metallic hydrates which they contain; all we can hope to discover is, that some of the peculiarities of the absorption by metallic hydrates are generally met with in cases of soil absorption.

I have no experiments of my own to quote; a collation of the results of others seems to indicate that in one peculiarity, the preference of the various salts in a certain order, the behaviour of soils very generally agrees with what we have seen to be the action of hydrated ferric oxide, namely, that more of the carbonate is absorbed than of the sulphate, and that more of the sulphate is absorbed than of either the chloride or nitrate.†

\* Humus appears to be capable of removing free ammonia from a watery solution. (Brustlein, Jahresbericht der Agrikultur-Chemie, 1859-60, p. 1.)

† In order to ascertain the comparative absorption of different salts, it is necessary that the same soil should be treated with equivalent quantities of those salts, the same proportion between the soil and the salt-solution being maintained in

With soil, however, the difference between the amount of the various salts absorbed is much smaller than is the case with the pure hydrated oxides. Only a trace of the chloride and nitrate of potassium or ammonium was removed from solution by ferric hydrate, while by most soils considerable quantities of these salts, or rather of the alkali they contain, are taken up. The reason is well known. The carbonate of calcium, or the calcium silicate of fertile soils, decomposes the chloride, nitrate, or sulphate brought in contact with it: the alkaline carbonate or silicate thus formed is absorbed by the soil, and the action continues till the soil is saturated, or the solution rendered too dilute for further change to take place. If the action of the calcium were *complete*, and in some soil experiments this may possibly happen, every salt of potassium and ammonium would be absorbed to the same extent, provided the salts were applied in equivalent proportions: but it is rarely that the action of the calcium goes as far as this, and consequently some margin is

every experiment. The following are the only experiments I have found which seem to satisfy these conditions: a great majority of the results will be seen to agree with the statement made in the text.

Henneberg and Stohmann experimented with a garden soil; the order of greatest absorption was, free ammonia, sulphate of ammonium, chloride and nitrate of ammonium about equal.—*Jahresbericht der Agrikulturchemie*, 1858-9, p. 25.

E. Peters, experimenting on a soil with potassium salts found the following order of greatest absorption; carbonate, nitrate, sulphate, chloride. The nitrate here unexpectedly breaks the order.—*Ibid.* 1860-1, p. 9.

Fraas applied equivalent quantities of carbonate, sulphate, and nitrate of potassium to soils placed above lysimeters in the open air; there passed through into the lysimeters for equal quantities of water, the following amounts of potash, the quantity yielded by unmanured soil being deducted:—From the carbonate 3·80 grm.; from the sulphate, 8·89 grm.; from the nitrate, 10·27 grm. of potash. In another series the potassium salts were mixed with superphosphate of lime: there passed into the lysimeters from the manure, for equal quantities of water, 9·33 grm. of potash from the sulphate, and 12·02 grm. from the nitrate. The absorption by the soil was, of course, inversely as the drainage into the lysimeter.—*Ibid.* 1861-2, p. 11.

Küllenbergh made elaborate experiments on one soil with salts of ammonium, potassium, sodium, magnesium, and calcium, each salt being used of five different strengths of solution. With salts of ammonium the order of greatest absorption was, carbonate, sulphate, chloride and nitrate about equal. With potassium salts the same order obtained; and with the salts of calcium and magnesium a like result. With sodium salts the order was to some extent inverted.—*Ibid.* 1865, p. 15.

Voelcker, experimenting with solutions of chloride and sulphate of potassium, obtained with a sandy soil rather more absorption of the chloride, and with a marl rather more absorption of the sulphate.—*Jour. R. Agricultural Soc.* xxv, 333.

left for the display of the particular affinities of the ferric and aluminic hydrates, the result being that some preference is shown for carbonates and sulphates over the chlorides and nitrates.

An account has been already given of the attempt made to imitate the conditions of a soil by adding carbonate of calcium to the ferric hydrate; the experiments, as already narrated, were attended with little success, the further absorption which took place on adding carbonate of calcium to the salt-solution being in every case very small. Can this result be consistently explained?

On testing the solution at the end of each experiment, a small quantity of lime was always found to have been dissolved; some carbonate of the alkali must therefore have been produced, but in so small an amount as to form an excessively dilute solution, from which no practical absorption could be expected. The difference in the case of soil I believe to be this. The particles of ferric hydrate are there already saturated with calcium, and the decomposition of the alkaline salt takes place consequently on their *surface*; the ferric hydrate thus absorbs from a thin film of concentrated salt-solution, and the absorption has thus no difficulty in keeping pace with the decomposition. Whether this theory be correct or not, it is evident that the ferric hydrate would have no difficulty in taking up potassium or ammonium from either the chloride or nitrate if these salts were effectually decomposed by carbonate of calcium, since we have seen that ferric hydrate has a powerful affinity for the carbonates of these bases.

The experiments of Henneberg and Stohmann, E. Peters, and Küllenberg show, that of all the salts of the alkalies experimented with, the phosphate was the salt from which the soil removed the largest quantity of base; the absorption from the phosphate even exceeding that from the carbonate. This fact agrees remarkably well with what we have now seen to be the properties of oxide of iron and alumina. The ferric hydrate and alumina of the soil would require no aid from a calcium-salt to enable them to decompose an alkaline phosphate, their own powerful affinity for phosphoric acid would immediately effect the decomposition of the salt, and liberate its base for absorption.

There appear then to be several facts in the chemical his-



tory of soil, the explanation of which is at once afforded by ascribing to the ferric oxide and alumina of soil those properties I have proved to be possessed by the artificially prepared hydrates of these oxides.

In advocating the claims of ferric oxide and alumina, as constituents of the soil, taking an active part in its absorption of potassium and ammonium, I am advancing no new idea. The belief that such is the case is to be found in several published papers discussing soil absorption; what I have tried to do has been to set the matter on an experimental basis. The present research, though touching only the outline of the subject, has I think shown that the hydrated ferric oxide and hydrated alumina of a soil perform most important functions. Their presence gives the soil its power of taking up phosphoric acid from solutions of basic phosphates, and in conjunction with the hydrated double silicates, it is the source of that property of the soil by which it absorbs alkalies and alkaline earths from the solutions of their salts. In these actions, the ferric oxide, as generally most abundant, and in regard to the alkaline salts more energetic in action than alumina, will usually have the greatest share; indeed for many soils it must be the chief promoter of the absorptive power. I need hardly say how opposed are the facts and arguments here advanced to the theory of physical attraction already referred to.

The experiments detailed in the present paper, were made in the laboratory of the Royal Agricultural College, Cirencester.

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## II.—*Analysis of the Water of the Holy Well, a Medicinal Spring at Humphrey Head, North Lancashire.*

By THOS. ED. THORPE, Dalton Scholar in the Laboratory of Owens College, Manchester.

HUMPHREY Head is a fine promontory of limestone, situated on the northern shore of Morecambe Bay, and the spring issues through a fissure of the rock within a few feet from its base. The well formerly belonged to the Priors of Cartmel, and its water has long been reputed to possess medicinal virtues. Camden, in the "Brittannia," states that so far back as in his

time, it was much used as an antarthritic, and for cutaneous disorders. The water is perfectly clear and colourless, and possesses a distinctly saline taste. It effervesces slightly on agitation, indicating the presence of free carbonic acid, and it exhibits a feebly alkaline reaction. On free exposure to the air it deposits a crystalline sediment, consisting principally of calcium carbonate. Frequent thermometric observations, made during the last two years, show that its temperature is very uniform; it rarely varies even one degree from the mean point, 11.5 C. (52.7 F.) The quantity discharged through the fissure amounts to about a gallon per minute, and this rate of flow is constant during the different seasons of the year. Moreover, although the spring rises within ten yards of the sea at high water, this amount is uninfluenced by the tide.

The specific gravity of the water at its ordinary temperature is 1005.83, as the mean of concordant determinations made on samples collected on different occasions, and during opposite seasons of the year.

A careful qualitative analysis indicated the presence of the following bodies in estimable quantity :—

Bases.	Acids or Elements replacing them.
Potash.	Chlorine.
Soda.	Bromine.
Lithia.	Sulphuric acid.
Lime.	Phosphoric acid.
Magnesia.	Carbonic acid.
Baryta.	Silicic acid.
Strontia.	
Ferrous oxide.	
Manganous oxide.	
Ammonia.	

In addition to the above were found traces of alumina, iodine, fluorine, volatile and non-volatile organic matter. A special examination, by means of the spectroscope, was made for the recently-discovered alkaline metals in the residue obtained by the evaporation of 21 litres of the water, but the search was unsuccessful.

The method of quantitative analysis employed differed in no important particular from that usually adopted. It was essentially that detailed by Fresenius under the head of "Analysis

of Mineral Waters," in the last edition of his Manual. To insure accuracy, at least two, in some cases three, determinations of each principal constituent were made and the amount of water taken for the several estimations was, whenever practicable, ascertained by weight.

The following synopsis shows the direct results of the determinations: the numbers express the means of the experiments, and give the amounts in grammes of the substances contained in 1000 grammes of water.

1. Chlorine.....	3·31800
2. Bromine.....	0·00034
3. Sulphuric acid .....	1·22749
4. Carbonic acid (total) .....	0·17259
5. Silicic acid.....	0·01753
6. Ferrous oxide .....	0·00193
7. Manganous oxide.....	0·00015
8. Lime and strontia together, expressed as carbonates... ..	1·05777
9. Magnesia (total) .....	0·24602
10. Lime and strontia retained in solution* after boiling the water, expressed as carbonates..	0·92668
11. Lime precipitated on boiling:—	
Total lime and strontia, expressed as carbonates.....	1·05777
Lime and strontia retained in solution after boiling, expressed as carbonates*.....	0·92668
	<hr/>
The remainder.....	0·13109
Gives in form of carbonate the amount of lime precipitated on boiling.	
This corresponds to lime ....	0·07341
12. Lime retained in solution after boiling:—	
Sum of the lime and strontia retained in solution, expressed as carbonates.....	0·92668
Deduct the strontia (13) calculated as carbonate .....	0·00333
	<hr/>
This remainder .....	0·92335
Corresponds to lime .....	0·51708

\* All the strontia was assumed to remain in solution on boiling the water.

13. Baryta and strontia :—		
(a) Baryta .....		0·00031
(b) Strontia .....		0·00234
14. Phosphoric acid .....		0·00017
15. Lithia .....		0·00066
Corresponding to lithium chloride .		0·00187
16. Sodium chloride and potassium chloride and lithium chloride .....		5·11537
17. Potash .....		0·06387
Corresponding to potassium chloride		0·10116
18. Soda :—		
Sum of the alkaline chlorides .....		5·11537
Deduct potassium chloride ..	0·10116	
,, lithium chloride.....	0·00187	
		<hr/>
		0·10303
	Remainder, sodium chloride ..	5·00234
	Corresponding to soda .....	2·65224
19. Ammonia .....		0·00016
20. Total of fixed constituents.....		7·19260

In order to facilitate reference and comparison with other mineral waters, the acids and bases are here associated after the method adopted by Fresenius, founded on the assumption that the strongest acid is combined with the strongest base, &c., due consideration being of course given to the fact that the greater or less degree of the solubility of the salts considerably modifies the manifestations of the affinities.

Comparison of the total amount of fixed constituents found directly with the sum of the several constituents associated in the above manner. (The manganese and iron are calculated to the degree of oxidation in which they occur in the residue dried at 180° C.)

Barium sulphate .....	0·00047
Strontium sulphate.....	0·00414
Calcium sulphate.....	1·25677
Potassium sulphate.....	0·13031
Sodium sulphate.....	0·34651
Magnesium bromide .....	0·00042
Lithium chloride .....	0·00201
Sodium chloride .....	4·71189
Ammonium chloride .....	0·00033
Magnesium chloride .....	0·61767
Calcium phosphate .....	0·00038
Calcium carbonate .....	0·13071
Ferric oxide .....	0·00214
Mangano-manganic oxide .....	0·00016
Silicic acid .....	0·01753
	<hr/>
	7·22144
The residue dried at 180° ..	7·19260

Amount of the several constituents in one litre and in one gallon of the water:—

	Gram. per litre.	Grains per gallon.
Barium sulphate .....	0·00047	0·0329
Strontium sulphate .....	0·00416	0·2912
Calcium sulphate .....	1·26414	88·4898
Potassium sulphate .....	0·13107	9·1749
Sodium sulphate .....	0·34853	24·3971
Magnesium bromide.....	0·00042	0·0294
Magnesium iodide .....	traces.	traces.
Lithium chloride .....	0·00202	0·1414
Sodium chloride .....	4·73932	331·7524
Ammonium chloride.....	0·00033	0·0231
Magnesium chloride.....	0·62126	43·4882
Calcium phosphate .....	0·00038	0·0266
Calcium fluoride .....	traces.	traces.
Calcium carbonate .....	0·13147	9·2029
Ferrous carbonate .....	0·00313	0·2191
Manganous carbonate ....	0·00024	0·0168
Silicic acid.....	0·01673	1·2341
Organic matter.....	traces.	traces.
	<hr/>	<hr/>
	7·26367	508·5199

	Cb. c.	Cb. in.
Gas dissolved in the water and expelled by ebullition in vacuo, measured at 11°·5 C. and 760 mm. barometer. . . . .	32·64	9·04

The above composition is perfectly uniform at the different seasons of the year, as will be seen from a comparison of the numbers obtained from the following determinations of the total amount of solid residue, sulphuric acid, and chlorine contained in water collected on (A) August 30th 1865, and on (B) January 1st 1867.

1. Estimation of the total amount of fixed constituents.

The weighed quantity of water was evaporated with a known weight of pure sodium carbonate in a platinum dish, and the residue dried at 180° C. until its weight appeared constant:—

	Water employed.	Residue obtained.	Amount in 1000 grm.
A.	50·1645	0·3607	7·1947
B.	66·0903	0·4755	7·1905

2. Determination of sulphuric acid.

Barium chloride producing an immediate precipitation in the water acidified with hydrochloric acid, the estimation of the sulphuric acid was effected without previous evaporation:—

	Water employed.	BaSO <sub>4</sub> obtained.	SO <sub>4</sub> H <sub>2</sub> in 1000 grms.
A.	135·390	0·3953	1·2281
B.	96·816	0·2824	1·2269

3. Determination of chlorine (together with traces of bromine and iodine).

By Mohr's volumetric method, *i.e.*, with standard silver solution and potassium chromate:—

	Water employed.	Silver required.	Chlorine, &c., in 1000 grms.
A.	39·2872	0·3969	3·3183
B.	22·7887	0·23025	3·3187

The constant composition and temperature, together with the uniform rate of flow of this spring, seem to indicate that it originates in a reservoir of considerable extent, situated probably in some extensive cavern or fissure at the junction of the slate and limestone formations. Its uniformity of composition, &c., cannot be attributed to the influence of the neighbouring

tion. That such is not the case is well seen from a comparison of the ratios of the amounts of sulphuric acid and chlorine contained in sea-water with the amounts of these bodies, determined as above, in the water of the Holy Well. In the former case the ratios are as 1 to 8, in the latter as 1 to 3. Lastly, the absence of nitric acid and the minute quantity of ammonia and organic matter present in the water indicate the comparative freedom from putrescible organic remains of the strata through which the spring rises.

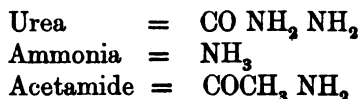
My best thanks are due to Dr. Roscoe for the use of his laboratory in the above analysis.

### III.—On the Action of Permanganate of Potash on Urea, Ammonia, and Acetamide in strongly Alkaline Solutions.

By J. ALFRED WANKLYN and ARTHUR GAMGEE.

It has been pointed out by Chapman and Smith,\* that permanganate of potash *in presence of excess of alkali* is an oxidizing agent of a most singular kind. It attacks alcohol much in the same way that nitric acid does, producing the diatomic acids glycollic and oxalic, but not aldehyde nor acetic acid. It is, at the same time, strangely inactive towards certain substances. Boiled with oxalic acid it does not suffer any decomposition; and, as is seen in the working of the† new method for the determination of albuminoid matter in waters, it may be boiled with ammonia without the occurrence of any chemical change.

The following experiments on the action of this re-agent on urea, ammonia, and acetamide:—



will serve as a contribution to its chemical history.

#### *Urea.*

The urea taken for this research was prepared by the well known process from ferrocyanide of potassium. One of the

\* Journ. of the Chemical Society [2], v, p. 302, June, 1867.

† Ibid., v, p. 449, Sept. 1867.

samples was proved to be pure by getting it to combine with the theoretical quantity of nitrate of mercury. Another sample was analysed by Dr. Affleck, who got from it the theoretical percentage of nitrogen by Dumas' method.

I.	0.100	grm. of urea,
	1.000	„ permanganate of potash,
	10.0	„ solid caustic potash,
	10.0	„ water,

was sealed up in a tube and heated to 130° C. for twelve hours. After the experiment the contents of the tube were free from unacted upon manganate or permanganate of potash—showing that much oxidation had taken place. On opening the tube under water there was an escape of 15.7 cub. cent. of gas.

In order to ascertain whether this evolution of gas was due to the permanganate giving up oxygen, or whether it was an evolution of nitrogen from the urea, a gas-analysis was made. (Frankland's apparatus was employed for this and the other gas-analyses given in this paper).

Volume taken.....	86
After adding hydrogen.....	139
After explosion .....	99

The gas therefore consisted of

Oxygen.....	15.50
Nitrogen .....	84.50
	<hr/>
	100.00

Obviously therefore, inasmuch as there was less oxygen than atmospheric air contains, the evolution of gas in our experiment was not evolution of oxygen but of nitrogen.

The space in the digestion tube unoccupied by liquid was measured and equalled 38.1 c.c. We are thus provided with data for determining whether the permanganate had evolved oxygen, and also how much nitrogen came from the urea.

	cub. c.
Volume of gas left in tube .....	38.1
Volume of gas escaped from tube .....	15.7
	<hr/>
Total volume of gas after experiment ....	53.8



consisting of 8·34 c.c. of oxygen and 45·46 c.c. of nitrogen.

Now the 38·1 c.c. of air originally present in the tube when it was sealed up contained 8·00 c.c. of oxygen and 30·1 c.c. of nitrogen.

We have therefore—

Oxygen present originally .....	8·00
Oxygen found after experiment.....	8·34

No oxygen, or only a trace of oxygen, was set free from the permanganate. Also the urea had evolved about 15 c.c. of nitrogen gas.

This amount of nitrogen is not half that which the urea contained (0·100 grm. urea contains 37·2 c.c. of nitrogen gas at 0°C. and 760 mm. pressure). A little of the nitrogen is accounted for as ammonia, for ·0032 grm. of nitrogen was found in the tube after the experiment in the form of ammonia, which was distilled off and estimated by titration. There thus remains about half of the total nitrogen to be accounted for, and which must have been converted into nitric acid. The circumstance that the 1 grm. of permanganate of potash had been completely reduced to the state of bi- or sesqui-oxide of manganese, and that there was no evolution of oxygen gas, is in itself sufficient proof that a considerable quantity of the nitrogen of the urea had been oxidized to nitric acid.

In this experiment, therefore, a little less than half of the nitrogen of the urea appeared as nitrogen gas, about half was oxidized to nitric acid, and a small portion was found as ammonia.

II. In a second experiment the proportion of permanganate was increased, the object proposed being to ascertain whether greater oxidizing effect would be the result of increasing the quantity of oxidizing agent.

0·050 grm. urea	
1·00	„ permanganate of potash
10·00	„ potash
10·	„ water

were sealed up and heated to 200° C. for four hours. After this treatment there remained much manganate still unreduced. On opening the tube there was a considerable escape of gas, which

was lost. Not so much as .0001 grm. of ammonia was to be found in the tube.

The experiment was repeated in order to have an opportunity of examining the gas.

0.100	grm. urea
2.00	„ permanganate of potash
10.00	„ caustic potash
12.	„ water

sealed up and heated to 160° C. for one hour. Abundance of manganate of potash remained after the experiment. On opening under water, there was an escape of gas. The total volume of gas was carefully measured and found to be 47 c.c. at 11° C. and 744 mm. pressure equal to 44.20 c.c. at 0° C. and 760 mm.

On analysis:—

Volume taken . . . . .	160
After adding hydrogen . . . . .	231.5
After explosion . . . . .	207.5

From which is deduced—

Oxygen . . . . .	5.00
Nitrogen . . . . .	95.00
	<hr/>
	100.00

Allowing for the nitrogen originally present in the tube when it was sealed up, which may be done by taking the 5 per cent. of oxygen to be the measure of atmospheric air, we shall arrive at the result that 33.68 c.c. at 0° C. and 760 mm. is the quantity of nitrogen furnished by the urea.

Thus we have:—

0.100 grm. urea give 33.68 c.c. of nitrogen.

Theory requires that 0.100 grm. urea contains 37.2 c.c. of nitrogen.

We arrive at the startling result that by increasing the proportion of permanganate, we put a stop to the oxidation.

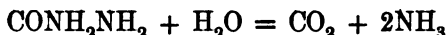
This fact, so singular at first sight, would appear to indicate that the oxidation of urea by permanganate is quick but superficial, whilst the oxidation at the expense of manganate is slower but deeper. Obviously (as will be apparent on referring to the actual quantities of permanganate and urea employed)

there would still remain unattacked urea in the first experiment after the permanganate had exhausted itself and passed into manganate. In the second experiment, on the contrary, there was enough permanganate to transform all the urea into carbonic acid, water, and nitrogen, without suffering deoxidation lower than to the stage of manganate, and nitrogen once in the free state is beyond the reach of oxidizing agents. For some interesting considerations concerning the difference of action between permanganates and manganates we would refer to Chapman and Smith's paper, which we cited at the beginning of this notice.

Thus far we have been dealing with very concentrated solutions at temperatures considerably above the boiling-point of water. Taking weaker solutions and operating at about 100° C., we meet with a similar decomposition, only slower. The following experiment illustrates this: we dissolved 4.75 milligrammes of urea in about 400 c.c. of pure water, added a little carbonate of soda, about 5 grm. of caustic potash, and about 0.5 grm. of permanganate of potash, and distilled for a very long time. A slow evolution of ammonia took place. Ultimately this evolution became very slow and then stopped. The quantity of ammonia obtained was estimated by the Nessler test, and amounted to 0.575 milligramme. Theory requires 2.692 milligrammes. About 22 per cent. of the nitrogen in the urea was obtained in the form of ammonia, the rest, of course, being either evolved as nitrogen gas, or converted into nitrate. An experiment on a still smaller quantity of urea gave a very similar result. Here the remark may be made that this result is hardly compatible with Mr. Dugald Campbell's statement, published in the "Laboratory," which is in effect that a weak solution of urea gives up all its nitrogen in the form of ammonia when it is partially decomposed with carbonate of soda, and then attacked with potash and permanganate of potash. If Mr. Campbell did not get off the full quantity of nitrogen in the form of ammonia by the treatment with carbonate of soda, he would not get the full quantity on employing permanganate.

#### *Ammonia.*

Urea being resolved into carbonic acid and ammonia by the simple assimilation of water,



it might be supposed that an oxidizing agent applied to urea in presence of water would, in effect, operate on the ammonia; and on this ground it was necessary to study the oxidation of ammonia.

*Experiment I.—*

0.050 grm. of  $\text{NH}_4\text{Cl}$   
 2.00 grm. of permanganate of potash  
 10.00 grm. of caustic potash  
 10. grm. of water

was heated to  $150^\circ\text{C}$ . for an hour and a half. Opened the tube; only minute traces of gas escaped. The gaseous contents of the tube were analysed:—

Oxygen	=	23.00
Nitrogen	=	77.00
		100.00

showing that the minute evolution of gas was evolution of oxygen, and not of nitrogen. The residue in the tube contained only .0033 grm. of nitrogen in the form of ammonia; therefore, there had been oxidation of most of the ammonia to the state of nitric acid.

In a second experiment sulphate of ammonia was substituted for the chloride of ammonium, the other things being the same, and the proportion the same. The temperature was a little higher than in the first experiment. Result: no ammonia and no gas.

*Acetamide.*

I. 0.050 grm. acetamide  
 1.00 grm. permanganate of potash  
 10. grm. caustic potash  
 10. grm. water

sealed up and heated to  $160^\circ\text{C}$ . for one hour.

After the experiment there remained abundance of manganate, but some peroxide of manganese had been deposited. No gas was given off, and only 0.0005 grm. of ammonia was found in the tube. The appearance of peroxide of manganese

proves that reaction had taken place Nitrates or nitrites must, therefore, have been formed.

The results arrived at in this paper are the following:—

Urea and great excess of permanganate, in presence of much caustic potash, gives all the nitrogen in the form of nitrogen gas.

Urea, with less permanganate, gives part of the nitrogen as gas, and part as nitric acid.

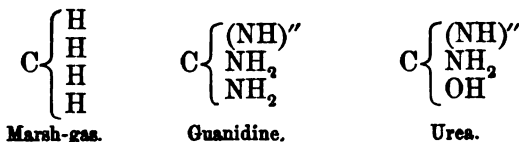
Ammonia, whether as chloride or sulphate, is totally oxidized to nitrates when heated with great excess of permanganate and alkali. Acetamide behaves like ammonia. These reactions occur at temperatures above the boiling-point of water.

The foregoing result has an important bearing on the rational formula for urea, and goes a long way to show that it is not the amide of carbonic acid. Ammonia and the amides yield nitrates on oxidation with alkaline permanganate. Urea, if it were really carbamide, should do the same, but it gives nitrogen gas instead. Moreover, urea, as is well known, is not resolved into ammonia and carbonic acid with anything like sufficient ease to admit of its being carbamide. We are,

therefore, led to write  $C \begin{cases} NH \\ NH_2 \\ OH \end{cases}$  for urea. It is marsh-gas

wherein imidogen, amidogen, and peroxide of hydrogen replace hydrogen. This formula is not new. Very simple and natural changes in this formula express the passage from urea to cyanate of ammonia and to carbamide.

The following formulæ express the relation between guanidine and urea:—




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#### IV.—*Synthesis of Caproic Acid.*

By J. ALFRED WANKLYN and ROBERT SOHENK.

CARBONIC acid attacks sodium-ethyl and sodium-methyl, forming propionate and acetate of soda respectively. It seemed to

us to be desirable to obtain a parallel reaction higher up in the series. We have selected the amylic group for this purpose.

Mercury-amyl was prepared by the process of Frankland and Duppa, from iodide of amyl and dilute sodium-amalgam, a little acetic ether being added, in order to effect the reaction. An analysis of the mercury-amyl gave the following result, proving the purity of the substance:—

0·3584 grm. taken gave 0·2082 grm. of metallic mercury.

Found. . . . . Hg per cent. = 58·09

Theory . . . . Hg per cent. = 58·50

From this mercury-amyl we prepared zinc-amyl by digesting it with zinc, as recommended by Frankland and Duppa.

The zinc-amyl was then sealed up with metallic sodium, and heated in the water-bath. Under these circumstances there was formation of sodium-amyl and precipitation of zinc.

On leading in carbonic acid gas there was evolution of heat, just as in the case of the ethyl or methyl compounds.

When the reaction was over, water was added, and the resulting solution of soda-salt evaporated to dryness in the water-bath.

The residue, distilled with dilute sulphuric acid, gave off an oily liquid having the smell of caproic acid. This oily distillate was dissolved in baryta-water, and formed a baryta-salt. About 3 grm. of baryta-salt was made.

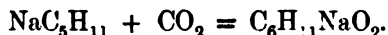
A barium determination was made on the dry salt. 0·2656 grm. gave 0·1697 grm. of sulphate of baryta. Ba per cent. = 37·56. Theory requires Ba per cent. = 37·33.

A silver-salt was also made and analysed. 0·0614 grm. gave 0·0298 grm. of silver.

Found. . . . . Ag per cent. = 48·53

Theory . . . . Ag per cent. = 48·43

The action of carbonic acid on sodium-amyl is expressed by the following equation:—



V.—*On the Origin of Muscular Power.*

By E. FRANKLAND, F.R.S.

[From the *Philosophical Magazine* for September 1866.]

UNDER this title there appeared in a recent number of the *Philosophical Magazine* an able article by Professors Fick and Wislicenus,\* in which these gentlemen describe the results of experiments made upon themselves before, during, and after an ascent of the Faulhorn in Switzerland. In these experiments the amount of measured work performed in the ascent of the mountain was shown to exceed, by more than three-fourths, the amount which it would be theoretically possible to realize from the maximum amount of muscle-oxidation indicated by the total quantity of nitrogen in the urine.

The data afforded by these experiments appear to me to render utterly untenable the theory that muscular power is derived from muscle-oxidation. Nevertheless, in the application of these data to the problem under consideration, one important link was found to be wanting, viz., the amount of actual energy generated by the oxidation of a given weight of muscle in the human body. Fick and Wislicenus refer to this missing link in the following words:—"The question now arises, what quantity of heat is generated when muscle is burnt to the products in which its constituent elements leave the human body through the lungs and kidneys? At present, unfortunately, there are not the experimental data required to give an accurate answer to this important question; for neither the heat of combustion of muscle, nor of the nitrogenous *residue* of muscle (urea), is known."

Owing to the want of these data, the numerical results of the experiment of Fick and Wislicenus are rendered less conclusive against the hypothesis of muscle-oxidation than they otherwise would have been; whilst similar determinations which have been made by Edward Smith, Houghton, Playfair, and others, are even liable to a total misinterpretation from the same cause.

I have endeavoured to supply this want by the calorimetrical determination of the actual energy evolved by the combustion

\* *Phil. Mag.*, vol. xxxi, p. 485.

of muscle and of urea in oxygen; but, inasmuch as uric and hippuric acids frequently appear in the urine as products of a less perfect muscle-oxidation, I have also determined the calorific value of these substances, and have added purified albumin and beef fat to the list. Creatine would also have been included; but, although I was furnished with an ample supply of this substance through the kindness of Mr. Dittmar, all attempts to burn it in the calorimeter were fruitless. In numerous trials under varied conditions it always exploded violently on ignition.

The determination of the actual energy developed by the combustion of the above-named substances is surrounded by formidable difficulties, which have probably prevented its previous execution. It is impossible to effect the complete combustion of these bodies in oxygen gas, under conditions which permit of the accurate measurement of the heat evolved; but preliminary experiments showed that complete oxidation could be secured by deflagration with potassic chlorate; and, although this method is doubtless inferior in accuracy to the calorimetric methods usually employed, it is hoped that, with the corrections described below, the results obtained merit sufficient confidence to render them useful in subsequent discussions of this and allied subjects. The determinations were made in a calorimeter devised some years ago by Lewis Thompson, and which I have repeatedly used with satisfaction in other estimations of a like kind. This instrument consists of a copper tube, which is made to contain a mixture of potassic chlorate with the combustible substance, and can be enclosed in a kind of diving-bell, also of copper, and so lowered to the bottom of a suitable vessel containing a known quantity (two litres) of water. The experiments were conducted in the following manner:—19.5 grams\* of potassic chlorate, to which about one-eighth of manganic oxide was added, were intimately mixed with a known weight (generally about two grms.) of the substance whose thermal value was to be determined; and the mixture being then placed in the copper tube above mentioned, a small piece of cotton thread, previously steeped in a solution of potassic chlorate and dried, was inserted in the mixture. The temperature of the water in the calorimeter was now carefully

\* I follow the example of the Registrar-General in abbreviating the French word *gramme* to gram.



ascertained by a delicate thermometer, and, the end of the cotton thread being ignited, the tube, with its contents, was placed in the copper bell, and lowered to the bottom of the water. As soon as the combustion reached the mixture, a stream of gases issued from numerous small openings at the lower edge of the bell, and rose to the surface of the water—a height of about 10 inches. At the termination of the deflagration, the water was allowed free access to the interior of the bell, by opening a stopcock connected with the bell by a small tube rising above the surface of the water in the calorimeter. The gases in the interior of the bell were thus displaced by the incumbent column of water; and by moving the bell up and down repeatedly, a perfect equilibrium of temperature throughout the entire mass of water was quickly established. The temperature of the water was again carefully observed; and the difference between this and the previous observation gives the calorific power, or the potential energy, of the substance consumed, expressed as heat.

The value thus obtained, however, is obviously subject to the following corrections:—

1. The amount of heat absorbed by the calorimeter and apparatus employed: *to be added.*

2. The amount of heat carried away by the escaping gases after issuing from the water: *to be added.*

3. The amount of heat due to the decomposition of the potassic chlorate employed: *to be deducted.*

4. The amount of heat equivalent to the work performed, by the gases generated, in overcoming the pressure of the atmosphere: *to be added.*

Although the errors due to these causes to some extent neutralize each other, there is still an outstanding balance of sufficient importance to require that the necessary corrections should be carefully attended to.

The amount of error from the first cause was once for all experimentally determined, and was added to the increase of temperature observed in each experiment.

The amount of heat carried away by the escaping gases after issuing from the water, may be divided into two items, viz. :—

- a.* The amount of heat rendered latent by the water which is carried off by the gases in the form of vapour.

- β.* The amount of heat carried off by these gases by reason of

their temperature being above that of the water from which they issue.

It was ascertained that a stream of dry air passed through the water of the calorimeter at about the same rate and for the same period of time as the gaseous products of combustion, depressed the temperature of the water by only  $0^{\circ}02$  C.

By placing a delicate thermometer in the escaping gases, and another in the water, no appreciable difference of temperature could be observed. Both these corrections may therefore be safely neglected.

The two remaining corrections can be best considered together, since a single careful determination eliminates both. When a combustible substance is burnt in gaseous oxygen, the conditions are essentially different from those which obtain when the same substance is consumed at the expense of the combined or solid oxygen of potassic chlorate. In the first case the products of combustion, when cooled to the temperature of the water in the calorimeter, occupy less space than the substances concerned in the combustion, and therefore no part of the energy developed is expended in external work—that is, in overcoming the pressure of the atmosphere. In the second case both the combustible and the supporter of combustion are in the solid condition, whilst a considerable proportion of the products of combustion are gases. The generation of the latter cannot take place without the performance of external work; for every cubic inch produced must obviously, in overcoming atmospheric pressure, perform an amount of work equivalent in round numbers to the lifting of a weight of 15lbs. to the height of 1 inch. In performing this work the gases are cooled, and consequently less heat is communicated to the water of the calorimeter. Nevertheless the loss of heat due to this cause is but small. Under the actual conditions of the experiments detailed below, its amount would only have increased the temperature of the water in the calorimeter by  $0^{\circ}07$  C. Even this slight error is entirely eliminated by the final correction which we have now to consider.

It is well known that the decomposition of potassic chlorate into potassic chloride and free oxygen is attended with the evolution of heat; if a few grains of manganic oxide, or, better, of ferric oxide, be dropped into an ounce or two of fused potassic chlorate, which is slowly disengaging oxygen, the evolution of

gas immediately proceeds with great violence, and the mixture becomes visibly red-hot, although the external application of heat be discontinued from the moment when the metallic oxide is added. The latter remains unaltered at the close of the operation. It is thus obvious that potassic chlorate, on being decomposed, furnishes considerably more heat than that which is necessary to gasify the oxygen which it evolves. It was therefore necessary to determine the amount of heat thus evolved by the quantity of potassic chlorate (9.75 grms.) mixed with one gram of the substance burnt in each of the following determinations. This was effected by the use of two copper tubes, the one placed within the other. The interior tube was charged with a known weight of the same mixture of potassic chlorate and manganic oxide as that used for the subsequent experiments, whilst the annular space between the two tubes was filled with a combustible mixture of chlorate and spermaceti, the calorific value of which had been previously ascertained. The latter mixture was ignited in the calorimeter as before; and the heat generated during its combustion effected the complete decomposition of the chlorate in the interior cylinder, as was proved by a subsequent examination of the liquid in the calorimeter, which contained no traces of undecomposed chlorate. The following are the results of five experiments thus made, expressed in units of heat, the unit being equal to 1 gram of water raised through 1° C. of temperature.

First experiment .....	340
Second experiment.....	300
Third experiment .....	375
Fourth experiment.....	438
Fifth experiment .....	438
	1891
Mean .....	378

This result was confirmed by the following experiments:—

(1) Starch was burnt, first, in a current of oxygen gas, and secondly by admixture with potassic chlorate and manganic oxide.

Heat-units furnished by 1 grm. of starch burnt with 9.75 grms. of potassic chlorate .....	} 4290
Heat-units furnished by the same weight of starch burnt in a stream of oxygen gas .....	
	3964
Difference .....	326

(2) Phenylic alcohol was burnt with potassic chlorate, and the result compared with the calorific value of this substance as determined by Favre and Silbermann.

Heat-units furnished by 1 grm. of phenylic alcohol burnt with 9.75 grms. potassic chlorate.....	} 8183
Heat-units furnished by 1 grm. of phenylic alcohol when burnt with gaseous oxygen (Favre and Silbermann) .....	
Difference .....	341

These three determinations of the heat evolved by the decomposition of 9.75 grms. of potassic chlorate, furnishing the numbers 378, 326, and 341, agree as closely as could be expected when it is considered that all experimental errors are necessarily thrown upon the calorific value of the potassic chlorate.

The mean of the above five experimental numbers was in all cases deducted from the actual numbers read off in the following determinations.

It was ascertained by numerous trials that all the potassic chlorate was decomposed in the deflagrations, and that but mere traces of carbonic oxide were produced.

Joule's mechanical equivalent of heat was employed, viz. 1 kilog. of water raised 1° C. = 423 metrekilogs.

The following results were obtained :—

*Actual Energy developed by 1 grm. of each substance when burnt in Oxygen.*

Name of substance (dried at 100° C.).	Heat-units.					Metre- kilogs. of force (Mean).
	1st Exp.	2nd Exp.	3rd Exp.	4th Exp.	Mean.	
Beef muscle purified by repeated washing with ether .....	} 5174	5062	5195	5088	5108	2161
Purified albumin ....		5009	4987	..	..	4998
Beef fat .....	9069	..	..	..	9069	3841
Hippuric acid.....	5330	5437	..	..	5383	2280
Uric acid.....	2645	2585	..	..	2615	1108
Urea .....	2121	2302	2207	2197	2206	984

It is evident that the above determination of the actual

energy developed by the combustion of muscle in oxygen represents more than the amount of actual energy produced by its oxidation within the body, because when muscle burns in oxygen its carbon is converted into carbonic anhydride, and its hydrogen into water, the nitrogen being to a great extent evolved in the elementary state; whereas when muscle is most completely consumed in the body the products are carbonic anhydride, water, and urea: the whole of the nitrogen passes out of the body as urea, a substance which still retains a considerable amount of potential energy. Dry muscle and pure albumin yield, under these circumstances, almost exactly one-third of their weight of urea; and this fact, together with the above determination of the actual energy developed in the combustion of urea, enables us to deduce with certainty the amount of actual energy developed by muscle and albumin respectively when consumed in the human body. It is as follows:—

*Actual Energy developed by 1 grm. of each substance when consumed in the body.*

Name of substance (dried at 100° C.).	Heat-units (Mean).	Metrekilogs. of force (Mean).
Beef muscle purified by ether ..	4868	1848
Purified albumin .....	4263	1803

Interpolating the data thus obtained into the results of Fick and Wislicenus's experiments, let us now compare the amount of measured and calculated work performed by each of the experimenters during the ascent of the Faulhorn, with the actual energy capable of being developed by the maximum amount of muscle that could have been consumed in their bodies, this amount being represented by the total quantity of nitrogen excreted in each case during the ascent and for six hours afterwards.

	Fick.	Wislicenus.
Weight of dry muscle consumed. . . . .	37·17 grms.	37·00 grms.
Actual energy capable of being produced by the consumption of 37·17 and 37·00 grms. of dry muscle in the body . . . . .	68,690 metrekilogs.	68,376 metrekilogs.
Measured work performed in the ascent (external work) . . . . .	129,096 metrekilogs.	148,656 metrekilogs.
Calculated circulatory and respiratory work performed during the ascent (internal work) . . . . .	30,541 metrekilogs.	35,681 metrekilogs.
Total ascertainable work performed..	{ 159,637 metrekilogs.	{ 184,287 metrekilogs.

The actual energy capable of being produced by the consumption of 37·17 and 37·00 grms. of dry muscle in the body was *estimated* by Fick and Wislicenus at 106,250 and 105,825 metrekilogs.

The experimental determination of the actual energy developed by the muscle-oxidation renders it now abundantly evident that the muscular power expended by these gentlemen in the ascent of the Faulhorn could not be exclusively derived from the oxidation either of their muscles or of other nitrogenous constituents of their bodies, since the maximum of power capable of being derived from this source, even under very favourable assumptions, is in both cases less than one-half of the work actually performed; but the deficiency becomes much greater if, as Fick and Wislicenus have done, we take into consideration the fact that the actual energy developed by oxidation or combustion cannot be wholly transformed into mechanical work. In the best-constructed steam engine, for instance, only one-tenth of the actual energy developed by the burning fuel can be obtained in the form of mechanical power; and in the case of man, Helmholtz estimates that not more than one-fifth of the actual energy developed in the body can be made to appear as external work. The experiments of Heidenhain, however, show that under favourable circumstances a muscle may be made to yield, in the shape of mechanical work, as much as one-half of the actual energy developed within it, the remainder assuming the form of heat.

Taking, then, this highest estimate of the proportion of mechanical work capable of being got out of actual energy, it becomes necessary to multiply by 2 the above numbers representing the ascertainable work performed, in order to express the actual energy involved in the production of that work. We then get the following comparison of the actual energy capable of being developed by the amount of muscle consumed, with the actual energy necessary for the performance of the work executed in the ascent of the Faulhorn.

	Fick.	Wislicenus.
	metrekiloga.	metrekiloga.
Actual energy capable of being produced by muscle-metamorphosis	68,690	68,376
Actual energy expended in work performed .....	319,274	368,574

Thus, taking the average of the two experiments, it is evident that scarcely one-fifth of the actual energy required for the work performed could be obtained from the amount of muscle consumed.

Interpreted in the same way, previous experiments of a like kind prove the same thing, though not quite so conclusively. To illustrate this, I will here give a summary of three sets of experiments,—the first, made by Dr. E. Smith upon prisoners engaged in treadmill labour; the second, by the Rev. D. Haughton upon military prisoners engaged in shot drill; and the third adduced by Playfair, and made upon pedestrians, pile-drivers, men turning a winch, and other labourers.

*Treadwheel Experiments.*

A treadwheel is a revolving drum with steps placed at distances of 8 inches, and the prisoners are required to turn the wheel downwards by stepping upwards. Four prisoners, designated below as A, B, C, and D, were employed in these experiments; and each worked upon the wheel in alternate quarters of an hour, resting in a sitting posture during the intervening quarters. The period of actual daily labour was 3½ hours. The total ascent per hour 2,160 feet, or per day 1·432 mile. The following are the results :—

*Treadwheel Work.* (E. Smith.)

	Weight in kilograms.	Ascent in metres.	Days occupied in ascent.	External work performed in metrekilogs.	Total nitrogen evolved.	Weight of dry muscle corresponding to nitrogen.
					grms.	grms.
A	47·6	23,045	10	1,096,942	171·3	1101·2
B	49	23,045	10	1,129,205	174·5	1121·7
C	55	20,741	9	1,140,755	168·0	1080·1
D	56	20,741	9	1,161,496	159·3	1024·3

In these experiments the measured work was performed in the short space of three and a-half hours, whilst the nitrogen estimated was that voided in the shape of urea in 24 hours. It will therefore be necessary to add to the measured work that calculated for respiration and circulation for the whole period of 24 hours. This amount of internal work was computed from the estimates of Helmholtz and Fick, as follows:—

*Internal Work.* (Helmholtz and Fick.)

	Work performed.	Actual energy required.
	metrekilogs.*	metrekilogs.
Circulation of the blood during 24 hours at 75 pulsations per minute	69,120	188,240
Respiration for 24 hours at 12 pulsations per minute	10,886	21,772
Statistical activity of muscles	Not determined	Not determined.
Peristaltic motion	" "	" "
	80,006	160,012

Taking this estimate for internal work, the average results of the treadwheel experiments may be thus expressed:—

*Treadwheel Work.*

Average external work per man per day	} 119,605 metrekilogs.
Average nitrogen evolved per man per day	

\* Since making use of this number I find that Donders estimates the work of the heart alone for twenty-four hours at 86,000 metrekilograms, a figure which is higher than that used above for the combined work of circulation and respiration.



*Treadwheel Work.*—(Continued.)

Weight of dry muscle corresponding to average nitrogen evolved per day	} 114 grms.
Actual energy producible by the con- sumption of 114 grms. dry muscle in the body .....	

Average actual energy developed in the body of each man,  
viz. :—

External work.....	119,605 × 2 =	239,210 metrekilogs.
Circulation .....	69,120 × 2 =	138,240 „
Respiration .....	10,886 × 2 =	21,772 „
		<hr/>
		399,222 „

In these experiments the conditions were obviously very unfavourable for the comparison of the amount of actual energy producible from muscle-metamorphosis with the quantity of actual energy expended in the performance of estimable work, since, during that portion of the 24 hours not occupied in the actual experiment, a large amount of unestimable internal work, such as the statical activity of the muscles, peristaltic motion, &c., was being performed. Nevertheless these experiments show that the average actual energy developed in producing work in the body of each man was nearly twice as great as that which could possibly be produced by the whole of the nitrogenous matter oxidized in the body during 24 hours. It must also be remarked that the prisoners were fed upon a nitrogenous diet containing six ounces of cooked meat without bone—a diet which, as is well known, would favour the production of urea.

*Shot-drill Experiments.*

The men employed for these experiments were fed exclusively upon a vegetable diet, and they consequently secreted a considerably smaller amount of nitrogen than the flesh-eaters engaged in the treadwheel work; the other conditions were,

however, equally unfavourable for showing the excess of work performed over the amount derivable from muscle-metamorphosis.

In shot drill each man lifts a 32-lb. shot from a tressel to his breast, a height of 3 feet; he then carries it a distance of 9 feet, and lays it down on a similar support, returning unloaded. Six of these double journeys occupy one minute. The men were daily engaged with

Shot drill.....	3 hours.
Ordinary drill.....	1½ „
Oakum-picking .....	3½ „

The total average daily external work was estimated by Houghton at 96,316 metrekilogs. per man. The following is a condensed summary of the results of these experiments:—

*Military Vegetarian Prisoners at Shot Drill.* (Houghton.)

Average external work per man per day.....	}	96,316 metrekilogs.
Average nitrogen evolved per man per day .....		
Weight of dry muscle corresponding to average nitrogen evolved per day	}	77.9 „
Actual energy producible by the consumption of 77.9 grms. of dry muscle in the body .....		
	}	143,950 metrekilogs.

Average actual energy developed daily in the body of each man, viz. :—

External work 96,316 × 2 .....	=	192,632 metrekilogs.
Internal work.....	=	160,012 „
		352,644 „

Owing chiefly to the vegetable diet of these prisoners, this result is more conclusive than that obtained upon the treadmill, the amount of work actually performed being considerably more than twice as great as that which could possibly be obtained through the muscle-metamorphosis occurring in the bodies of the prisoners.

*Playfair's Determinations.*

In these determinations the number 109,496 metrekilograms was obtained as the average amount of daily work performed by pedestrians, pile-drivers, porters, paviors, &c.; but as the amount of muscle consumption is calculated from the nitrogen taken in the food, the conditions are as unfavourable as possible with regard to the point I am seeking to establish; for it is here assumed, not only that all the nitrogen taken in the food enters the blood, but also that it is converted into muscle, and is afterwards oxidized to carbonic anhydride, water, and urea.

The following are the results, expressed as in the previous cases:—

*Hard-worked Labourer (Playfair).*

	Work performed.	Actual energy required.
	metrekilogs.	metrekilogs.
Daily labour (external work) ..	109,496	218,992
Internal work.....	80,006	160,012
	189,502	379,004

Actual energy capable of being produced from 5·5 oz. (155·92 grms.) of flesh-formers contained in the daily food of the labourer..... 288,140 metrekils.

Thus, even under the extremely unfavourable conditions of these determinations, the actual work performed exceeded that which could possibly be produced through the oxidation of the nitrogenous constituents of the daily food by more than 30 per cent.

We have seen, therefore, in the above four sets of experiments, interpreted by the data afforded by the combustion of muscle and urea in oxygen, that the transformation of tissue alone cannot account for more than a small fraction of the muscular power developed by animals; in fact this transformation goes on at a rate almost entirely independent of the amount of muscular power developed. If the mechanical work of an animal be doubled or trebled, there is no corresponding increase of nitrogen in the secretions; whilst it was proved, on the other hand, by Lawes and Gilbert, as early as the year 1854,

that animals under the same conditions as regarded exercise, had the amount of nitrogen in their secretions increased two-fold by merely doubling the amount of nitrogen in their food. Whence, then, comes the muscular power of animals? What are the substances which, by their oxidation in the body, furnish the actual energy whereof a part is converted into muscular work? In the light of the experimental results detailed above, can it be doubted that a large proportion of the muscular power developed in the bodies of animals has its origin in the oxidation of non-nitrogenous substances? For, whilst the secretion of nitrogen remains nearly stationary under widely different degrees of muscular exertion, the production of carbonic anhydride increases most markedly with every augmentation of muscular work, as is shown by the following tabulated results of E. Smith's highly important experiments upon himself, regarding the amount of carbonic anhydride evolved under different circumstances.\*

Excretion of carbonic anhydride during rest and muscular exertion:—

	Carbonic anhydride per hour.
During sleep .....	19·0 grams.
Lying down, and sleep approaching ..	23·0    "
In a sitting posture .....	29·0    "
Walking at the rate of 2 miles per hour	70·5    "
Walking at the rate of 3 miles per hour	100·6   "
On the treadmill, ascending at the rate of 28·65 feet per minute .....	189·6   "

It is admitted on all hands that food, and food alone, is the ultimate source from which muscular power is derived; but the above determinations and considerations prove conclusively, first, that the non-nitrogenous constituents of the food, such as starch, fat, &c., are the chief sources of the actual energy which becomes partially transformed into muscular work; and secondly, that the food does not require to become organized tissue before its metamorphosis can be rendered available for muscular power, its digestion and assimilation into the circulating fluid (the blood) being all that is necessary for this purpose. It is, however, by no means the non-nitrogenous portions of food alone

\* Phil. Trans., for 1859. p. 709.

that are capable of being so employed—the nitrogenous also, inasmuch as they are combustible, and consequently capable of furnishing actual energy, might be expected to be available for the same purpose; and such an expectation is confirmed by the experiments of Savory upon rats,\* which show that these animals can live for weeks in good health upon food consisting almost exclusively of muscular fibre. Even supposing these rats to have performed no external work, nearly the whole of their internal muscular work must have had its source in the actual energy developed by the oxidation of their strictly nitrogenous food.

It can scarcely be doubted, however, that the chief use of the nitrogenous constituents of food is for the renewal of muscular tissue—the latter, like every other part of the body, requiring a continuous change of substance; whilst the chief function of the non-nitrogenous is to furnish, by their oxidation, the actual energy which is in part transmuted into muscular force.

The combustible food and oxygen coexist in the blood which courses through the muscle; but when the muscle is at rest, there is no chemical action between them. A command is sent from the brain to the muscle, the nervous agent determines oxidation. The potential energy becomes actual energy, one portion assuming the form of motion, another appearing as heat. *Here is the source of animal heat, here the origin of muscular power!* Like the piston and cylinder of a steam-engine, the muscle itself is only a machine for the transformation of heat into motion; both are subject to wear and tear, and require renewal; but neither contributes in any important degree, by its own oxidation, to the actual production of the mechanical power which it exerts.

From this point of view it is interesting to examine the various articles of food in common use, as to their capabilities for the production of muscular power. I have, therefore, made careful estimations of the calorific value of different materials used as food, with the same apparatus and in the same manner as described above for the determination of the actual energy in muscle, urea, &c. The results are embodied in the following series of tables; but it must be borne in mind that it is only on the condition of the food being digested and passed into the

\* The Lancet, 1863, pages 381 and 412.

blood, that the results given in these tables are realized. If, for instance, sawdust or paraffin oil had been experimented upon, numbers would have been obtained for these substances, the one about equal to that assigned to starch, and the other surpassing that of any article in the tables; but these numbers would obviously have been utterly fallacious, inasmuch as neither sawdust nor paraffin oil is, to any appreciable extent, digested in the alimentary canal. Whilst the force-values experimentally obtained for the different articles in these tables must, therefore, be understood as the maxima assignable to the substances to which they belong, yet it must not be forgotten that a large majority of these substances appear to be completely digestible under normal circumstances.

TABLE I.—*Results of Experiments with Food dried at 100° C., in heat-units.*

Name of Food.	Heat-units. 1st Exp.	Heat-units. 2nd Exp.	Heat-units. 3rd Exp.	Heat-units. (Mean.)
Cheshire cheese.....	6080	6149	..	6114
Potatoes .....	3752	..	..	3752
Apples.....	3776	3562	..	3669
Mackerel.....	5994	6134	..	6064
Oatmeal (not dried) .....	4148	4018	3857	4004
Lean beef .....	5271	5260	5410	5313
White of egg .....	4823	4940	4927	4896
Carrots .....	3776	3759	..	3767
Pea-meal (not dried) .....	3866	4006	..	3936
Flour (not dried) .....	3941	3931	..	3936
Arrowroot (not dried) .....	3923	3902	..	3912
Butter .....	7237	7291	..	7264
Ham boiled and lean .....	4188	4498	..	4343
Lean veal .....	4459	4595	4488	4514
Hard-boiled egg.....	6455	6187	..	6321
Yolk of egg .....	6460	..	..	6460
Isinglass .....	4520	4520	..	4520
Cabbage .....	3809	3744	..	3776
Whiting .....	4520	4520	..	4520
Ground rice (not dried).....	3802	3824	..	3813
Cod-liver oil .....	9134	9080	..	9107
Cocoa nibs (not dried) .....	6809	6937	..	6873
Residue of milk.....	5066	5120	..	5093
Bread crumb .....	3984	3984	..	3984
Bread crust (not dried).....	4459	..	..	4459
Lump sugar (not dried).....	3403	3294	..	3348
Commercial grape-sugar (not dried) .....	3277	3277	..	3277
Residue from bottled ale .....	3776	3744	..	3760
Residue from bottled stout .....	6348	6455	..	6401

TABLE II.—*Actual Energy developed by 1 gram of various Articles of Food when burnt in Oxygen.*

Name of Food.	Heat-units.		Metrekilograms of force.		Percent. of water.
	Dry.	Natural condition.	Dry.	Natural condition.	
Cheese (Cheshire) .....	6114	4647	2589	1969	24·0
Potatoes .....	3752	1013	1589	429	78·0
Apples .....	3669	660	1554	290	82·0
Oatmeal .....	..	4004	..	1696	
Flour .....	..	3936	..	1669	
Pea-meal .....	..	3936	..	1667	
Ground rice .....	..	3813	..	1615	
Arrowroot .....	..	3912	..	1657	
Bread crumb .....	3984	2231	1687	945	44·0
Bread crust .....	..	4459	..	1888	
Beef (lean) .....	5313	1567	2250	664	70·5
Veal .....	4514	1314	1912	556	70·9
Ham (boiled) .....	4343	1980	1839	839	54·4
Mackerel .....	6064	1739	2568	758	70·5
Whiting .....	4520	904	1914	388	80·0
White of egg .....	4896	671	2074	294	86·3
Hard-boiled egg .....	6321	2333	2677	1009	62·3
Yolk of egg .....	6460	3423	2737	1449	47·0
Iainglass .....	4520	..	1914	..	
Milk .....	5093	662	2157	280	87·0
Carrots .....	3767	527	1595	223	86·0
Cabbage .....	3776	434	1599	184	88·5
Cocoa nibs .....	..	6878	..	2911	
Beef fat .....	9069	..	3841	..	
Butter .....	..	7264	..	3077	
Cod-liver oil .....	..	9107	..	3557	
Lump sugar .....	..	3343	..	1418	
Commercial grape-sugar .....	..	3277	..	1388	
Bass's ale (alcohol reckoned) ..	3760	775	1599	328	88·4
Guinness's stout ..	6401	1076	2688	455	88·4

TABLE III.—*Actual Energy developed by 1 gram of various Articles of Food when oxidized in the Body.*

Name of Food.	Metrekilograms of force.	
	Dry.	Natural condition.
Cheshire cheese .....	2429	1846
Potatoes .....	1563	422
Apples .....	1516	273
Oatmeal .....	..	1665

TABLE III—*continued.*

Name of Food.	Metrekilograms of force.	
	Dry.	Natural condition.
Flour .....	..	1627
Pea-meal.....	..	1598
Ground rice .....	..	1591
Arrow-root .....	..	1657
Bread crumb .....	1625	910
Lean of beef .....	2047	604
Lean of veal .....	1704	496
Lean of ham (boiled).....	1559	711
Mackerel.....	2815	683
Whiting .....	1675	335
White of egg .....	1781	244
Hard-boiled egg.....	2562	966
Yolk of egg .....	2641	1400
Gelatin .....	1550	
Milk .....	2046	266
Carrots .....	1574	220
Cabbage .....	1543	178
Cocoa-nibs .....	..	2902
Butter .....	..	3077
Beef fat .....	3841	
Cod-liver oil .....	3857	
Lump sugar .....	..	1418
Commercial grape-sugar .....	..	1888
Bass's ale (bottled).....	1559	328
Guinness's stout „ .....	2688	455

TABLE IV.—*Weight and Cost of various Articles of Food required to be oxidized in the body in order to raise 140 lbs. to the height of 10,000 feet.*

External Work = one-fifth of Actual Energy.

Name of Food.	Weight in lbs. required.	Price per lb.		Cost.	
		<i>s.</i>	<i>d.</i>	<i>s.</i>	<i>d.</i>
Cheshire cheese .....	1·156	0	10	0	11½
Potatoes .....	5·068	0	1	0	5½
Apples.....	7·815	0	1½	0	11½
Oatmeal .....	1·281	0	2½	0	3½
Flour .....	1·311	0	2½	0	3½
Pea-meal.....	1·335	0	3½	0	4½
Ground rice .....	1·341	0	4	0	5½
Arrowroot .....	1·287	1	0	1	3½
Bread .....	2·345	0	2	0	4½



TABLE IV—*continued.*

Name of Food.	Weight in lbs. required.	Price per lb.		Cost.	
		s. d.	s. d.		
Lean beef .....	3·532	1 0	3 6½		
Lean veal .....	4·800	1 0	4 3½		
Lean ham (boiled).....	3·001	1 6	4 6		
Mackerel.....	3·124	0 8	2 1		
Whiting .....	6·369	1 4	9 4		
White of egg .....	8·745	0 6	4 4½		
Hard-boiled egg.....	2 209	0 6½	1 2½		
Isinglass .....	1·377	16 0	22 0½		
Milk .....	8·021	5d. per quart.	1 3½		
Carrots .....	9·685	0 1½	1 2½		
Cabbage .....	12·020	0 1	1 0½		
Cocoa nibs .....	0·735	1 6	1 1½		
Butter .....	0·693	1 6	1 0½		
Beef fat .....	0·555	0 10	0 5½		
Cod-liver oil .....	0·553	3 6	1 11½		
Lump sugar .....	1·505	0 6	1 3		
Commercial grape-sugar ....	1·537	0 3½	0 5½		
Bass's pale ale (bottled) ....	9 bottles.	0 10	7 6		
Guinness's stout „ .....	6½ „	0 10	5 7½		

TABLE V.—*Weight of various Articles of Food required to sustain Respiration and Circulation in the Body of an average Man during twenty-four hours.*

Name of Food.	Weight in ozs.	Name of Food.	Weight in ozs.
Cheshire cheese .....	3·0	Whiting .....	16·8
Potatoes .....	13·4	White of egg .....	23·1
Apples.....	20·7	Hard-boiled egg .....	5·8
Oatmeal .....	3·4	Gelatin .....	3·6
Flour .....	3·5	Milk .....	21·2
Pea-meal.....	3·5	Carrots .....	25·6
Ground rice .....	3·6	Cabbage .....	31·8
Arrowroot .....	3·4	Cocoa nibs.....	1·9
Bread .....	6·4	Butter .....	1·8
Lean beef .....	9·3	Cod-liver oil.....	1·5
Lean veal .....	11·4	Lump sugar .....	3·9
Lean ham (boiled).....	7·9	Commercial grape-sugar....	4 0
Mackerel.....	8·3		

These results are fully borne out by experience in many instances. The food of the agricultural labourers in Lancashire contains a large proportion of fat. Besides the very fat bacon which constitutes their animal food proper, they consume large

quantities of so-called apple dumplings, the chief portion of which consists of paste in which dripping and suet are large ingredients; in fact, these dumplings frequently contain no fruit at all. Egg and bacon pies and potatoe pies are also very common *pièces de résistance* during harvest time, and whenever very hard work is required from the men. I well remember being profoundly impressed with the dinners of the navigators employed in the construction of the Lancaster and Preston Railway; they consisted of thick slices of bread surmounted with massive blocks of bacon, in which mere streaks of lean were visible. These labourers doubtless find that from fat bacon they obtain at the minimum cost the actual energy required for their arduous work. The above tables affirm the same thing. They show that .55 lb. fat will perform the work of 1.15 lb. cheese, 5 lbs. potatoes, 1.3 lb. of flour or pea-meal, or of 3½ lbs. of lean beef. Donders, in his admirable pamphlet "On the Constituents of Food, and their relation to Muscular Work and Animal Heat," mentions the observations of Dr. M. C. Verloren on the food of insects. The latter remarks, "many insects use, during a period in which very little muscular work is performed, food containing chiefly albuminous matter; on the contrary, at a time when the muscular work is very considerable, they live exclusively, or almost exclusively, on food free from nitrogen." He also mentions bees and butterflies as instances of insects performing enormous muscular work, and subsisting upon a diet containing but the merest traces of nitrogen. The following conclusions, may, therefore, be drawn from the foregoing experiments and considerations:—

1. A muscle is a machine for the conversion of potential energy into mechanical force.

2. The mechanical force of the muscles is derived chiefly from the oxidation of matters contained in the blood, and only in a very subordinate degree from the oxidation of the muscles themselves.

3. In man, the chief materials used for the production of muscular power are non-nitrogenous; but nitrogenous matters can also be employed for the same purpose, and hence the greatly increased evolution of nitrogen under the influence of a flesh diet, even with no increase of muscular exertion.

4. Like every other part of the body, the muscles are constantly being renewed; but this renewal is scarcely perceptibly

more rapid during great muscular activity than during comparative quiescence.

5. After the supply of sufficient albuminoid matters in the food of man to provide for the necessary renewal of the tissues, the best materials for the production both of internal and external work are non-nitrogenous matters, such as oil, fat, sugar, starch, gum, &c.

6. The non-nitrogenous matters of food which find their way into the blood yield up all their potential energy as actual energy; the nitrogenous matters, on the other hand, leave the body with a portion (at least one-seventh) of their potential energy unexpended.

7. The transformation of potential energy into muscular power is necessarily accompanied by the production of heat within the body, even when the muscular power is exerted externally. This is doubtless the chief, and probably the only, source of animal heat.

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## VI.—*On the Artificial Production of Coumarin and Formation of its Homologues.*

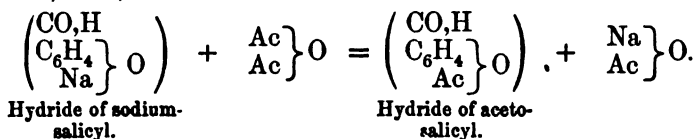
By W. H. PERKIN, F.R.S.

It is well known that coumarin, when fused with hydrate of potassium, yields salicylic and acetic acids. This fact has naturally led chemists to assume that there must exist a close relationship between this body and the salicylic series. No one, however, appears to have studied this subject, and, in fact, when we consider the formula of coumarin and compare it with that of any member of that series, we see that there is but little room for speculation; for example, if we compare the formula of coumarin with that of the hydride of salicyl, it will be seen that there exists only a difference of two equivalents of carbon, but it must be remembered that salicylic acid does not result from the action of hydrate of potassium upon coumarin, but is, in fact, a product of the decomposition of coumaric acid, therefore, speaking correctly, it is coumaric acid, and not coumarin, which is related to the salicylic series.

Under the name of aceto-salicylol, is described a body isomeric with coumaric acid, and this substance, being an acetyl derivative of the hydride of salicyl, should yield, if fused with hydrate of potassium, exactly the same products of decomposition as coumaric acid would, if treated in a similar manner.

In a paper I lately had the honour of reading before this Society, I mentioned that I was unable to obtain aceto-salicylol, or, more correctly, the hydride of aceto-salicyl, by the method of Cahours, and also that my endeavours to prepare it by the action of acetic anhydride upon the hydride of salicyl were unsuccessful.

It then appeared to me probable that if the hydride of salicyl were replaced by its sodium derivative, I might expect a better result, thus,—



On performing this experiment, the following results were obtained.

The hydride of sodium-salicyl, when submitted to the action of acetic anhydride, rapidly loses its yellow colour, and then dissolves; this change is attended with a very considerable elevation of temperature, the mixture becoming quite hot. After this reaction has moderated, the product, when boiled for a few minutes, and then poured into water, sinks as an oil, acetate of sodium dissolving. On distilling this oil, any acetic anhydride that may have escaped decomposition comes over at first, then hydride of salicyl; the temperature then rises rather quickly, and when it has reached 290°, all the remaining product on being distilled into a separate receiver, solidifies to a crystalline mass on cooling.

This product, when purified by pressure between bibulous paper, and recrystallised two or three times from alcohol, gave the following number on analysis:—

- I. .2396 of substance gave  
     .6508 of CO<sub>2</sub> and  
     .0942 of H<sub>2</sub>O.
- II. .2387 of substance gave  
     .6467 of CO<sub>2</sub> and  
     .0920 of H<sub>2</sub>O.

These numbers give percentages agreeing with the formula—



as the following comparisons will show :—

	Theory.		Experiment.	
			I.	II.
C <sub>9</sub> . . . . .	108	73·97	74·07	73·87
H <sub>6</sub> . . . . .	6	4·11	4·36	4·28
O <sub>2</sub> . . . . .	32	21·92	—	—
	<hr/>	<hr/>		
	146	100·00		

It will be seen that this formula is not that of the hydride of aceto-salicyl, being deficient by an equivalent of water. It is, however, the formula of *coumarin*.

To prove that this substance is in reality pure coumarin, and identical with the natural product, the following comparisons of its properties with those of a specimen prepared from the Tonka bean, were made.

I. When crystallised from water, side by side, these two products could not be distinguished the one from the other, the appearance of the crystals and their grouping being identical.

II. Crystallised from alcohol, side by side, they appeared perfectly alike.

III. Their melting points were also the same.

IV. Their boiling points were also the same.

V. When heated with strong aqueous hydrate of potassium, each yielded coumaric acid, and moreover the acid prepared from both specimens possessed the same melting point.

VI. Fused with hydrate of potassium, they yielded salicylic acid.

VII. They also possessed exactly the same odour.

It will be remembered that some time since I made a verbal communication to the Society, upon the artificial formation of this body,\* but stated that I had not had an opportunity of ascertaining whether it was identical, or only isomeric with the natural product; from the foregoing comparisons; however, I think I may safely conclude that this artificial coumarin is the same as that obtained from the Tonka bean.

It will not, perhaps, be out of place to make a few obser-

\* Laboratory, vol. i, p. 136.

vations respecting the properties of coumarin, which I have found to differ somewhat from those described in chemical works. The melting point of this substance is nearly  $20^{\circ}$  higher than that recorded, being between  $67^{\circ}$  and  $67^{\circ}5$  C. Its boiling point is also much higher, my experiments giving  $290^{\circ}5$  to  $291^{\circ}$  C. as the temperature, whereas it is generally stated as  $270^{\circ}$  C. It is also mentioned that coumarin is easily soluble in a solution of hydrate of potassium; this remark is perfectly true when applied to boiling, but not to cold solutions of that alkali; the slender crystals obtained by crystallising this substance from water, dissolving only with extreme slowness in a strong, cold, aqueous solution of hydrate of potassium.

The melting point of coumaric acid I have found to be between  $207^{\circ}$  and  $208^{\circ}$  C.,  $190^{\circ}$  C. being the temperature usually given.

The production of coumarin by means of acetic anhydride and the hydride of sodium-salicyl, made it appear probable that if other anhydrides were substituted for the acetic, a whole series of bodies homologous with coumarin, might be produced.

This anticipation has been verified by experiment.

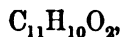
#### *Butyric Coumarin.*

Butyric anhydride acts but slowly upon the hydride of sodium-salicyl, unless heat be applied, the sodium compound then loses its colour, and gradually dissolves; after boiling for a few minutes, the product, if poured into water, separates as an oil, the butyrate of sodium which has been formed dissolving. On rectifying this oil, butyric anhydride and a little hydride of salicyl at first come over, the temperature then rapidly increases, and all the product distilling above  $290^{\circ}$  C. crystallises on cooling. This is rendered perfectly pure by pressure between bibulous paper and two or three crystallisations from alcohol. In one experiment I obtained three grammes of this substance from twelve grammes of the hydride of sodium-salicyl. When submitted to analysis, it gave the following numbers:—

- I.  $\cdot 1976$  of substance gave  
 $\cdot 5474$  of  $\text{CO}_2$  and  
 $\cdot 1049$  of  $\text{H}_2\text{O}$ .

II. ·2125 of substance gave  
 ·5902 of CO<sub>2</sub> and  
 ·1115 of H<sub>2</sub>O.

These numbers give percentages agreeing with those required by the formula—



as the following comparisons will show :—

	Theory.		Experiment.	
			I.	II.
C <sub>11</sub> .....	132	75·86	75·55	75·74
H <sub>10</sub> ....	10	5·75	5·89	5·82
O <sub>2</sub> .....	32	18·39	—	—
	<hr/>	<hr/>		
	174	100·00		

The formula of this substance is C<sub>2</sub>H<sub>4</sub> higher than that of coumarin, the difference being the same as that existing between acetic and butyric acids; this body is in fact a *butyric coumarin*, homologous with the natural product.

Butyric coumarin melts at from 70° to 71° C., and on cooling solidifies to a beautiful crystalline mass; at 296° to 297° C. it distils with slight decomposition. It is but little soluble in boiling water, the solution becoming milky as it cools, and after a time depositing a small quantity of crystals in the form of minute needles. In boiling alcohol it dissolves freely, and on standing separates from this solvent in large semi-opaque prisms. It is easily soluble in ether.

This body possesses the odour of ordinary coumarin, and also of fresh honey.

Butyric coumarin is nearly insoluble in cold aqueous hydrate of potassium, and even when gently heated with a saturated solution of that alkali, it only melts and floats as an oil upon its surface; if more strongly heated, however, it dissolves perfectly, forming a pale yellow solution; this, on being further concentrated, becomes opaque, and on standing a few moments an oily fluid rises to the surface, which, upon cooling, changes to a tenacious mass; it can then easily be separated from the excess of hydrate of potassium which remains fluid. This substance is a compound of butyric coumarin and hydrate of potassium; it is deliquescent and very soluble in water; acids

easily decompose it, with separation of butyric coumarin. When heated, this compound dries up to a yellow amorphous mass, and then undergoes decomposition, being converted into the potassium salt of a new acid, apparently homologous with coumaric acid; in fact, the coumaric acid of butyric coumarin. This acid is crystalline and easily soluble in carbonate of sodium and ammonia. For want of sufficient substance I have not been able to analyse this acid.

The addition of bromine to this coumarin causes it to liquefy, and on distilling the product, a tough resinous mass is obtained, giving, when digested with alcoholic hydrate of potassium, an acid which may be separated from the alkaline solution by means of hydrochloric acid. Ordinary coumarin, when treated with bromine, yields a similar product.

Butyric coumarin, when heated with fused hydrate of potassium, decomposes, yielding salicylic acid, together with hydrate of phenyl, and apparently butyric acid; but the odour of this latter compound is much masked by the presence of the hydrate of phenyl.

#### *Valeric Coumarin.*

The hydride of sodium-salicyl appears to be scarcely affected by valeric anhydride in the cold, but upon the application of heat, these two substances gradually react upon each other, forming a clear liquid. In performing this experiment I prefer to add the sodium compound to the boiling anhydride, and then to digest the mixture for a few minutes. The oily product of this reaction, after being agitated with water to remove valerate of sodium, is collected and distilled, the portion boiling above 290° C. being kept separate. This distillate, unlike those obtained in the preceding experiments, does not crystallise, even after standing for days, and it was only by repeated trials, that I succeeded in obtaining a method for its purification.

This process is based upon the property of coumarins to dissolve in boiling solutions of hydrate of potassium, and was carried out in the following manner:—

The above oily distillate, after being well agitated with a strong boiling solution of hydrate of potassium, was diluted with



water, and then mixed with ether, to separate all oily products, the clear aqueous solution, when acidified with hydrochloric acid, liberated the new coumarin, which was taken up with ether, and the ethereal solution agitated with carbonate of sodium, to remove any acids that might be present. On evaporating this solution, the new product was obtained as an oil solidifying to a crystalline mass upon cooling. It was then separated from oily impurities by pressure between bibulous paper; two or three crystallisations from alcohol then rendered it perfectly pure. From twelve grammes of the hydride of sodium-salicyl and about 14 grammes of valeric anhydride, I have obtained, by the above method, two grammes of this new coumarin. Two combustions of separate preparations of this body gave the following numbers :—

- I. .1990 of substance gave  
     .5600 of CO<sub>2</sub> and  
     .1153 of H<sub>2</sub>O.
- II. .2725 of substance gave  
     .7630 of CO<sub>2</sub> and  
     .1610 of H<sub>2</sub>O.

These numbers give percentages agreeing with the formula—



as the following comparisons will show.

	Theory.		Experiment.	
			I.	II.
C <sub>12</sub>	144	76.59	76.74	76.36
H <sub>12</sub>	12	6.38	6.43	6.56
O <sub>2</sub>	32	17.03	—	—
	188	100.00		

This substance is therefore *valeric coumarin*.

Valeric coumarin melts at 54° C., and on cooling solidifies to a splendid crystalline mass; at 301° C. it boils and distils with slight decomposition. It possesses a coumaric odour, but not to the same extent as the butyric coumarin. In boiling water it dissolves to a small extent, but is apparently insoluble in cold water. It is very soluble in alcohol, from which it crystallises in splendid transparent prisms nearly three-quarters of an

inch in length; they appear to be oblique six-sided prisms. This body is also very soluble in ether.

This coumarin appears to be insoluble in cold solutions of the alkalis. If added to a concentrated solution of hydrate of potassium, diluted with about a fourth of its volume of water, and gently heated, it melts and floats as an oil, but when heated further, perfectly dissolves. This solution, on being concentrated, becomes milky, and after standing a few moments, an oily layer forms on its surface, becoming a tenacious mass upon cooling; this is a compound of valeric coumarin and hydrate of potassium. This product is very deliquescent and easily soluble in water. Hydrochloric acid decomposes it, liberating the valeric coumarin. If heated strongly it decomposes, yielding an acid most probably valeric coumaric.

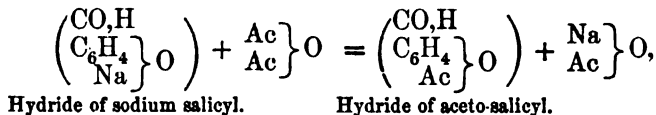
With fused hydrate of potassium this coumarin yields salicylic acid, hydrate of phenyl, and apparently a small quantity of valeric acid.

When distilled with pentachloride of phosphorous it yields a viscid oil, which, if gently heated, emits a turpentic odour, and when burnt, communicates a green colour to the edges of the flame, showing it to be a chlorinated body.

From the preceding results we see that coumarin is but a member of a whole series of homologous bodies producible from the hydride of sodium-salicyl by means of anhydrides. The question, therefore, which presents itself for consideration is, what is the nature of the reaction by which these bodies are formed, and their consequent constitution?

In this inquiry it will be well to consider the formation of ordinary coumarin, as the history of this substance is more complete than that of its homologues.

In the reaction by which this body is formed, there would appear to be two distinct stages, the first being the formation of the hydride of aceto-salicyl, thus:—



Hydride of sodium salicyl.

Hydride of aceto-salicyl.

the second consisting in the formation of coumarin from this hydride of aceto-salicyl by the separation of an equivalent of water.

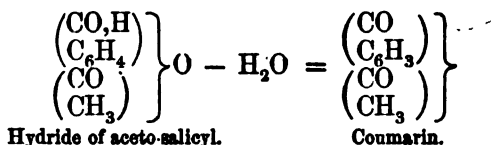
Respecting the first change I have found that by treating the hydride of sodium salicyl in a very careful manner the hydride of aceto-salicyl is actually formed.\*

The second part of this reaction is not so easy of explanation, viz., from what part of the hydride of aceto-salicyl is the equivalent of water removed.

Seeing that this change must be effected either by the dehydrating power of boiling acetic anhydride, or by a temperature not exceeding 300° C., it would not appear very probable that the acetylic radical was interfered with, especially as acetic acid is produced when coumarin or coumaric acid is decomposed with hydrate of potassium.

It is also evident that the hydride of aceto-salicyl loses its character as an acetate on changing into coumarin; otherwise, when dissolved in a strong solution of hydrate of potassium, coumarin should entirely split up, instead of forming coumaric acid.

Further, it is evident that it has lost its typical aldehydic hydrogen, otherwise coumarin would be an aldehyde. Assuming these considerations to be correct, the change which the hydride of aceto-salicyl undergoes on losing an equivalent of water, and thereby being converted into coumarin, may be represented thus:—

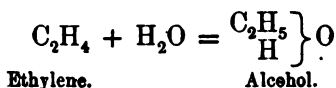
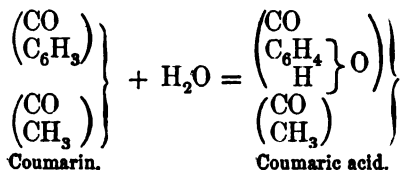


According to this formula, coumarin is a mixed acid radical, consisting of a molecule of acetyl, jointed to a molecule of a radical C<sub>7</sub>H<sub>3</sub>O. This would belong to the same series as cinnamyl, and I propose to name it *Diptyl*.

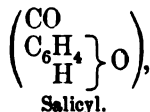
It will be well to see in what way the reactions of coumarin may be explained by this formula. I will first take the formation of coumaric acid.

\* This substance possesses all the properties pointed out by theory, namely, those of an aldehyde and an acetate. It freely combines with bisulphites and, with alcoholic hydrate of potassium, easily decomposes, yielding acetate of potassium, and the hydride of potassium-salicyl. I hope shortly to give a full account of this body.

This acid is formed by the assimilation of an equivalent of water by coumarin, through the intervention of hydrate of potassium, in the same way that alcohol is formed from ethylene by the intervention of sulphuric acid.

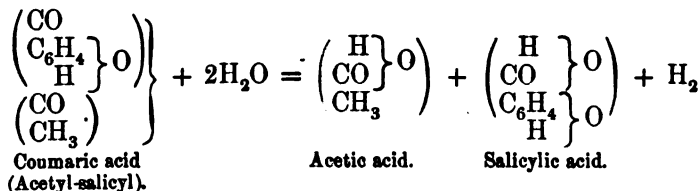


Thus expressed coumaric acid would be a phenol and not a true acid, and, if we regard the radical salicyl as a phenol as well as an acid radical,—



coumaric acid likewise becomes a mixed acid radical acetyl-salicyl.

The second reaction it will be well to consider is, the transformation of coumaric acid into acetic and salicylic acids. It will be seen that this change is easy of comprehension, the two radicals simply becoming hydrated.



To express the formation of the homologues of coumarin it is evidently only necessary to replace acetyl by other acid radicals.

Coumarin and its homologues probably have several isomers corresponding in number to the acids isomeric with salicylic, and

if coumarins are simply acid radicals, the possible number of such substances capable of existence is enormous.

The following is a table of the bodies described in this paper, written out according to the foregoing theoretical views. Also of coumaric acid, and its probable homologues not yet analyzed—

Acetic coumarin (Coumarin)	} C <sub>9</sub> H <sub>6</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>3</sub> O } C <sub>2</sub> H <sub>3</sub> O }	Acetyl-diptyl.
Propionic coumarin, wanting.			
Butyric coumarin ..	C <sub>11</sub> H <sub>10</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>3</sub> O } C <sub>4</sub> H <sub>7</sub> O }	Butyl-diptyl.
Valeric coumarin ..	C <sub>12</sub> H <sub>12</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>3</sub> O } C <sub>5</sub> H <sub>9</sub> O }	Valyl-diptyl.
Acetic coumaric acid } (Coumaric acid)	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	C <sub>2</sub> H <sub>3</sub> O } C <sub>7</sub> H <sub>4</sub> (HO)O }	Acetyl- salicyl.
Propionic coumaric acid, wanting.			
Butyric coumaric acid	C <sub>11</sub> H <sub>12</sub> O <sub>3</sub>	C <sub>4</sub> H <sub>7</sub> O } C <sub>7</sub> H <sub>4</sub> (HO)O }	Butyl- salicyl.
Valeric coumaric acid	C <sub>12</sub> H <sub>14</sub> O <sub>3</sub>	C <sub>5</sub> H <sub>9</sub> O } C <sub>7</sub> H <sub>4</sub> (HO)O }	Valyl- salicyl.

I am at present studying some new derivatives of coumarin and its homologues, with a view of obtaining a clearer insight into their nature.

## VII.—*Note on the Preparation of Urea.*

By JOHN WILLIAMS.

HAVING had occasion to prepare rather large quantities of urea, I found that the result constantly fell considerably short of what I considered a satisfactory one. This led me to consider if the ordinary mode of preparation could not be improved upon.

The result of my experiments is, that cyanate of lead is

better adapted for the purpose than the mixture of salts generally present in solution, when the usual process is adopted. I proceed in the following manner:—

I prepare the cyanate of lead by fusing cyanide of potassium, of the best commercial quality (containing about 90 per cent. of real cyanide), at a very low red heat, in a shallow iron vessel; red lead is added in the usual manner, by small quantities at a time, with constant stirring, so as to prevent the temperature rising too much during the operation. I prefer cyanide of potassium to ferrocyanide for many reasons, but mainly because the temperature can be kept down to the lowest point.

The cooled and finely powdered product is exhausted with successive portions of *cold* water, the liquid filtered, and nitrate of barium added. Carbonate of barium is thus precipitated. The mother-liquid, treated with nitrate of lead, yields pure cyanate of lead; this can be washed thoroughly, and dried at a gentle heat, and preserved for use. Unlike cyanate of potassium it is a permanent salt, and could be produced as a commercial product at a moderate price, if required.

To prepare urea, it is simply necessary to digest with sufficient water, at a gentle heat, equivalent quantities of cyanate of lead and sulphate of ammonium, filter and evaporate. I have found the result most satisfactory.

The compound ureas may in like manner be produced by substituting the sulphates of the compound ammonias for the ordinary sulphate of ammonium; the experiment has been tried and found successful.

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### VIII.—*On the Pyrophosphoric Amides.*

By J. H. GLADSTONE, Ph.D., F.R.S.

IN former communications\* I have described three acid bodies which may be viewed as pyrophosphoric acid in which one, two,

\* Quart. Journal Chem. Soc. Vol. III, pp. 135 and 353.  
 Do. do. „ XVII, p. 225.  
 Do. do. „ XIX, pp. 1 and 290.

or three semi-molecules of amidogen have displaced an equal number of molecules of hydroxyl. Their composition and their relation to the original acid may be thus exhibited:—

Pyrophosphoric acid	.. ..	$P_2H_4O_7$
Pyrophosphamic acid	.. ..	$P_2(NH_2)H_3O_6$
Pyrophosphodiamic acid	.. ..	$P_2(NH_2)_2H_2O_5$
Pyrophosphotriamic acid	.. ..	$P_2(NH_2)_3HO_4$

The basic hydrogen of these acids decreases as the amidogen increases, but in the case of the last one, half the hydrogen combined with the nitrogen may also be replaced by certain metals.

Since these papers were written, I have come across some additional facts, and have formed a more precise conception of the rational formulæ of these bodies. I propose to narrate these facts first, and then to develop the more complete theory.

*Pyrophosphamic Acid.*—This acid had hitherto been formed only by the breaking down of the higher amide under the influence of a metallic salt and heat. There is also another series of bodies—the tetraphosphamides—which yield it by decomposition; and in some cases I have found that a solution containing free pyrodiamic acid gave indications of its presence after standing for some weeks at the ordinary temperature. The following experiments led me at first to believe that it might be produced synthetically, but there is no conclusive proof that the compounds are not a peculiar series of double ammonium salts.

I. Ordinary pyrophosphoric acid was saturated with ammonia, and to this solution hydrate of barium was added, not in excess. A precipitate was obtained which, when well washed and dried, gave the indications of a pyrophosphamate; that is, when heated *per se* it turned black and gave off ammonia and a peculiar sublimate. When excess of hydrate of barium was added, nothing but the pyrophosphate was obtained.

II. Similar experiments were tried with acetate of lead, and ferric chloride, instead of hydrate of barium, and with like results.

III. The insoluble modification of ferric pyrophosphate was prepared in the presence of a quantity of chloride of ammonium. The well-washed precipitate gave the ordinary indications of

the pyrophosphamate. In one experiment 0.427 grm. of the salt thus produced was decomposed by boiling with hydrochloric acid, and gave 0.200 grm. of ammonio-chloride of platinum, which is equal to 2.93 per cent. of nitrogen. Had the whole precipitate been the pyrophosphamate, the nitrogen would have been 5.65 per cent., or nearly double that found.

IV. 0.355 grm. of ferric pyrophosphate was dissolved in ammonia and reprecipitated by dilute sulphuric acid. The salt thus obtained was well washed and decomposed by hydrochloric acid, when it gave 0.234 grm. of ammonio-platinum salt, equivalent to 4.13 per cent. of nitrogen.

V. This experiment was repeated with copper instead of iron salt, and with a similar result.

VI. The converse of these last experiments was tried. 0.333 grm. of ferric pyrophosphate (soluble modification) was dissolved in dilute sulphuric acid, and reprecipitated by ammonia, of course not in excess. The well-washed precipitate gave 0.170 grm. of ammonio-platinum salt, equivalent to 3.14 per cent. of nitrogen.

That the azotized ferric compound contained in these precipitates is not the ordinary pyrophosphamate is shown by the following properties:—It is soluble in excess of either pyrophosphate of sodium or ferric chloride; it is decomposed by cold dilute sulphuric acid; and moreover it is somewhat soluble in pure water. But while these properties distinguish it from the insoluble ferric pyrophosphamate previously known, they are rather suggestive of the idea that it may be a soluble modification analogous to the soluble ferric pyrophosphate. An attempt was made to convert it into the ordinary salt by boiling its solution in very dilute sulphuric acid, but without success. Ferric pyrophosphamate formed in the cold by the double decomposition of pyrophosphamate of potassium and ferric chloride was found to be identical in properties with the ordinary salt.

The action of heat upon this ferric compound is similar to its action on the pyrophosphamate, but even the production of water and of the white sublimate must be taken as evidence with considerable reserve; at any rate these substances are formed when the compound of pyrophosphoric acid and ammonia is heated *per se*.

For analysis it would, of course, be necessary to prepare this



compound free from pyrophosphate or any other salt. The fact that it is somewhat soluble in water, but not in a solution of chloride of ammonium, was taken advantage of for this purpose. An aqueous solution was, in fact, precipitated by the addition of the concentrated chloride, and the white flocculent compound was quickly washed with as little water as possible. Of what remained on the filter, 0.390 grm. decomposed by hydrochloric acid gave 0.334 grm. of ammonio-chloride of platinum, which is equivalent to 5.35 per cent. of nitrogen. This agrees nearly with the amount contained in ferric pyrophosphamate, viz., 5.65 per cent., but no ultimate analysis can decide between the formula  $P_2(NH_2)Fe_3O_6 \cdot H_2O$ , and a possible double ammonium salt of the composition  $P_2(NH_4)Fe_3O_7$ .

*Pyrophosphodiamic Acid.*—I formerly published a characteristic test of this acid, founded on the fact that when a solution containing it is rendered strongly acid, and is heated with a few drops of a ferric salt, the flocculent white pyrophosphamate makes its appearance. Precautions were given so as to avoid mistaking for pyrophosphodiamic acid, two others which I have since called tetraphosphoric compounds. With my further knowledge of these amides, I still think that the process may be looked upon as furnishing a characteristic test, but a chemist inexperienced in these compounds might easily be misled by the formation of the insoluble ferric pyrophosphate, which so closely resembles the pyrophosphamate. Hence it will be generally desirable, if not necessary, to dry a portion of the precipitate, and examine which compound it is, by heating it *per se* in a test tube, when the pyrophosphate simply fuses, and the pyrophosphamate does not fuse, but turns black at first and gives off ammonia and a little white volatile salt. This sublimate is very soluble in water, not so in alcohol: its aqueous solution contains ammonia, and some acid that gives a brown-black precipitate with nitrate of silver, like phosphorous acid. It may also be borne in mind that the pyrophosphamate will separate from a solution so acid as to prevent the formation of the insoluble pyrophosphate. A large excess of acid will also nearly, if not entirely, prevent the formation of the compound resulting from pyrophosphoric acid and ammonia in juxta-position. So there is little fear of error from this source.

Still as the proof that this acid may be prepared by the

eleven methods noted in my paper rests mainly on the evidence of this test, I thought it well to repeat the principal experiments, examining whether it was the pyrophosphamate that was really produced. I have found it to be so in all cases, and I have no reason to doubt that in each instance it had been formed by the decomposition of pyrophosphodiamic acid.

*Pyrophosphotriamic Acid.*—The method formerly given for preparing this body was not a productive one, and the acid was apt to be contaminated with another compound, unless great attention was paid to the temperature. The following is a far more productive and a better process:—Saturate oxychloride of phosphorus with dry ammonia gas, without regard to the rise of temperature; heat the resulting mass at about 220°C.; add water to it; and boil for about a minute. This will convert the whole of the insoluble portion into pyrophosphotriamic acid, with very little loss from the production of other phosphoric compounds.

This acid has also been met with among the products of decomposition of one of the tetraphosphoric amides that remain to be described at some future time. Its formation, along with other compounds, when pentachloride of phosphorus is thrown into the strongest aqueous ammonia, has been already noted.

#### *Theoretical Constitution.*

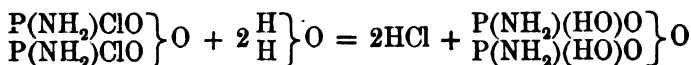
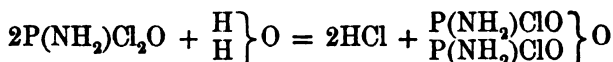
In my last communication to this Society,\* I suggested as the rational formula of pyrophosphoric acid, — $P_2(HO)_4O_3$ — or at greater length,  $\left. \begin{array}{l} P(HO)_2O \\ P(HO)_2O \end{array} \right\} O$ ;—and I expressed my conviction that when this acid is produced by the mutual action of water and oxychloride of phosphorus, the two atoms of hydrogen in the molecule of water are attacked simultaneously by two molecules of the chloride, and the water type is preserved in the new phosphorus compound.

A similar explanation will hold good in the formation of these amides from oxychloride of phosphorus, ammonia, and water. When the oxychloride is exposed to a current of the alkaline gas at a low temperature, it absorbs two equivalents, giving doubtless the first amide thus:—



\* Journ. Chem. Soc., vol. xx, p. 435.

When the oxychloride is dropped into the strongest aqueous solution of ammonia, it seems probable that the first action is the same. In both cases the production of the second pyrophosphoric amide by the action of water (or alkaline hydrate) may be well explained on the assumption that the two atoms of hydrogen (or ammonium) are attacked simultaneously by the chloride. The reaction must be expressed on paper in two successive stages, though they probably take place together in reality:—



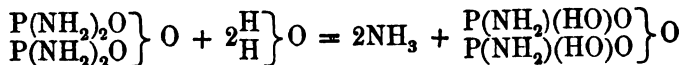
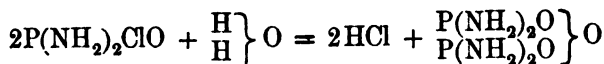
or  $\text{P}_2(\text{NH}_2)_2\text{H}_2\text{O}_5$ , *pyrophosphodiamic acid*.

These formulæ are precisely analogous to those by which the formation of pyrophosphoric acid was sought to be explained.

But the above is not the only amidated oxychloride from which the pyro-diamic acid may be produced. Oxychloride of phosphorus combines with 4 equivalents of ammonia gas, giving rise doubtless to a second amide, thus:—



When this is treated with water, it is only necessary to suppose that the action is precisely similar to that given above, the two stages being probably simultaneous, and the reaction being favoured in this instance by the affinity of the resulting acid and alkali for one another.

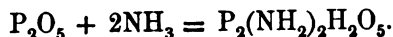


or,  $\text{P}_2(\text{NH}_2)_2\text{H}_2\text{O}_5$ , *pyrophosphodiamic acid*.

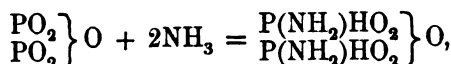
It will be perceived that this pyro-diamic acid is the sym-

metrical one, and that the unsymmetrical pyro-amic and pyro-triamic acids are not to be produced by this kind of reaction.

This acid is also formed directly by the mutual action of ammonia and phosphoric anhydride. Nothing can be simpler.

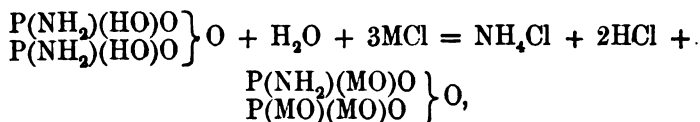


But  $P_2O_5$  is probably also constructed on the water-type, and in that case we shall have—



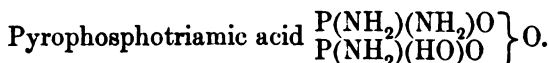
or,  $P_2(NH_2)_2H_2O_5$ , *pyrophosphodiamic acid*.

The unsymmetrical pyro-amic acid is produced by breaking down the symmetrical pyrophosphodiamic acid.



or,  $P_2(NH_2)M_3O_6$ , a *pyrophosphamate*.

The unsymmetrical pyro-triamic acid is produced from an amidated oxychloride of unknown composition, or by the breaking down of tetraphosphoric compounds. As these have not yet been described, I will content myself with writing down the formula of this acid in a manner analogous to its congeners:—



It is easy to understand how a substance of this composition, when boiled for a long time with water, or heated with sulphuric acid, parts with one of its nitrogen constituents and becomes the symmetrical pyrophosphodiamic acid.

IX.—*Freezing of Water and Bismuth.*

By ALFRED TRIBE, F.C.S.

PROFESSOR TYNDALL, in his work entitled "Heat considered as a mode of Motion," after speaking of the anomalous expansion of water prior to solidification, and the importance of this property in the economy of nature, controverts the generally received opinion that no other bodies possess the same properties in this respect, and cites bismuth as a case in point.

He says, at page 84: "The fact, however, is, that the case is not an isolated one. You see this iron bottle, rent from neck to bottom; I break it with this hammer, and you see a core of metal within. This is the metal bismuth, which, when it was in a molten condition, was poured into this bottle, the bottle being closed by a screw, exactly as in the case of the water. The metal cooled, solidified, expanded, and the force of its expansion was sufficient to burst the bottle. There are no fish here to be saved, still the molten bismuth acts exactly as the water acts."

The experiment, as above detailed, shows conclusively that molten bismuth expands either on cooling or freezing; but it affords very little or no proof of that which has been inferred from it.

The real question obviously is, not whether the fluid metal in returning to the solid condition rends an "iron bottle from neck to bottom," but whether the freezing of water and bismuth are analogous.

The results and details of the experiments which have been made with a view to answer this question form the subject of the present communication.

To ascertain the general mode of solidification, paraffin, nitrate chlorate and hydrate of potassium, and nitrate of sodium were experimented with.

The first experiments were made by simply melting bismuth, paraffin, &c., in good sized test-tubes. The solidification of the transparent molten substances, on cooling, could easily be observed to start from the bottom. The solidification of *bismuth*, likewise, was found to commence at the bottom, which

was ascertained by pouring off the fluid metal, after it had somewhat cooled.

Water was observed by placing tubes about three-quarters full of the liquid in a freezing mixture—taking care to have the mixture some little distance above the surface of the water. In every experiment solidification began at the surface; but in one especially, ice was seen gradually to descend, while in the freezing mixture, to the bottom. Two or three times during the descent, the tube was removed from the freezing mixture, which instantly stopped the formation of ice.

Thinking the tubes employed favoured the solidification of bismuth, &c., at the bottom (there being comparatively a larger surface exposed to the cooling action of the air), the experiments were repeated in U-shaped tubes, but with the same results.

The experiments were likewise made in crucibles, again with the same practical results. A slight modification of this form of experiment submitted the metal to a severe, and, what was considered, conclusive test. A crucible three-quarters filled with molten bismuth was placed over a small Bunsen's gas jet, and in this way allowed to cool extremely slowly—at the same time cold air was blown upon its surface. It will be seen that this experiment decidedly favoured solidification on the surface; but the freezing of the metal commenced in every case at the bottom—the process being repeated several times.

At this stage of the inquiry the question presented itself: Have the air-currents produced by the heated tubes, &c., anything practically to do with solidification at the bottom. To ascertain this, tubes filled with melted bismuth and paraffin were placed horizontally in the centre of a cylinder, which was then immediately closed. The solidification of the paraffin—it being transparent—could be distinctly seen to start from the bottom. The bismuth was ascertained, as before, by pouring off the surface metal.

From the foregoing experiments it appears that, as a rule, substances solidify upwards—water being *the* exception. Whether water be the only exception, it is certain that bismuth follows the rule.

With regard to those bodies which commence solidifying at the bottom we are entitled to reason as follows:—

As soon as a liquid begins to cool, its temperature ceases

to be uniform, some particles being more exposed to cooling influences than others. The necessary consequence of this must be, a difference in the specific gravity of the different particles, which will arrange themselves accordingly. It may be assumed, therefore, that after a short time, the denser particles will be found at the bottom, and as solidification begins there, the conclusion may be drawn that the point of greatest density coincides with that of solidification, and it stands to reason that the particles which solidify first are the coldest. It may be concluded from this that molten bismuth, on cooling, does not expand before freezing, as is the case with water, but that it continues to contract down to the solidifying point. The rapid expansion, which is well known to all chemists, is due to the act of crystallisation. The reason why the metal does not rise to the surface as soon as it becomes solid, although specifically lighter, is simply because it adheres to the bottom and sides of the vessel.

The two following experiments confirm in a great measure the above deductions: Melted paraffin and water at  $100^{\circ}$  C. were placed in tubes about six inches long, closed at both ends with corks, and then completely immersed, vertically, in cold water for a few minutes. It was found by a thermometer, that the top of each liquid was about  $3^{\circ}$  C. higher than the bottom.

Hence the analogy of bismuth with water is not perfect, but fails just in that point which causes our rivers and lakes to freeze from the surface and thus protect animal life.

The above experiments were principally, through the kindness of Dr. Gladstone, made in his laboratory, and I am much indebted to him for many valuable suggestions.

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X.—*On the Isomeric forms of Valeric Acid.*

By ALEXANDER PEDLER, Esq.

IN the concluding pages of Frankland and Duppa's memoir on Synthetical researches on Ethers,\* the authors state that ordinary valeric acid rotates a ray of polarized light to the right; whilst Wurtz had previously asserted that ordinary valeric acid is without any action upon a polarized ray. To reconcile these discrepant observations, Frankland and Duppa suggested that active amylic alcohol yields an active valeric acid when oxidized, and inactive amylic alcohol an inactive acid, and that the sample of amylic alcohol from which Wurtz's valeric acid had been prepared, was the inactive variety.

To test the validity of this suggestion, the two amylic alcohols were first separated by Pasteur's process, and then individually oxidized with a mixture of dipotassic dichromate and sulphuric acid in the usual manner. Equal weights of concentrated sulphuric acid and amylic alcohol were mixed together, the amylic alcohol being added very gradually; the mixture was then allowed to stand for 24 hours, and neutralized with baric carbonate, so as to form baric sulphamylate. The baric sulphamylate obtained from the active amylic alcohol, is, as stated by Pasteur, about two and a half times as soluble as that obtained from the inactive amylic alcohol; the mixed sulphamylates were consequently separated by fractional crystallisation, which was continued until the two salts were obtained in a state of purity.

Care must be taken to keep the solutions alkaline by baric hydrate, or the sulphamylates will decompose when heated. This process is long and tedious, as numerous crystallisations have to be made before the perfect separation of the sulphamylates is effected.

The two amylic alcohols were obtained by decomposing the baric sulphamylates with sodic carbonate, and again decomposing the sodic sulphamylates by ebullition with excess of

\* Chem. Soc. Journ., vol. xx, p. 102.



sulphuric acid. The amylic alcohols thus obtained were purified by drying and rectification; they then exhibited the following characters:—

The amylic alcohol obtained from the less soluble sulphamylate, was found to boil at  $129^{\circ}$  C., and to have a penetrating and oppressive odour which produces coughing, and a burning taste. In the polariscope, when tested with a yellow sodium flame, it was found to be perfectly incapable of rotating the ray of polarized light.

The alcohol obtained from the soluble sulphamylate, had a boiling point of  $128^{\circ}$  C., and an odour resembling that of the inactive alcohol, but more fruity; it was, however, equally irritating, and had a burning taste. It was found to rotate a yellow ray of polarized light  $17^{\circ}$  to the left in a tube 50 centimetres long.

For the conversion of these alcohols into valeric acid, a hot oxidizing mixture was used, made by dissolving two parts of dipotassic dichromate in moderately hot water, and then adding three parts of concentrated sulphuric acid. The alcohol was added through a funnel tube slowly, the vessel containing the mixture being also connected with a condenser.

The inactive alcohol when oxidized was converted into valeric acid and amylic valerate, which latter was decomposed by sodic hydrate, and the resulting amylic alcohol again oxidized. There was no effervescence when the alcohol was added to the hot oxidizing mixture.

The active amylic alcohol when added to the nearly boiling oxidizing mixture, was found to effervesce strongly from the evolution of carbonic anhydride. On allowing the oxidizing mixture to cool, and then adding more of the alcohol, scarcely any effervescence was observed. It was allowed to stand for some hours, and then distilled, and the distillate was found to contain valeric acid and amylic valerate, which latter was again decomposed and oxidized as before.

The two valeric acids were freed from the accompanying water, which had distilled over with them, by neutralizing with pure sodic carbonate, evaporating to dryness, and decomposing with sulphuric acid. When dried and distilled, they had the following characters:

The valeric acid obtained from the inactive variety of amylic alcohol, boiled at  $175^{\circ}$  C., and had the characteristic persistent

odour and taste of ordinary valeric acid. It was found when tested in the polariscope, not to possess the slightest action on the polarized ray. It is highly probable that this acid is identical

with the isopropacetic acid  $\left\{ \begin{array}{l} \text{CPr}\beta\text{H}_2 \\ \text{COH}_0 \end{array} \right.$  or  $\left\{ \begin{array}{l} \text{C}(\text{CMe}_2\text{H})\text{H}_2 \\ \text{COH}_0 \end{array} \right.$

obtained by Frankland and Duppa, and described in their memoir before mentioned. The boiling points of inactive valeric acid and of isopropacetic acid are identical.

The valeric acid from the rotating amylic alcohol boiled at about  $170^\circ\text{C}$ . and had the same disagreeable odour and taste as the inactive acid. When tested with the ray of polarized light, it gave a right-handed rotation of 43 degrees in a tube 50 centimetres long.

The above observations with the polariscope were most kindly taken by Dr. Frankland, to whom my most cordial thanks are due.

In order to ascertain the products of the graduated oxidation of the two amylic alcohols, some experiments were made by digesting them in sealed tubes at  $100^\circ\text{C}$ . with ordinary chromic acid oxidizing mixture.

When the rotating alcohol was thus treated, it evolved abundance of carbonic anhydride, and produced a large amount of acetic acid; while the inactive alcohol, which, when similarly digested, gave a mere trace of carbonic anhydride, seemed to produce scarcely anything but valeric acid.

The above experiments therefore indicate, either that the non-rotating valeric acid of Wurtz had been made, as suggested by Frankland and Duppa, from a non-rotating sample of amylic alcohol; or that the acid made from the mixed alcohols had been allowed to remain in contact with the hot oxidizing mixture sufficiently long to destroy the whole of the less stable rotating acid.

In a future paper I hope to be able to give a more detailed description of the oxidation products of the two alcohols, together with a comparison of the properties of the salts obtained from the two acids.

XI.—*On the Analysis of Potable Waters.*

By E. FRANKLAND, F.R.S., and H. E. ARMSTRONG, Esq.

ALTHOUGH the analysis of potable waters has received no inconsiderable amount of attention, the subject is surrounded with such formidable difficulties, that, at the time we undertook its investigation, it was generally regarded as one of the least satisfactory of analytical operations. The difficulties concentrate themselves chiefly upon the determination of the organic matters contained in all potable natural waters, and of the mineral compounds derived from the decomposition of these organic matters, viz., nitrous and nitric acids, and ammonia; the processes used for the estimation of the remaining mineral ingredients leaving little to be desired.

In the year 1856 Hofmann and Blyth\* drew attention to the defects of the processes then in use, and showed that the loss experienced on ignition by the solid residue of a water could be made more nearly than before to represent the organic matters, by excluding from this loss ammoniacal salts, moisture, and hydrochloric acid, an improvement which they effected by the addition of a known weight of sodic carbonate to the water before evaporation. These chemists also pointed out the great desirability of determining the amount of nitrogen entering into the composition of the organic matters contained in waters, although they did not succeed in devising any process by which this could be accomplished. In 1864 Weltzien† described a new process for determining the amount of nitric acid in waters by the ignition of the water-residue with finely divided metallic copper. He also employed, for the first time, a process for the estimation of organic carbon, which consisted in acidulating the water with sulphuric acid, evaporating to dryness, and then igniting the residue with cupric oxide, as in an ultimate organic analysis. It is obvious, however, that this latter process could only make a distant approach to accuracy, because the sulphuric acid would not only expel volatile organic acids if pre-

\* Report to the President of the General Board of Health on the Metropolis Water Supply, by Hofmann and Blyth.

† Ann. Chemie u. Pharm. cxxxii, 215.

sent, but, by liberating nitrous and nitric acids, could scarcely fail to cause the oxidation and loss of other forms of organic matter. Nevertheless, Weltzien's memoir on the well waters of Carlsruhe is one of the most important contributions ever made to this branch of analysis.

In the following year W. A. Miller\* gave an elaborate *resumé* of the processes which he considered to be most worthy of confidence, together with some important modifications and valuable suggestions; and in the same year Dr. Angus Smith† recommended and described certain modifications in the use of potassic permanganate in the examination of water for sanitary purposes.

In the monthly examination of waters supplied to London, one of us had frequently occasion to notice the serious imperfections which still attached themselves to the best processes of water analysis hitherto employed for the determination of the organic matter and of the products of its decomposition. Since the autumn of 1866 we have been occupied with the critical examination of these processes, and with attempts to place this branch of chemical analysis upon a more satisfactory basis. In laying the results of our inquiries before the Society, it will be most convenient first to discuss the merits of the processes in general use up to the commencement of our investigation, and then to describe the method of analysis which we now venture to recommend in dealing with the particular class of constituents above mentioned.

The following is a list of the determinations which are usually made in the so-called partial analysis of potable waters, and which have been submitted by us to examination:—

1. Estimation of total solid constituents.
2. Estimation of organic and other volatile matter.
3. Determination of amount of oxygen required to oxidize the organic matter.
4. Estimation of nitrous and nitric acids.
5. Estimation of ammonia.

We will examine these seriatim.

I. *Estimation of total Solid Constituents.*—This operation is usually performed by evaporating a given volume of the water

\* Journ. Chem. Soc., vol. xviii, p. 117.

† Estimation of Organic Matter in Water, by R. Angus Smith, Ph.D., F.R.S., &c., 1865.

to apparent dryness, with a known weight of sodic carbonate, upon a steam bath; and, as the residue so obtained is generally employed for the determination of the organic and other volatile matters expelled on ignition, it is dried at  $120^{\circ}$ — $130^{\circ}$  C., before being weighed. This process involves two errors: in the first place the salts of ammonia are decomposed by the sodic carbonate, the ammoniac carbonate formed being expelled during evaporation; and, secondly, urea, if present in the water, is slowly decomposed during evaporation with sodic carbonate, ammoniac carbonate being expelled. The loss of weight in the solid residue arising from the latter cause is seen from the following determinations:—

I. 1.505 grm. sodic carbonate, and .038 grm. urea, were dissolved in 1 litre of distilled water; the solution was evaporated on the steam-bath, and the residue dried at  $100^{\circ}$  C. The latter weighed 1.526 grm., showing a loss of .017 grm., or 44.7 per cent. of the urea employed.

II. .1 grm. sodic carbonate, and .05 grm. urea, on being similarly treated, left a residue which weighed .1205 grm., showing a loss of .0295 grm., or 59 per cent. of the urea present.

It is difficult, if not impossible, entirely to avoid this loss, but it is much lessened by omitting the sodic carbonate, and drying the residue at  $100^{\circ}$  C. By this modification of the process, the elements of water which would be expelled at  $120^{\circ}$ — $130^{\circ}$  C. are sometimes retained in the residue, but as such water is in chemical combination, it may be fairly said to belong to the solid constituents. It is only in the residues of waters containing much calcic and magnesian sulphates and chlorides that the weight of the elements of water so retained is considerable. Its small amount in the case of Thames water is seen from the following determinations made upon three different samples:—

	Solid residue dried at $100^{\circ}$	Solid residue dried at $120^{\circ}$ — $130^{\circ}$ C.
100,000 parts of Thames water gave	27.02 pts.	26.54
100,000           "           "	26.70   "	26.20
100,000           "           "	26.10   "	26.02

II. *Estimation of Organic and other Volatile Matter.*—This determination is effected by the gentle ignition in contact with air,

of the solid residue obtained by evaporation and subsequent drying at  $120^{\circ}$ — $130^{\circ}$  C., as above described. After being allowed to cool, the residue is repeatedly treated with a saturated solution of carbonic anhydride in water, until, on being again dried at  $120^{\circ}$ — $130^{\circ}$ , it ceases to gain weight. The loss in weight experienced by a water residue on incineration, although now no longer regarded as an exact ponderal expression of the organic matter present in the original water, is yet considered by many chemists to afford at least an approximate indication of the amount of organic impurity. How far any reliance can be placed upon it in this respect may be judged of by the consideration of the following sources of error which we have found in the examination of this process. We have already shown that urea, when present in water contaminated with sewage, is partially dissipated during evaporation with sodic carbonate; thus a portion of the organic impurity of a water may be lost before the determination of the "organic and other volatile matter" is made, but this error is still further increased in the case of urea, and probably also in that of other nitrogenous organic compounds, by the impossibility of expelling the whole of the organic matter on ignition, as is seen from the following experiments:—

I. A water-residue consisting of .997 grm. sodic carbonate, and .0205 grm. urea, lost on ignition .003 grm.

II. A water-residue consisting of 1.542 grm. sodic carbonate, and .039 grm. urea, lost on ignition .011 grm.

III. A water-residue consisting of 1.505 grm. sodic carbonate, and .038 grm. urea, lost on ignition .016 grm.

The results of these experiments may be thus expressed:—

	I.	II.	III.
Percentage of organic matter expelled			
on ignition	14.6	28.2	42.1
left in			
residue	85.4	71.8	57.9

It is probable that the organic matter left in the residue is in the form of sodic cyanate or cyanurate.

Another source of error which we have repeatedly encountered in the use of this process consists in a continued increase of weight by successive treatments of the incinerated residue with an aqueous solution of carbonic anhydride, until in some cases

the weight of the incinerated residue even exceeds that which was observed before incineration. This remarkable phenomenon does not arise from any solid residue left by the solution of carbonic anhydride itself, because this source of fallacy was carefully eliminated, and moreover it occurs only with particular samples of water, but with these samples it is always observed when the determination is repeated. It occurs also in an equal degree when a solution of ammoniac carbonate is substituted for one of carbonic anhydride. It is difficult to account for this increase in weight, but, when it occurs, the determination of the loss by ignition becomes impossible, because the analyst does not know when to discontinue the treatment of the residue with solution of carbonic anhydride. These facts show how difficult it is to interpret the meaning of the loss on ignition experienced by a water-residue; it may arise entirely from organic matter, or it may be exclusively due to the dissipation of mineral ingredients. On the one hand, there may be much more organic matter in a water than is represented by the total loss on ignition, indeed; we have not unfrequently observed in the analysis of waters, greatly contaminated with sewage, that the loss on ignition has actually been considerably less than the weight of the carbon alone contained in the organic matters. On the other hand, this determination may indicate the presence of a considerable amount of organic matter in a water which is wholly free from it. All that can be inferred from the loss on ignition is that, when it is large, the water is probably contaminated with animal or vegetable organic matter, or has been previously in contact with decaying animal matters.

III. *Determination of amount of Oxygen necessary to Oxidise the Organic Matter.*—The uncertainty which surrounds the determination of the organic and other volatile matter by the ignition of the dried water-residue, has led to attempts being made to estimate indirectly, by means of potassic permanganate, the amount of organic matter present in the water before evaporation. Potassic permanganate, when dissolved in water, readily yields oxygen to many substances capable of combining with this element; thus if it be added to water acidulated with sulphuric acid, and containing oxalic acid in solution, the latter is completely and rapidly converted into carbonic anhydride and water, at the expense of oxygen derived from the perman-

ganate; and it is found that eight parts by weight of oxalic acid, in being thus oxidised, abstract almost exactly one part by weight of oxygen from the permanganate, the latter being converted into manganic sulphate. In undergoing this chemical change the rich violet colour of the solution of potassic permanganate, vanishes, and it is thus easy to ascertain, by the non-disappearance of the characteristic tint of the permanganate, when the oxidation of the oxalic acid is complete. Now, a similar disappearance of colour occurs when the solution of potassic permanganate is added to an acidulated sample of potable water containing organic matter, and it has been assumed that, as in the case of the oxalic acid, the organic matter contained in the water is completely oxidised by the permanganate, which is thus thought to indicate the amount of oxygen required for this purpose. Dr. Letheby has even employed this reaction for the estimation of the *actual weight* of organic matter contained in a known volume of water, on the assumption that every eight grains of organic matter contained in a sample of water, rob the permanganate solution of one grain of oxygen. Such a method of ascertaining the actual amount of organic matter in a water, or even the amount of oxygen required to convert this organic matter into its final products of oxidation, would be invaluable on account of the extreme facility with which it can be applied; but, unfortunately, the further study of this process reveals its utter untrustworthiness.

By the addition of known weights of different organic substances to equal volumes of pure distilled water, the latter was artificially contaminated with a known proportion of each kind of organic matter. Every sample of water so contaminated was made to contain three parts of organic matter in 100,000. The amount of oxygen which this organic matter abstracted from the potassic permanganate was first carefully ascertained, and then the actual amount of organic matter present in the water was calculated, on the assumption that eight parts by weight of organic matter consumed one part by weight of oxygen from the permanganate. The same test was also applied to another sample of distilled water, from which all organic matter was carefully excluded, but to each 100,000 parts of which, three parts of sodic nitrite were added. The importance of the last experiment will be evident when it is



remembered how frequently nitrites are present in potable waters. The amount of oxygen consumed was determined for two different periods of time, viz. :—First, for a period, at the end of which the acidulated and contaminated water remained tinted with permanganate for ten minutes after the addition of the latter; and secondly, for a period of six hours, during the whole of which time the permanganate was present in excess.

The results are contained in the following table, where they are compared with the known amount of organic matter present, and the known amount of oxygen, which that organic matter would require for its complete oxidation :—

1	2	3	4	5	6	7
Name of Substance, 3 parts of which were contained in 100,000 parts of water.	Oxygen absorbed in 10 minutes. (Experiment.)	Oxygen absorbed in 6 hours. (Experiment.)	Oxygen required to oxidize organic matter. (Calculated.)	Amount of organic matter present. (Calculated from Column No. 2.)	Amount of organic matter present. (Calculated from Column No. 3.)	Amount of organic matter actually present.
Gum arabic.....	·0102	·0350	3·55	·082	·280	3·0
Cane sugar.....	·0064	·0162	3·37	·051	·111	3·0
Starch.....	·0148	·0302	3·55	·114	·241	3·0
Gelatin.....	·0792	·1886	6·76	·634	1·469	3·0
Creatin.....	·0080	·0172	6·59	·064	·138	3·0
Alcohol.....	·0093	·0164	6·26	·074	·131	3·0
Urea.....	·0092	·0119	6·40	·074	·095	3·0
Hippuric acid.....	·0828	·0600	5·90	·262	·480	3·0
Oxalic acid (crystallised)	·3747	·3750	·88	2·998	3·000	3·0
Sodic nitrite.....	·6910	·6918	0·00	5·521	5·580	0·0

From this table, it is seen that, of the nine kinds of organic matter operated upon, only one was completely oxidized by potassic permanganate, even after the lapse of six hours; whilst it will be remarked that urea, hippuric acid, and creatin—three organic substances likely to be present in water recently contaminated with sewage—suffer an oxidation which, even in the most favourable case, only reaches  $\frac{1}{30}$ th of complete oxidation; whilst if the attempt be made to calculate the amount of these substances present in the water, from the quantity of oxygen so absorbed, instead of finding three parts of each in 100,000 of water, we obtain only ·138 part of creatin,

·095 part of urea, and ·480 part of hippuric acid. On the other hand, the mineral salt, sodic nitrite, weight for weight, surpasses every form of organic matter experimented upon in the avidity with which it absorbs oxygen; and three parts of this inorganic substance in 100,000 of water would actually, by the mode of calculation above described, indicate no less than  $5\frac{1}{2}$  parts of organic matter. Thus it is evident, that for the estimation of the amount of organic matter in water, or the quantity of oxygen necessary to oxidise that organic matter, permanganate of potash is utterly untrustworthy. The fallacy of the permanganate test has often been suspected, but it was imagined that, although not to be relied on for quantitative estimations, yet its rapid decoloration afforded positive evidence of the presence of organic matter in actual putrescence, and consequently in its most dangerous condition. We fear, however, that, even for this subsidiary purpose, the permanganate is not sufficiently trustworthy. Fresh urine contains no organic matter in a state of putrescence, but, even when largely diluted, it decolorises the permanganate with almost the same rapidity as potassic nitrite. With all these defects, however, this reagent may still be used in certain cases as a qualitative test where there is no opportunity for accurate analytical examination. Thus, if a clear and colourless water, decolorises much of the permanganate solution, the water ought to be rejected for domestic use as being of *doubtful* quality; for although such a water may be absolutely free from nitrogenous organic impurity, yet its decolorising action upon the permanganate would indicate with considerable certainty that it had been in contact with decaying animal matters. Should the water, however, instead of being colourless, be tinged of a yellow or brownish yellow colour, when viewed through a considerable stratum, as in a quart decanter, for instance, its capability of decolorising a considerable amount of permanganate solution ought not to be regarded with the same suspicion as a similar reaction with a colourless water, because the yellow tint of such waters is generally owing to the presence of peaty matter, which, though innocuous, has the power of decolorising potassic permanganate.

The depth of colour which a sample of water exhibits when viewed through a stratum some two feet in thickness, has also been regarded as an indication of the amount of organic matter

contained therein. It appears to be so regarded for instance by Dr. Letheby, who thus speaks of the use of this test:—"The oxidizable organic matter is determined by a standard solution of permanganate of potash—the available oxygen of which is to the organic matter as 1 is to 8; and the results are controlled by the examination of the colour of the water when seen through a glass tube two feet in length, and two inches in diameter."\*

The tinctorial power of many colouring matters is so great as to render them distinctly appreciable to the eye when their amount is far too minute to be detected gravimetrically; thus a litre of water distinctly tinted with ink or magenta, contains an amount of either of these colouring matters too small to be appreciated by the most delicate balance. The yellowish or brownish colour of water appears also to be of this character, for it may be removed completely by agitation with aluminic hydrate, and yet a considerable amount of organic matter is still left in the water. Thus a sample of water which had been so treated, and which exhibited the blue-green tint of distilled water when viewed through a thick stratum, still contained  $\cdot 160$  part of organic carbon in 100,000 parts. It is, therefore, evident that no reliance can be placed upon colour as an indication of the amount of organic matter in waters, for although a dark-tinted water probably contains a considerable amount of organic matter, it by no means follows that a colourless water may not contain even a larger proportion. Thus a sample of peaty water, possessing a decided brown tinge, contained but  $\cdot 256$  part of organic carbon in 100,000 parts, whilst a sample of water from North Wales, which had been in contact with the fine mud of the stamping-engines of mines, was perfectly colourless, although it contained no less than  $\cdot 544$  part of organic carbon in 100,000 parts.

IV. *Estimation of Nitrous and Nitric Acids.*—The best process hitherto employed for this estimation is that proposed by the late Dr. Pugh. It depends upon the conversion of stannous chloride into stannic chloride in the presence of free nitric acid, whilst the latter is transformed into ammonia. The application of this process to water analysis has been described by Miller.†

\* Dr. Letheby's reports, on the Metropolitan Waters, to the Association of Medical Officers of Health.

† Journ. Chem. Soc., vol. xviii, p. 117.

If nitrites be also present, they may be converted into nitrates by the cautious addition of potassic permanganate to the water previously slightly acidified. The process is easy of execution, and extremely delicate; but unfortunately, as Messrs. Chapman and Schenk have shown, stannous chloride is converted into stannic chloride by many organic substances containing oxygen, such as starch, sugar, &c. The following experiments prove that this effect of starch and sugar takes place to such an extent as to render the process entirely untrustworthy.

I. 100 grm. starch was digested for 20 minutes in a sealed tube with 3 c.c. of stannous chloride solution, at a temperature of  $170^{\circ}\text{C}$ . Before digestion 3 c.c. of the same solution of stannous chloride required 17.85 c.c. of a standard solution of dipotassic dichromate to oxidize it. After digestion it required only 14.1 c.c. The oxidizing action of the starch was equivalent to that of .00375 grm. of  $\text{N}_2\text{O}_5$ .

II. 100 grm. sugar, similarly treated at  $150^{\circ}\text{C}$ ., oxidized an amount of stannous chloride equivalent to 7.0 c.c. of the standard solution of dipotassic dichromate, corresponding to .007 grm. of  $\text{N}_2\text{O}_5$ .

III. 100 grm. starch, similarly treated at  $150^{\circ}\text{C}$ ., oxidized an amount of stannous chloride equivalent to 4.2 c.c. of the standard dipotassic dichromate solution, corresponding to .0042 grm. of  $\text{N}_2\text{O}_5$ .

IV. 100 grm. starch, digested at  $120^{\circ}\text{C}$ ., oxidized an amount of stannous chloride equivalent to 2.5 c.c. of the standard dipotassic dichromate solution, corresponding to .0025 grm. of  $\text{N}_2\text{O}_5$ .

V. The last experiment repeated, with .1 grm. of sugar instead of starch, at  $120^{\circ}\text{C}$ ., gave results corresponding to .0058 grm. of  $\text{N}_2\text{O}_5$ .

Experiments II, III, IV, and V, were made in order to ascertain whether the oxidizing action of sugar and starch could not be prevented by operating at lower temperatures, but they show that these substances still oxidize very powerfully, even at a temperature below the minimum required, according to Pugh, for the performance of his reaction.

V. *Estimation of Ammonia.*—The determination of ammonia in potable waters is usually made by rendering the water alkaline either by baric hydrate or sodic carbonate, and then distilling off about one-fourth of its volume. In the distillate,

the ammonia is then estimated either by neutralisation with a standard solution of dilute acid, or by Hadow's modification of Nessler's reaction. In its application to waters recently contaminated with sewage, this process is liable to considerable inaccuracy, owing to the gradual production of ammonia when an alkaline solution of urea is boiled. Thus the ammonia found exceeds that originally contained in the water. This error has already been pointed out by Mr. Chapman, who recommends that the ammonia determination should be made by the application of Nessler's solution directly to the water. We find, however, that the yellowish colour of many potable waters presents a formidable obstacle to success; unless the water be first decolorised as we recommend below; besides, waters containing chalk in solution become turbid on the addition of the Nessler test, and any turbidity is utterly fatal to accuracy in this determination.

Having thus pointed out the inaccuracies which attach themselves to the usual determinations in a water analysis, we will now describe the processes which we propose as substitutes for, or modifications of, those which have been hitherto employed. They may be thus enumerated:—

1. Estimation of total solid constituents.

2. Estimation of the carbon and nitrogen contained in the organic portion of the solid constituents (organic carbon and nitrogen).

3. Estimation of nitrogen in the form of nitrates and nitrites.

4. Estimation of ammonia.

1. *Estimation of total Solid Constituents.*—Half a litre of water is evaporated to dryness as rapidly as possible in a weighed platinum capsule on a steam- or water-bath; after drying the residue at 100° C., the capsule is again weighed. We have already given our reasons for the non-addition of sodic carbonate to the water before evaporation, and also for drying the residue at 100° instead of 120°—130° C. As we propose to abolish altogether the fallacious estimation of "loss on ignition," the retention of the elements of water in this residue is of no moment; they always exist there in the solid condition, and are hence quite legitimately included amongst the solid constituents.

2. *Estimation of Organic Carbon and Nitrogen.*—No process has yet been devised by which the amount of organic matter in

water can be even approximately estimated, but we have now to describe a method by which the two most important elements—carbon and nitrogen—can be determined with considerable accuracy.

The estimation of the organic carbon in a water containing both carbonates and carbonic anhydride in solution is, as might be anticipated, an operation of more than ordinary difficulty. It is obviously necessary, in the first place, to expel both combined and dissolved carbonic anhydride, and this must be done in such a manner as to prevent the organic matter from being subject to the oxidising action which would necessarily result from the liberation of nitric and nitrous acids, which are probably never entirely absent from potable waters. We endeavoured to effect this by the addition of boric acid to the water during evaporation. Bloxam has shown\* that for the expulsion of one molecule of carbonic anhydride from alkaline carbonates, six molecules of boric acid are necessary. Approximately this appears to be true also of the carbonates of the alkaline earths; nevertheless after the addition of six molecules of boric acid to each molecule of combined carbonic anhydride, we still found an amount of carbonate in the residue, which, though small, was sufficient seriously to vitiate the result of the subsequent determination of organic carbon. After many abortive attempts to overcome this difficulty, we found in sulphurous acid a re-agent, which not only completely expels carbonic anhydride from the water but also permits of the simultaneous determination of organic nitrogen with great accuracy, by completely removing, during evaporation, every trace of the nitrogen existing in the form of nitrates and nitrites, and thus leaving in the dry residue the organic nitrogen associated only with one remaining nitrogenous body, viz., ammonia. For the successful application of sulphurous acid to this purpose, it is not sufficient to add an excess of this acid to the potable water and then evaporate to dryness, since under these circumstances traces of carbonates are always found in the residue. It is, in fact, necessary after the addition of excess of sulphurous acid, to boil the water for two minutes in order to insure the complete expulsion of carbonic anhydride before evaporation on the steam-bath begins. If this precaution be

\* Journ. Chem. Soc., vol. xii, p. 177.

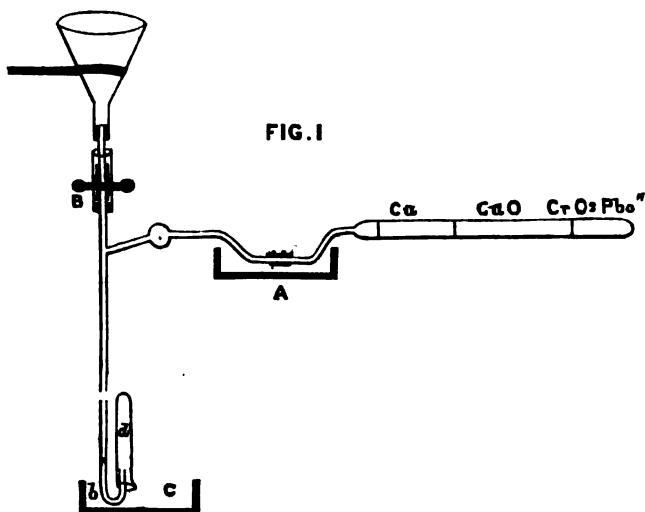
observed, numerous experiments have shown that no trace of carbonic anhydride is evolved on adding hydrochloric acid to the dry residue. By availing ourselves of that admirable instrument the Sprengel-pump, we are able to combine in one operation the determination of carbon and nitrogen in a water-residue, by an analytical process of such simplicity and extreme delicacy, that we believe it will be found generally useful in the analysis of all organic compounds containing nitrogen, which are not volatile at ordinary temperatures. By this process  $\cdot 000001$  grm. of nitrogen and  $\cdot 0000005$  grm. of carbon are distinctly measurable quantities.

The following is the mode of conducting this operation:— As soon as possible after the collection of the sample of water, 2 litres are poured into a convenient stoppered bottle, and 60 c.c. of a recently prepared saturated solution of sulphurous acid are added. Should the water contain oxidizable or putrescible organic matter, this addition of sulphurous acid promptly arrests any further change, and the remaining operations may now be conducted at leisure. One-half of this sulphurized water is now boiled for two or three minutes,\* and unless it contained a considerable amount of carbonates,  $\cdot 2$  grm. of sodic sulphite is to be added during the boiling, so as to secure the saturation of the sulphuric acid formed during the subsequent evaporation. To secure the expulsion of the nitrogen existing as nitrates, it is also desirable to add a couple of drops of solution of ferrous or ferric chloride. The boiled water is then evaporated to dryness in a hemispherical glass capsule, of about 100 c.c. capacity, upon a steam- or water-bath, care being taken to keep the capsule well covered with a disc of filter paper stretched over a light cane hoop, and also to preserve the atmosphere of the room in which the operation is performed as free from ammonia as possible. If the first-mentioned precaution be neglected, the access of floating particles of dust during the evaporation will introduce a considerable error into both carbon and nitrogen determinations. At one period of our investigations we feared that it would be necessary to perform the evaporation in vacuo, but we prove below that this would be an unnecessary precaution, for if the evaporation be conducted under paper, the

\* In operating with waters strongly contaminated with sewage, it is desirable that the flask in which this operation is performed should be furnished with an inverted Liebig's condenser, in order to prevent the loss of volatile organic constituents and ammonia. With all ordinary waters this precaution is unnecessary

amount of nitrogen introduced by atmospheric dust and ammonia (and this in the worst of all possible localities, the middle of London) only amounts to a maximum of  $\cdot 00002$  grm. per litre of water evaporated: consequently when this is deducted from the amount of nitrogen actually obtained by combustion the residual error is almost a vanishing quantity. The process of evaporation under a paper cover fitting tightly upon the edge of a glass dish *without a lip*, is in fact one of diffusion, in which the atmospheric air, constantly being exchanged for aqueous vapour, is filtered through a porous diaphragm.

The evaporation being completed, and the glass capsule placed upon a sheet of glazed paper, a few grammes of powdered plumbic chromate are to be introduced, and gently trituated with the dry residue by means of an agate or glass pestle. When the mixture has been made as perfect as possible, the contents of the capsule are to be transferred to a combustion tube, about 16 inches long and sealed at one end, the capsule is then rinsed two or three times with fresh quantities of chromate, which are also transferred to the combustion tube. The latter is then charged, in the usual manner, with granulated cupric oxide, and about 3 inches of bright copper turnings. The open end must now be drawn out before the blow-pipe, as shown in figure I, and the tube being laid in a



combustion-furnace, the drawn out extremity is to be connected with a Sprengel-pump by means of a piece of india-rubber



tubing, care being taken that the extremities of the two glass tubes touch each other, or nearly so, within the caoutchouc connector. The latter being then plunged beneath water in the vessel A, and the furnace around the front part of the combustion-tube lighted, the pump is to be worked until the tube is exhausted as completely as possible, an operation which requires from five to ten minutes.\* The flow of mercury is then stopped.

The recurved delivery end of the pump, *b*, dips into a mercurial trough, C, and an inverted tube, *d*, filled with mercury is placed over it in a convenient position for receiving the gaseous products of the ignition. The combustion must now be conducted in the usual manner, care being taken that, when the organic matter begins to burn, the operation proceeds very slowly until the vacuum becomes considerably impaired; otherwise traces of carbonic oxide may be produced. A combustion usually lasts from three-quarters of an hour to an hour; at its conclusion, unless the water-residue contained much organic matter, no gas will have passed into the inverted tube. The pump is again set to work, and in from five to ten minutes the whole of the gases will be transferred into the vessel placed for their reception. Unless the heat of the furnace be excessive, the combustion-tube will rarely collapse; but if it should do so, the metallic copper and granulated cupric oxide support the glass and prevent any obstruction to the passage of the gases. In many scores of combustions made by this process, no single instance of vitiated result has occurred from this cause. The gases collected consist of carbonic anhydride, nitric oxide, and nitrogen. The separation and determination of these, by well-known methods, is exceedingly simple, and in a manometric gas apparatus, such as that described by one of us,† is the work of a few minutes only.

\* As it is obviously necessary that the leakage of atmospheric air into the pump should be rendered impossible, the caoutchouc pinch-cock, at B, should be enclosed in a wide piece of vulcanized tube, the annular space between the two tubes being filled with glycerin. The clamp is placed outside both tubes. The wide piece of tube is fastened upon the glass tube below the pinch-cock, by the aid of an india-rubber cork, whilst it terminates considerably above the joint; the interior caoutchouc-joint is, therefore, entirely immersed in glycerin, and all possibility of leakage of air entirely prevented. We find, in fact, that by this arrangement the vacuum is still perfect after the lapse of several days. The calibre of the pump-tube, which we prefer, is one millimetre, and it is advisable to allow the mercury to flow very slowly until the exhaustion is nearly complete, when a rapid stream is necessary to expel the remaining traces of air or gas.

† Journ. Chem. Soc., vol. vi, p. 197.

A simplified form of this apparatus, designed especially for the examination of all gaseous mixtures incident to water analysis, is described in the memoir immediately following the present, where the method of analysing these mixtures is also given. The weights of carbon and nitrogen contained in the carbonic anhydride, nitric oxide, and nitrogen gases, having been deduced from the respective volumes of these gases, the numbers so obtained are expressed in parts of these elements contained in 100,000 parts of the water. The nitrogen thus found may have been present in the water, first as a constituent of organic matter (organic nitrogen), and secondly as a constituent of ammonia. The latter, if present, is determined in the original water by Nessler's test, as described below, and the nitrogen existing in this form being deducted from that obtained on combustion, gives the amount, if any, of organic nitrogen present.

It is obvious that the accuracy of this method of combustion will depend in a great measure upon the perfection of the vacuum obtained by the Sprengel pump. In order to ascertain the error due to this cause, the following experiments were made:—

I. .01 grm. sugar was burnt in the same way as a water residue. After absorption of carbonic anhydride, there remained .019 c.c. of nitrogen at 0° C., and 760 mm. pressure.

II. .01 grm. sugar similarly treated gave .013 c.c. of nitrogen at 0° C., and 760 mm. pressure.

If these numbers be referred to the residue of one litre of water (the quantity usually operated upon) the excess of nitrogen due to the imperfection of the Sprengel vacuum would be—

I. .0024 part of nitrogen in 100,000 parts of water.

II. .0016 part of nitrogen in 100,000 parts of water.

It will be seen that this error, which includes also any nitrogen retained or occluded in the cupric oxide, &c., is very insignificant; nevertheless it would be necessary to allow for it, if it were not included in another correction, which consists in evaporating a litre of distilled water,\* acidified as usual

\* This distilled water should be previously purified by boiling, for 24 hours, with alkaline potassic permanganate. It should then be distilled, the first portions of the distillate being rejected so long as they show any reaction with Nessler's test. Finally, this distillate should be slightly acidified with sulphuric acid and rectified.

with 15 c.c. of sulphurous acid, and containing about .1 gm. of recently ignited sodic chloride. The residue from this water must now be burnt in vacuo in the usual manner, and the carbon and nitrogen deducted from the amount of these elements obtained from the residues of other waters submitted to analysis.

It is advisable that each analyst should perform several blank operations of this kind, so as to be able accurately to correct for the combined errors of his own manipulation and apparatus. In our own case we find these errors on the average of four blank analyses to amount to—

Carbon .00032 gm. in 1 litre of water.

Nitrogen .000045 gm. in 1 litre of water.

It is scarcely necessary to add that, to insure a minimum in these errors, it is of the utmost importance, carefully to guard against every access of organic matter, and especially of nitrogenous compounds, to the water and the substances used in the analysis. Cupric oxide prepared from the nitrate should on no account be used, since, even after being actually fused, it evolves considerable quantities both of carbonic anhydride and nitrogen when ignited in vacuo. The oxide must be made by igniting sheet copper in a current of air, in a muffle or other convenient apparatus. This oxide, in a coarsely granular or scaly condition, should be at once transferred to a stoppered bottle, over the neck of which a small beaker is inverted to protect it from dust. The fused plumbic chromate should be heated to redness with frequent stirring for a couple of hours, and then carefully transferred to another bottle similarly protected. As these substances do not require to be either dried or ignited again before use, they should be transferred as required, from their respective bottles, direct to the capsules or combustion tubes, and any portion of them once removed from the bottle should on no account be returned there without being first ignited for two hours.

The extent to which this method can be depended upon for the determination of the minute amounts of carbon and nitrogen contained in a water residue was tested by the following experiments:—

I. .0352 gm. sugar was dissolved in one litre of distilled water, together with about .5 gm. of sodic carbonate, previously

converted into sulphite, 15 c.c. of a saturated solution of sulphurous acid were then added, and the liquid boiled for three minutes. The residue left after evaporation to dryness on the steam-bath gave, on combustion, an amount of carbonic anhydride corresponding to ·01463 grm. carbon.

II. ·0347 grm. sugar similarly treated gave ·01386 grm. carbon.

III. ·0114 grm. sugar similarly treated gave ·00440 grm. carbon.

IV. ·0122 grm. sugar similarly treated gave ·00530 grm. carbon.

V. ·0115 grm. sugar ·0094 grm. ammoniac chloride, and ·8 grm. sodic carbonate (previously converted into sulphite) treated in like manner, gave ·004344 grm. carbon, and ·0025415 grm. nitrogen.

VI. ·010 grm. urea, and ·8 grm. sodic carbonate similarly treated gave ·0017704 grm. carbon, and ·00463 grm. nitrogen.

VII. ·01025 grm. urea and ·8 grm. sodic carbonate treated as before gave ·00211 grm. carbon, and ·00357 grm. nitrogen.

VIII. ·0104 grm. urea and ·8 grm. sodic carbonate similarly treated gave ·0023865 grm. carbon, and ·004675 grm. nitrogen.

IX. ·0202 grm. urea, and one litre of solution of dihydric calcic dicarbonate boiled with 15 c.c. of sulphurous acid solution, and evaporated gave ·00452 grm. carbon and ·00887 grm. nitrogen.

X. ·025 grm. hippuric acid and ·5 grm. sodic carbonate (converted into sulphite) dissolved in one litre of water, boiled with 10 c.c. of sulphurous acid solution, and evaporated to dryness gave ·01386 grm. carbon, and ·00203 grm. nitrogen.

Expressed in parts per 100,000 of water evaporated, the following are the results of these experiments:—

		Calculated.	Found.
No. I.	Organic carbon . . . . .	1·482	1·463
No. II.	"    "    . . . . .	1·460	1·386
No. III.	"    "    . . . . .	·480	·440
No. IV.	"    "    . . . . .	·514	·530
No. V.	"    "    . . . . .	·484	·434
	{ Nitrogen . . . . .	·246	·254
No. VI.	{ Organic carbon . . . . .	·200	·177
	{ "    nitrogen . . . . .	·466	·463

		Calculated.	Found.
No. VII.	{ Organic carbon . . . . .	·205	·211
	{ „ nitrogen . . . . .	·478	·357
No. VIII.	{ „ carbon . . . . .	·208	·239
	{ „ nitrogen . . . . .	·484	·468
No. IX.	{ „ carbon . . . . .	·404	·452
	{ „ nitrogen . . . . .	·942	·887
No. X.	{ „ carbon . . . . .	1·508	1·386
	{ „ nitrogen . . . . .	·195	·203

When it is considered that these results were obtained from very minute amounts of the respective organic matters, which were first dissolved in a large quantity of water, and then recovered by evaporation, and, further, that some of the organic substances experimented upon are exceedingly prone to change, the correspondence of the experimental with the calculated numbers is as close as could be anticipated. The following results, obtained with actual waters, also tend to inspire confidence in this method of analysis:—

XI. Two litres of the same sample of water were successively analysed five days apart. They gave the following amounts of organic carbon and nitrogen in 100,000 parts:—

	No. I.	No. II.
Organic carbon . . . . .	1·030	1·010
Organic nitrogen . . . . .	·198	·207

XII. Three mixtures of sewage and distilled water were made in such proportions that 1 litre contained respectively 100 c.c., 10 c.c., and 1 c.c. of sewage. Some solution of dihydric calcic dicarbonate was added to the second and third to form a tangible residue. They were then treated with sulphurous acid in the manner above described, and evaporated to dryness. Their residues gave, on combustion, the following results per 100,000 parts of water evaporated:—

	100 c.c. sewage. 900 c.c. water.	10 c.c. sewage. 990 c.c. water.	1 c.c. sewage. 999 c.c. water.
Organic carbon in } 100,000 parts of } the mixture . . . . }	·302	·033	·005
Organic nitrogen } and nitrogen of } ammonia . . . . . }	·330	·033	·004

It has been already stated that the nitrogen obtained on the combustion of a water-residue is made up of the organic nitrogen plus the nitrogen of any ammonia that may have been contained in the water, but that it includes no trace of the nitrogen which may have been present in the form of nitrates and nitrites, the latter having been completely destroyed during the evaporation with excess of sulphurous acid. Such an expulsion of the nitrogen of nitrates and nitrites is a remarkable reaction, and could scarcely have been predicted; indeed, it takes place to a very partial extent only when a nitrate is dissolved in water, and evaporated with excess of sulphurous acid, in imitation of a natural water; neither is the result very different when sodic chloride or calcic or magnesian carbonate is added. Thus the residue from half a litre of distilled water, to which had been added  $\cdot 05$  gm. potassic nitrate (=  $\cdot 007$  gm. nitrogen),  $\cdot 0001$  gm. ammonia,  $\cdot 1$  gm. sodic chloride, and 15 c.c. of a saturated solution of sulphurous acid, yielded  $\cdot 00161$  gm. nitrogen.

One litre of distilled water, containing  $\cdot 1$  gm. sodic chloride,  $\cdot 1$  gm. potassic nitrate (=  $\cdot 014$  gm. nitrogen), one drop of a strong solution of soluble glass, and 15 c.c. of a saturated solution of sulphurous acid, treated like a natural water, yielded, on combustion,  $\cdot 00222$  gm. nitrogen.

One litre of distilled water, containing  $\cdot 1$  gm. sodic chloride,  $\cdot 1$  gm. potassic nitrate, and 15 c.c. sulphurous acid solution, similarly treated, gave  $\cdot 00259$  gm. nitrogen.

The presence of a minute amount of iron, or of a phosphate, reduces to zero the amount of nitrogen retained from nitrates. Thus 1 litre of distilled water,  $\cdot 1$  gm. sodic chloride,  $\cdot 1$  gm. potassic nitrate (=  $\cdot 014$  gm. N.), 2 drops of a moderately concentrated solution of hydric sodic phosphate, and 15 c.c. of sulphurous acid solution, gave no nitrogen on combustion of the solid residue.

Half a litre of distilled water, containing  $\cdot 1$  gm. potassic nitrate, and 2 drops of a solution of ferric chloride, evaporated with 10 c.c. of sodic sulphite solution and 15 c.c. of a saturated solution of sulphurous acid, gave no nitrogen on combustion.

One litre of distilled water containing  $\cdot 1$  gm. sodic chloride,  $\cdot 1$  gm. potassic nitrate, 1 drop of solution of ferric chloride, and 15 c.c. of sulphurous acid solution, gave no trace of nitrogen on combustion, and the same result was obtained in a duplicate

experiment. Three drops of a solution of ferric chloride also removed all traces of nitrates from half a litre of a natural water when evaporated in vacuo, although the water contained no less than 2·466 parts of nitrogen as nitrates and nitrites in 100,000 parts.

The nitrogen was also completely expelled during the evaporation of an artificial water, to which the following ingredients were added:—·01 grm. magnesia, ·1 grm. calcic carbonate, ·1 grm. sodic chloride, ·01 grm. potassic chloride, 1 drop of solution of soluble glass, 1 drop of solution of ferric chloride, 2 drops of solution of hydric sodic phosphate, ·1 grm. potassic nitrate, and 15 c.c. of sulphurous acid solution.

There is probably no natural water containing an appreciable quantity of nitrates or nitrites which does not also contain either iron or phosphoric acid; nevertheless, it is advisable to add one or two drops of ferrous or ferric chloride to the portion of water which is evaporated for combustion, in order to place beyond the possibility of doubt the complete expulsion of the nitrogen of nitrates and nitrites.

Since we began to use this process for the estimation of organic carbon and nitrogen in waters, Messrs. Wanklyn, Chapman, and Smith have proposed a new method for the determination of the latter element in potable waters. Their process is founded upon a highly remarkable change which albumin and some other organic substances undergo during prolonged ebullition with an alkaline solution of potassic permanganate, by which their nitrogen is converted into ammonia. Unfortunately, however, this conversion is never complete; neither is there any guarantee that all the different forms of nitrogenous organic substances in water will thus yield up their nitrogen in the form of ammonia. That some such substances do not thus evolve their nitrogen when submitted to this process is evident from the following results, obtained with three bodies taken at random from a collection of chemicals:—

I. ·01 grm. strychnine, dissolved in 1 litre of distilled water (not previously purified), and distilled nearly to dryness with caustic potash and potassic permanganate, gave ·00032 grm. ammonia.

II. ·02 grm. narcotine, similarly treated, gave ·000312 grm. ammonia.

III. ·02 grm. quinine sulphate gave ·000728 grm. ammonia.

The following comparison of the amounts of ammonia actually obtained, with those which ought to be yielded by the weights of the respective substances operated upon, shows that in each case a large proportion of nitrogen was not evolved as ammonia :—

	Ammonia evolved.	
	Calculated.	Found.
Strychnine .....	·00101 grm.	·00032 grm.
Narcotine.....	·00068 „	·000312 „
Quinine sulphate .....	·00128 „	·000728 „

We have also tested the permanganate process by applying it to a form of nitrogenous organic matter which is very frequently met with in natural waters, viz., peaty matter.

Some peat, collected by one of us from Leyland moss at a depth of three feet below the surface, and placed immediately in a well-corked glass vessel, was digested at 100° C. for a couple of hours in distilled water, rendered slightly alkaline by caustic soda. 100 c.c. of the dark-coloured liquid so obtained was made up to one litre with distilled water, and after the determination of ammonia by ebullition with sodic carbonate, was submitted to the permanganate process so long as ammonia was evolved. Another 100 c.c. of the same liquid was acidified with sulphurous acid, boiled for two minutes, then evaporated to dryness in vacuo, and the dry residue submitted to combustion in vacuo. The following amounts of *organic* nitrogen per 100,000 parts of liquid were obtained :—

Permanganate Process.	Combustion Process.
·308	1·015

Another portion of the same liquid was acidified with dilute sulphuric acid; the copious brown precipitate which separated was collected on a filter, and, after being dried at 100° C., was reduced to fine powder. Two separate centigrms. of this precipitate were respectively submitted to the permanganate and combustion processes. Two equal volumes (100 c.c.) of the filtered liquid were also respectively treated by the two processes, the portion used for combustion being evaporated under paper upon a steam-bath. The ammonia was determined in this liquid as usual. The following are the amounts of *organic* nitrogen obtained :—



ON THE ANALYSIS OF POTABLE WATERS.



	Permanganate process.	Combustion process.
·01 grm. of peat precipitate yielded of organic nitrogen .....	·000052 grm.	·0001188 grm. N <sub>2</sub>
100,000 parts of filtrate from peat precipitate gave of organic nitrogen .....	·108	·291

200 c.c. of another sample of peat solution, treated by the two processes, yielded the following amounts of organic nitrogen per 100,000 parts of liquid :—

Permanganate process.	Combustion process.
·422	1·175

Two separate litres of an artificial water, made by diffusing some peat in distilled water for several days (without the addition of alkali), and then filtering, were treated by the two processes, and yielded the following amounts of organic nitrogen per 100,000 parts of water :—

Permanganate process.	Combustion process.
·022	·076

The extension of this comparison of the two processes to natural waters confirms, in a large majority of cases, the conclusion which is forced upon us by the above experiments, viz., that nitrogenous organic substances do not uniformly yield up the whole, or nearly the whole of their nitrogen in the form of ammonia when boiled with alkaline potassic permanganate; indeed Wanklyn has recently discovered that, even in regard to albumen itself, his first statement in reference to this point requires modification, and he now states\* “The ‘albuminoid ammonia’ is not the total amount of ammonia which the albumen is capable of giving, but appears to be two-thirds of the total quantity, being at any rate a constant fraction of the total quantity.” Neither the above nor the following results show, either that two-thirds of the total nitrogen is evolved in the shape of ammonia, or that the fraction of the total nitrogen evolved in the permanganate process is a constant one. We have tested the two processes side by side upon more than 100 different samples of natural waters, and we

\* Journ. Chem. Sec., vol. xx, p. 593.

find that as a rule, to which, however, there are some exceptions, the permanganate process gives results considerably below those obtained by combustion, as in the following cases :—

Organic nitrogen in 100,000 parts of water.			Organic nitrogen in 100,000 parts of water.		
By permanganate process.		By combustion.	By permanganate process.		By combustion.
·006	....	·010	·002	....	·010
·006	....	·011	·002	....	·008
·006	....	·010	·003	....	·008
·002	....	·011	·016	....	·068
·016	....	·042	·003	....	·006
·002	....	·009	·001	....	·012
·006	....	·022	·002	....	·011
·000	....	·007	·000	....	·007
·013	....	·043	·011	....	·058
·012	....	·027	·024	....	·061
·006	....	·031	·030	....	·062

In some cases where, as a rule, the amount of organic nitrogen was very small, the two processes yielded accordant results, as in the following cases :—

Organic nitrogen in 100,000 parts of water.			Organic nitrogen in 100,000 parts of water.		
By permanganate process.		By combustion.	By permanganate process.		By combustion.
·001	....	·001	·004	....	·004
·001	....	·001	·003	....	·004
·004	....	·004	·002	....	·001
·010	....	·009	·003	....	·004
·012	....	·012	·002	....	·001
·001	....	·001	·002	....	·002

In a few other cases, however, the amount of organic nitrogen obtained by the permanganate process was higher than that yielded by combustion, as for instance :—

Organic nitrogen in 100,000 parts of water.			Organic nitrogen in 100,000 parts of water.		
By permanganate process.		By combustion.	By permanganate process.		By combustion.
·010	....	·007	·004	....	·000
·009	....	·005	·002	....	·000
·005	....	·000	·003	....	·000

These last results are to some extent explained by the fact, that distilled water purified by boiling with alkaline potassic permanganate, for a long time after ammonia has ceased to be evolved, always yields ammonia when again treated with alkaline potassic permanganate. Thus in four experiments made with such purified water, the following quantities of ammonia per 100,000 parts of water were obtained:—

No. I.	....	·002 part		No. III.	....	·002 part
No. II.	....	·001 „		No. IV.	....	·002 „

### 3. Estimation of Nitrogen in the form of Nitrates and Nitrites.

This determination can be made with very great accuracy by a modification of a process proposed twenty years ago by Walter Crum, for the refraction of nitre.\* It consists in agitating with mercury a concentrated solution of the nitrate or nitrite, with a large excess of concentrated sulphuric acid, when the whole of the nitrogen is evolved as nitric oxide. We find that, for the success of this process, it is absolutely necessary that no chlorides should be present, and also that the mixed liquids should be *violently* agitated with mercury, so as to break up the latter into minute globules.

The following determinations show the accuracy of this process:—

I. ·02 grm. of nitre gave 75·48 c.c. nitric oxide at 49 mm. mercurial pressure, and 16°·4 C.

II. ·01 grm. of nitre, dissolved in a saturated solution of sodic sulphate, gave 75·48 c.c. of nitric oxide at 24·2 mm. mercurial pressure, and 17°·8 C.

	Weight of nitrogen.	
	Calculated.	Found.
No. I. ....	·002772	·002897
No. II ....	·001386	·001424

It was ascertained that uric acid, hippuric acid, urea, and creatin when agitated with concentrated sulphuric acid and mercury gave no trace of gas.

The following is the mode in which this process is applied to the estimation of nitrogen existing as nitrates and nitrites in potable waters. The solid residue from the half litre of water

\* Phil. Mag., xxx, 426.

used for determination No. 1 (estimation of total solid constituents)\* is treated with a small quantity of distilled water, a very slight excess of argentic sulphate is added to convert the chlorides present into sulphates, and the filtered liquid is then concentrated by evaporation in a small beaker until it is reduced in bulk to two or three cubic centimetres. The liquid must now be transferred to a glass tube, Fig. 2, and furnished at



FIG. 2

its upper extremity with a cup and stopcock previously filled with mercury at the mercurial trough, the beaker being rinsed out once or twice with a very small volume of recently boiled distilled water, and finally with pure and concentrated sulphuric acid in somewhat greater volume than that of the concentrated solution and rinsings previously introduced into the tube. By a little dexterity it is easy to introduce successively the concentrated liquid, rinsings, and sulphuric acid into the tube by means of the cup and stopcock, without the admission of any trace of air. Should, however, air inadvertently gain admittance, it is easily removed by depressing the tube in the mercury trough, and then momentarily opening the stopcock. If this be done within a minute or two after the introduction of the sulphuric acid, no fear need be entertained of the loss of nitric oxide, as the evolution of this gas does not

begin until a minute or so after the violent agitation of the contents of the tube.

The acid mixture being thus introduced, the lower extremity of the tube is to be firmly closed by the thumb, and the contents violently agitated by a simultaneous vertical and lateral movement, in such a manner that there is always an unbroken column of mercury, at least an inch long, between the acid liquid and the thumb. From the description, this manipulation may appear difficult, but in practice it is extremely simple, the acid liquid never coming in contact with the thumb. In about a minute from the commencement of the agitation a

\* If the water contain nitrites, a separate half litre should be taken for this determination, otherwise there is a risk of loss of nitrogen during evaporation. The nitrites in this half litre of water must be transformed into nitrates by the cautious addition of potassic permanganate to the slightly acidified water before the evaporation is commenced. Immediately after the action of the permanganate the water must, of course, be again rendered slightly alkaline.

strong pressure begins to be felt against the thumb of the operator, and mercury spurts out in minute streams, as nitric oxide gas is evolved. The escape of the metal should be gently resisted, so as to maintain a considerable excess of pressure inside the tube, and thus prevent the possibility of air gaining access to the interior during the shaking. In from three to five minutes the reaction is completed, and the nitric oxide may then be transferred to a suitable measuring apparatus, where its volume is to be determined over mercury. As half a litre of water is used for the determination, and as nitric oxide occupies exactly double the volume of the nitrogen which it contains, the volume of nitric oxide read off expresses the volume of nitrogen existing as nitrates and nitrites in one litre of the water. From the number so obtained, the weight of nitrogen in these forms in 100,000 parts of water is easily calculated.

#### 4. *Estimation of Ammonia.*

Unless the amount of ammonia obtained by distillation alone, or with sodic carbonate, be considerable (above  $\cdot 01$  part in 100,000 parts of water), Hadow's modification of Nessler's process is all that could be desired for its accurate determination. But if a larger proportion than this be obtained, the presence of urea may be suspected, and it becomes necessary to make the Nessler ammonia determination directly, in the original water, without the intervention of distillation. For this purpose, however, the water should be colourless, and free from calcic and magnesian carbonates. Any tint which is appreciable in a stratum 6 or 8 inches thick would obviously vitiate the result of a colour-test; whilst if calcic or magnesian carbonate be present, the addition of the Nessler solution will infallibly produce turbidity; moreover, we find that the slightest opalescence in the water, under these circumstances, is absolutely incompatible with an accurate determination. Both these difficulties might be effectually removed by adding to the water, first a few drops either of ferric chloride or aluminic chloride in solution, and then a few drops of a solution of sodic carbonate so as to precipitate ferric hydrate or aluminic hydrate. The precipitate completely decolorises the water, and no turbidity is caused by the subsequent addition of the Nessler solution; but unfortunately the precipitate carries down with it an amount

of ammonia which, in the case of the ferric hydrate, sometimes amounts to one-third of the total quantity present. Remembering the beautiful blue-green tint—the natural colour of absolutely pure water—which is presented by a reservoir of water that has been softened by Clark's process, we tried, upon peaty water, the effect of precipitating in it calcic carbonate, and found that the decolorisation was as complete as could be desired, and that no appreciable amount of ammonia was carried down with the precipitate. The amount of calcic carbonate present in a coloured water is rarely sufficient to enable the operator to carry out this reaction with sufficient rapidity and completeness; it is therefore best in all cases to add a few drops of a concentrated solution of calcic chloride, to half a litre of the water. The subsequent addition of a slight excess of sodic carbonate then produces a copious precipitate of calcic carbonate, which should be allowed to subside for half an hour before filtration. 100 c.c. of the filtrate is a convenient quantity to take for the direct Nessler determination of ammonia. To this volume of the filtrate 1 c.c. of the Nessler solution is added, and the colour observed in the usual manner (see Miller on the Analysis of Potable Waters. Jour. Chem. Soc., vol. xviii, p. 125). By this direct process the ammonia in fresh urine can be readily estimated, for this purpose 5 c.c. of the urine should be diluted with 95 c.c. of water free from ammonia. We have ascertained that known quantities of ammonia, added in the form of ammonic chloride to urine, can be determined with great accuracy.

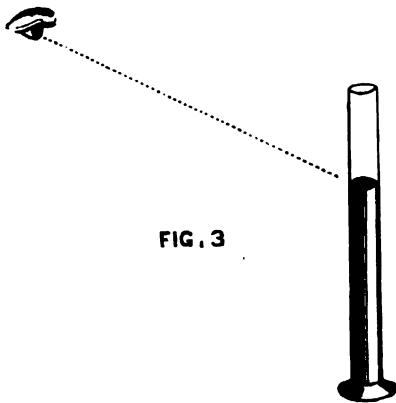


FIG. 3

The colour observations of the Nessler determination are best made in narrow glass cylinders of such a diameter that 100 c.c. of the water to be tested form a stratum about seven inches deep. The depth of tint is best observed by placing these cylinders upon a sheet of white paper near a window, and looking at the *surface* of the liquid obliquely; thus, Fig. 3.

The nitrogen existing as nitrates, nitrites, and ammonia, in potable waters, is derived partly from the atmosphere and partly from the decomposition of nitrogenous organic matters previously existing, either in the water, or in the soil with which the water has been in contact. In view of the opinions now very generally entertained, with regard to the propagation of certain forms of disease by means of spores or germs contained in excrementitious matters, the search for nitrates, nitrites, and ammonia, is second only in importance to that for actual sewage contamination; because, although these substances are in themselves innocuous, unless present in excessive quantity, yet, when contained in a water in more than a certain proportion, they betray previous contamination by sewage or by manured land. The nitrogenous organic matters contained in sewage or manure, undergo slow oxidation and conversion into mineral compounds when mixed with water; their carbon is converted into carbonic anhydride, and their hydrogen into water. These mineral products can no longer be identified in the aerated waters of a river, spring, or lake, but the nitrogen is transformed into ammonia, nitrous acid, and nitric acid; the two latter combine with the bases contained in most waters, and, together with the ammonia, constitute a record of the sewage, or other analogous contamination from which the water has suffered. With certain corrections, mentioned below, the determination of the nitrogen contained in these mineral compounds proclaims the previous history of the water as regards its contact with decomposing nitrogenous organic matters. We propose to employ this determination for the expression of the previous sewage contamination of a water, in terms of average filtered London sewage, which, if thus oxidised, would yield a like amount of nitrogen in the form of ammonia, nitrites, and nitrates. For this purpose average filtered London sewage may be assumed to contain 10 parts of combined nitrogen in 100,000 parts, as deduced from the numerous analyses of Hofmann and Witt, and of Way and Odling.

The number so obtained as the previous sewage contamination of a water requires, however, a correction, since rain water itself contains combined nitrogen as ammonia, nitrite of ammonia, and nitrate of ammonia. The amount of these substances present in the rain which falls at Rothamstead has been determined by a series of monthly analyses made inde-

pendently, on the one hand, by Messrs. Lawes and Gilbert, and on the other by Mr. Way, and extending over two years. The results of these chemists give, as the average amount of combined nitrogen, '0985 part in 100,000 parts of rain water. But as only a very small proportion of the rain water which supplies a river falls directly into the stream, and as rain water is very rapidly deprived of its ammonia, and to some extent also of its nitrites and nitrates, by contact with vegetation, this number, as representing the amount of combined nitrogen, conveyed into a river from *ærial* sources must obviously be too high; indeed, the experience gained in the examination of fifty samples of water collected near the source of streams, proves this to be the case, for the maximum amount of nitrogen as ammonia contained in any of these samples was only '008 part in 100,000, whilst the average amount of nitrogen in the form of nitrous and nitric acids observed by Messrs. Lawes, Gilbert, and Way, and this in thunder rain only, was but '024 part in 100,000. It may, therefore, be safely assumed that the maximum amount of combined nitrogen, derived by natural waters from *ærial* sources, does not exceed  $\cdot 024 + \cdot 008 = \cdot 032$  part in 100,000; and we, therefore, propose to deduct this amount from the quantity of nitrogen present in a water in the form of ammonia and of nitrites and nitrates, and to employ the remainder, if any, for the calculation of the previous sewage contamination, on the basis that 10 parts of nitrogen correspond to 100,000 parts of such contamination. If we represent the nitrogen existing in 100,000 parts of water as nitrates and nitrites by N, and the nitrogen present as ammonia in the same quantity of water by N', the previous sewage contamination of 100,000 parts of the water is denoted by the following expression:—

$$10,000 (N + N' - \cdot 032).$$

Thus a water which contains in 100,000 parts '339 part of nitrogen as nitrates and nitrites, and '001 part of ammonia, has a previous sewage contamination of 3,080 parts; that is, 100,000 parts of the water have been previously contaminated with sewage or manure matter equivalent to 3,080 parts of average filtered London sewage. *Previous* must not be confounded with *actual* or *present* sewage contamination; the latter is caused by unchanged or unoxidized sewage, whilst the former



denotes sewage completely resolved, so far as its dead and unorganised organic constituents are concerned, into perfectly or comparatively innocuous mineral compounds. But although this change has been effected at the time the sample of water was collected for analysis, it by no means follows that it will be equally complete under future altered conditions as regards temperature, exposure to air or vegetation, and comparative volume of pure water. Previous sewage contamination must, therefore, to some extent, be regarded as possible actual sewage contamination at some future time, at the place where the sample was taken. There is also another aspect in which the previous sewage contamination of a water assumes a high degree of importance: if the shell of an egg were broken, and its contents beaten up with water and thrown into the Thames at Oxford, the albumen would probably be entirely converted into mineral compounds before it reached Teddington; but no such destruction of the nitrogenous organic matter would ensue if the egg were carried down the stream unbroken for the same distance; the egg would even retain its vitality under circumstances which would break up and destroy dead or unorganized organic matter. Now, excrementitious matters certainly, sometimes, if not always, contain the germs or ova of organized beings; and as many of these can doubtless retain their vitality for a long time in water, it follows that they can resist the oxidizing influences which destroy the excrementitious matters associated with them. Hence great previous sewage contamination in a water means great risk of the presence of these germs, which, on account of their sparseness and minute size, utterly elude the most delicate determinations of chemical analysis.

These considerations respecting the import of the previous sewage contamination of a water, lead us to regard, from a sanitary point of view, the accurate determination of the nitrogen in the form of nitrates, nitrites, and ammonia, as being, next to the organic carbon and nitrogen determinations—by far the most important datum in water analysis.

In illustration of our mode of expressing the results of water analyses, the following table is subjoined. The degrees of hardness which we employ express the number of parts of calcic carbonate, or its equivalent of other hardening salts in 100,000 parts of water; they harmonize better than Clark's with the

decimal arrangement of the rest of the analytical results, and, if it be desired, they are readily converted into Clark's degrees by multiplying by .7. The numbers opposite Thames water are the means of analyses of the water delivered by the Chelsea, West Middlesex, Southwark, Grand Junction, and Lambeth Companies on the 21st of January last. The New River, East London, and Kent Companies' waters were collected about the same time. The lake waters were analysed for the Royal Commission on Water Supply by Dr. Odling and one of us. The results yielded by the Caterham Company's water are interesting, as an example of the great improvement effected in a chalk water by the application of Clark's process. Unfortunately, this last sample was not taken under our supervision, and we cannot, therefore, vouch for its authenticity.

Names of Waters.	Total solid impurity in 100,000 parts.	Organic carbon.	Organic nitrogen.	Nitrogen as nitrates and nitrites.	Ammonia.	Total combined nitrogen.	Previous sewage contamination.	Hardness.
Thames water, as delivered in London .....	30·94	·399	·048	·346	·001	·395	3150	17·3
River Lea water, as delivered by New River Company .....	30·20	·115	·014	·361	·001	·376	3300	20·5
Ditto, delivered by the East London Company .....	36·00	·147	·024	307	·001	·332	2760	22·8
Chalk water, delivered by the Kent Company .....	44·80	·064	·013	·408	·001	·422	3770	26·2
Ditto, delivered by the South Essex Company .....	37·98	·164	·000	·848	·006	·852	8205	21·6
Ditto, supplied by Caterham Water Works .....	12·60	·064	·007	·000	·009	·014	0	7·0
Ditto, supplied to Worthing .....	36·70	·162	·000	·428	·000	·426	3940	23·8
Glasgow, from Loch Katrine .....	3·28	·256	·008	·031	·002	·041	0	3
Manchester, from Derbyshire Hills .....	6·80	·242	·026	·001	·001	·028	0	2·7
Lancaster, from Bleasdale Fells .....	3·54	·157	·001	·036	·001	·038	50	1
Preston, from Longridge Fells .....	14·70	·515	·040	·001	·003	·044	0	6·7
Leicester, waterworks supply .....	23·70	·506	·020	·001	·001	·022	0	13·4
Bala Lake .....	2·79	·227	·001	·000	·001	·002	0	4
Ulswater Lake .....	3·63	·067	·000	·005	·003	·007	0	1·9
Thirlmere Lake .....	2·66	·194	·004	·002	·003	·008	0	7
Haweswater Lake .....	3·56	·158	·004	·000	·004	·007	0	1·3
Well water, from Leyland, near Preston, Lancashire .....	54·40	·325	·056	2·466	·003	2·324	24960	17·5
Ditto, from Ledbury .....	65·30	·145	·030	1·575	·001	1·806	15440	25·1
Ditto, from Redhill .....	43·60	·224	·021	1·446	·002	1·469	14160	25·1

XII.—*On a Simple Apparatus for determining the Gases incident to Water Analysis.*

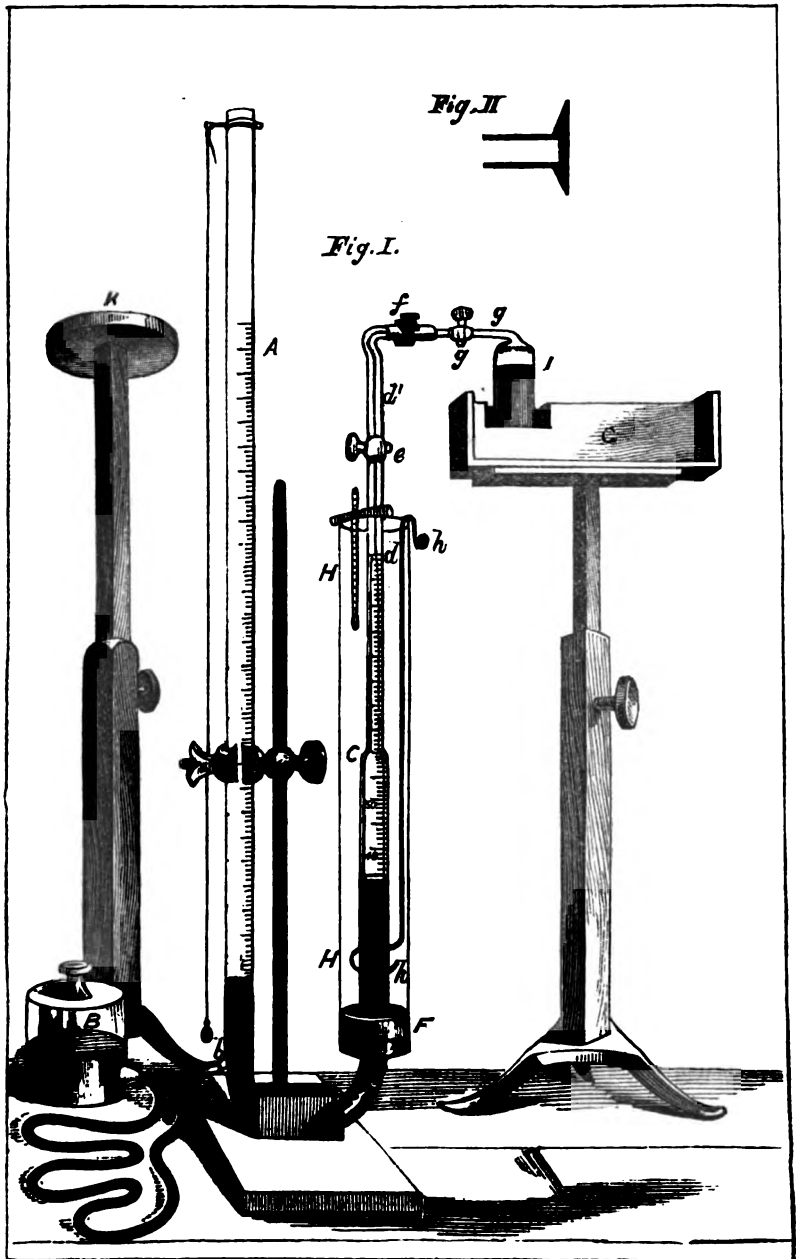
By E. FRANKLAND, F.R.S.

THE manometric gas-analysis apparatus described by Mr. Ward and myself,\* enables the operator to make all the gaseous determinations connected with water-analysis with a rapidity, delicacy, and precision, leaving little to be desired; nevertheless, as this instrument is also designed for the analysis of gaseous mixtures of greater complexity, its construction is more elaborate than is necessary for the investigation of such gases as require to be dealt with in water-analysis. I have, therefore, devised a more simple, and much less costly apparatus, which permits of the rapid and accurate analysis of such gaseous mixtures as require to be submitted only to the action of absorbents,—a category which includes all the gases appertaining to ordinary water-analysis.

This apparatus is represented in fig. 1.

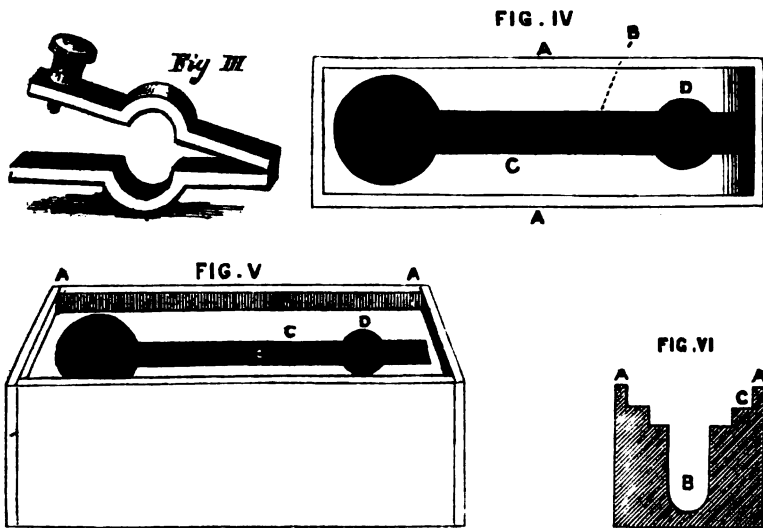
A is a U-shaped glass tube 16 mm. internal diameter, supported in a perfectly perpendicular position by a convenient clamp. Its longer limb stands 1.1 metre high, its shorter limb 350 mm. measured to C. In the longer limb, just above the bend, is inserted a short glass tube *b*, 1 centimetre long, and 2 mm. internal diameter; it is attached to a doubly tubulated bottle, B, by a piece of strong caoutchouc tube  $1\frac{1}{2}$  metre long, and 2 mm. internal diameter. This bottle and tube serve for the supply of the apparatus with mercury. The shorter limb of the tube A, is contracted at C, and joined to a tube 220 mm. long, the bore of which does not exceed  $1\frac{1}{2}$  mm. To the upper extremity of C is joined the capillary tube *d d'*, carrying a glass stopcock, *e*. The upper extremity of *d d'* is bent horizontally, and is carefully cemented into the steel cap and clamp-joint *f*, the structure of which is shown in section in figs. 2 and 3. *g g* represents a similar steel cap, glass stopcock, and capillary tube connected with the small absorbing jar I, 100 mm. high, and 38 mm. internal diameter. The two steel caps permit of being joined gas-tight into a continuous capillary tube by a

\* Journ. Chem. Soc., vi, 197.



small screw clamp, fig. 3, as originally devised by Regnault. The jar, I, stands firmly upon the shelf of a wooden mercury trough, G. The construction of this trough is shown by figures IV, V, and VI. It is 265 mm. long, 80 mm. broad, and 90 mm. deep outside measure. The rim, AA, is 8 mm. broad, and 15 mm. deep. The excavation B, is 230 mm. long, 26 mm. broad, and 65 mm. deep. The shelf or bottom of the circular cavity, on which the jar, I, rests, is sunk to a depth of 20 mm. below the top of the trough, C, or 35 mm. below the top of the rim, A (Fig. vi). At D, in the excavation, are two slight lateral indentations for the convenient transference of tubes containing specimens of gas from their capsules to the trough.

Both limbs of the U-shaped tube are graduated in millimetres from below upwards, care being taken that, when the tube is placed perpendicularly, the zeros on both limbs are exactly at the same level. HH is a glass cylinder fixed upon the tube, C by a perforated, caoutchouc cork, F, slipped over the top of the tube. To facilitate the placing of the cork and cylinder in position, the horizontal portion of the capillary tube, *d*, should be as short as possible. The cylinder, HH, serves to contain water intended to give, without delay, a definite temperature to



gases which have to be measured in the limb, C. To secure a uniform temperature in this column of water an agitator, *h h*,

consisting of a copper wire, flattened and bent into the form of a ring at its lower extremity, is employed. Before this instrument is ready for use, its shorter limb, C, requires calibration, which is effected with great facility and accuracy in the following manner. The instrument is filled with mercury, by placing the reservoir, B, upon the stand, K, opening the clamp at *b*, and the stopcock, *e*, after disconnecting *g* I, at *f*. When mercury drips from the orifice at *f*, the cock, *e*, is shut. The jar, I, is now to be filled with mercury, by applying suction to the orifice of its capillary tube, until mercury issues from it, and then closing the glass stopcock, *g*. The tubes, *d* and *g*, must now be joined by the clamp *f*, and sufficient distilled water thrown up into I to fill completely the shorter limb of the U-shaped tube. The stopcocks, *e* and *g*, being opened, and B again placed upon the table, the clamp at *b* is to be unscrewed, so as to allow mercury to flow from both limbs of the U-tube, and thus to draw over the water from I into C. When the latter is so far filled with water as to depress the level of the mercury below the zero of the graduation, the cock, *e*, is closed, I is disconnected at *f*, and removed, and the mercury reservoir, B, again placed upon the stand, K. The cock, *e*, is now cautiously opened, and water allowed to drip from *f* until the convex surface of the mercury in C exactly marks the zero of the graduated scale. By greasing the face of the steel cap at *f*, the water will flow down it in minute globules without wetting its surface. The temperature of the water in the cylinder HH, being now noted, the calibration may be commenced. A small and light glass flask, the weight of which has been accurately ascertained is placed in such a position as to receive the drops of water when the latter are made to flow from *f*. The cock, *e*, is then cautiously opened, and water allowed to drop into the flask until the mercury has risen in C a certain number of millimetres, when the weight of water collected in the flask is ascertained. If the tube be of tolerably uniform bore, it will be sufficient to weigh the water at each rise of mercury through 100 millimetres, but the last reading of mercury in C should be taken at the highest point at which the calibre has remained unaltered in attaching the narrower tube, and the next reading should, in like manner, be taken at the lowest point of the narrow tube, where the bore has not been deformed by the glass-blower. It is obvious that between these two points no gaseous volume

can be determined, but the gas can always be either compressed into the narrower tube or expanded into the wide one by lengthening or shortening the column of mercury in the other limb of the apparatus. The operation of weighing the water expelled between observed divisions of the scale, is continued, until the last drop is expelled from the capillary tube *d*. If the temperature of the water in H H be 4° C., the weight of water in grammes expelled from known lengths of the tube, C, expresses in cubic centimetres the respective capacities of those lengths of the tube. If the temperature of the water be not 4° C., the necessary correction must be made. It now only remains to calculate the volume-value of each millimetre in the different calibrated spaces, and to prepare a table showing the volume of gas contained in the tube when the apex of the mercury stands at each individual millimetre from zero to *d*. The capillary depression of the mercury in the narrow tube must also be estimated by taking several readings in the two limbs when they are both freely open to the air. With a narrow tube of the diameter recommended above, this capillarity, will amount to about 3·4 millimetres, which must therefore be deducted from the pressure in all determinations of gaseous volumes made within the narrow tube. The instrument is now ready for use. To preserve the mercury in the open limb of the U-shaped tube and in the reservoir B, from dust and atmospheric impurity, it is advisable to close their mouths with a loose plug of cotton wool.

The following is the mode of conducting, with this apparatus, the analysis of a gaseous mixture obtained in the combustion of a water residue. The gas is carefully transferred without loss to the jar, I, and thence for measurement into C,\* where the apex of the mercury is brought to coincide with any millimetre mark. Let us suppose that the following observations are made:

Height of mercury in C .....	250 mm.
Corresponding vol. of gas as per calibration table	19·200 c.c.
Height of mercury in A .....	130·4 mm.
Temperature of water in H H .....	16·4° C.
Height of barometer .....	763·1 mm.

\* In the calibration, the internal walls of C are moistened with distilled water; they are also ever afterwards kept moist, so that the gases when measured are always saturated with aqueous vapour.

From these data the pressure upon the gas will be as follows:—

Height of barometer .....	763·1 mm.
Deduct height of mercury column in A from height in C, viz: 250 — 130·4 =	119·6
Plus tension of aqueous vapour at 16°·4 C. =	13·9
	----- 133·5 mm.
Pressure on dry gas.....	629·6 mm.

Hence we have 19·200 c.c. of dry gas at 16°·4 C. and 629·6 mm. pressure.

Two or three drops of a concentrated solution of caustic potash having been introduced by means of a small pipette into I, the gas is now brought over into contact with it by placing the reservoir, B, upon the stand, K, and opening the clamp, *b*, and the stopcocks, *e* and *g*. The absorption of carbonic anhydride is complete in about three minutes. The gas is again passed into C for measurement, as before, the difference between the two measurements giving obviously the volume of carbonic anhydride in the original mixture.\* The residual gas now consists of nitric oxide and nitrogen. Whilst it is still in the measuring tube, C, about an equal volume of oxygen is passed up into I, and the gas being now brought over into the latter, the nitric oxide is instantly transformed into nitric peroxide, and absorbed by the excess of caustic potash present. But as excess of oxygen must be employed in this operation, it is necessary to get rid of this gas before the volume of residual nitrogen can be determined. For this purpose, two or three drops of a concentrated solution of pyrogallic acid are passed up into I. The oxygen is soon absorbed, but its removal is much hastened by agitating the liquid so as to cause it again and again to moisten the surface of the glass receiver I. By dexterously causing the stand supporting the trough G to vibrate slightly, this agitation of the enclosed liquid can be readily effected,

\* If the combustion of the water residue be not pushed on too rapidly every trace of sulphurous anhydride will be absorbed by the metallic copper in front of the cupric oxide, but it has occasionally happened in combustions, very carelessly made, that some sulphurous anhydride has escaped absorption. If such a result be suspected, it is only necessary to introduce two or three drops of a saturated solution of dipotassic dichromate into I before the original gas is transferred for measurement.



without exposing the capillary tubes to the risk of fracture. The absorption of oxygen is known to be complete when the dark-coloured liquid thrown by agitation upon the sides of the glass runs off again without leaving a dark, blood-red stain. The operation is usually complete at the expiration of five minutes. It now only remains to determine, in C, the volume of the residual nitrogen, and the analysis is finished.

The operations have furnished three uncorrected gaseous volumes, viz., A, volume of the three mixed gases; B, volume of nitric oxide and nitrogen; and C, volume of nitrogen. By the usual calculations these volumes may be reduced to 0° C. and 760 mm. pressure, and then from the corrected volumes A', B', and C', so obtained, the quantities of carbonic anhydride and nitrogen may be deduced as follows:—

$$A' - B' = \text{vol. of carbonic anhydride.}$$

$$\frac{C' + B'}{2} = \text{vol. of nitrogen.}$$

From these corrected volumes of carbonic anhydride and nitrogen the weights of carbon and nitrogen can, of course, be readily calculated. This final and sole object of the analyst may, however, be obtained by a much shorter process; that is, by dispensing altogether with the intermediate determination of the corrected volumes, which is only necessary in the foregoing method of calculation, in order to enable the operator to arrive at the corrected volumes of carbonic anhydride and nitrogen. In fact, if the original gaseous mixture be treated, so far as volume-weight is concerned, as nitrogen, the calculations become greatly simplified. They depend upon the following data:—

1. The weights of carbon and nitrogen contained in equal volumes of carbonic anhydride and nitrogen gases measured at the same temperature and pressure, are to each other as 6:14.

2. The weights of nitrogen contained in equal volumes of nitrogen and nitric oxide are as 2:1.

Now, if we assume, for the purposes of calculation, that the gaseous mixture submitted to analysis consists entirely of nitrogen, and that two successive portions of this nitrogen are removed from it by the action of reagents, then, if A be, the

weight of the total gas calculated as nitrogen, B the weight after absorption of the first portion ( $\text{CO}_2$ ), and C the weight after the absorption of the second portion ( $\text{N}_2\text{O}_2$ ); further, if  $x$  and  $y$  represent respectively the weights of carbon and nitrogen actually contained in the gaseous mixture, then the following simple equations express the values of  $x$  and  $y$ :—

$$x = \frac{3(A - B)}{7}$$

$$y = \frac{C + B}{2}$$

By the use of the logarithmic table given below for the reduction of cubic centimetres of nitrogen to grms. for each tenth of a degree centigrade by the formula  $\frac{\cdot 0012562}{(1 + \cdot 00367t)760}$  the labour of calculation is reduced to a minimum. An example will perhaps render the whole method of calculation here proposed more intelligible. For this purpose, let us suppose the following values to have been obtained from readings such as those described at p. 113:—

Vol. of original gas = A.

19·200 c.c. of dry gas at 16°·4 C. and 629·6 mm. pressure.

Vol. after first absorption (of  $\text{CO}_2$ ) = B.

3·342 c.c. of dry gas at 16°·7 C. and 324·5 mm. pressure.

Vol. after second absorption (of  $\text{N}_2\text{O}_2$ ) = C.

1·631 c.c. of dry gas at 16°·9 C. and 298·4 mm. pressure.

A =

$$\log. 19\cdot200 = 1,28830$$

$$,, 629\cdot6 = 2,79906$$

$$\log. \frac{\cdot 002562}{(1 + \cdot 00367 t) 760} \text{ for } 16\cdot4 \text{ C} = - 6,19286$$

$$- 2,27522 = \cdot 01885 \text{ grm.}$$

B =

$$\log. 3\cdot342 = 0,52401$$

$$,, 324\cdot5 = 2,51121$$

$$\log. \frac{\cdot 0012562}{(1 + \cdot 00367 t) 760} \text{ for } 16\cdot7 \text{ C} = - 6,19241$$

$$- 3,22768 = \cdot 001689 \text{ grm.}$$

C =

$$\log. 1\cdot631 = 0,21245$$

$$,, 298\cdot4 = 2,47480$$

$$\log. \frac{\cdot 0012562}{(1 + \cdot 00367 t) 760} \text{ for } 16\cdot9 \text{ C} = - 6,19211$$

$$- 4,87986 = \cdot 0007575 \text{ grm.}$$

Introducing these values for A, B, and C, into the above equations, we get the following values for  $x$  (carbon) and  $y$  (nitrogen) :—

$$x = \cdot 007355 \text{ grm.}$$

$$y = \cdot 00122325 \text{ grm.}$$

If these results had been obtained by the combustion of the solid residue from one litre of water, then by moving the decimal point two places to the right, the values for  $x$  and  $y$  just quoted are transformed into parts by weight of carbon and nitrogen in 100,000 parts of the water ; thus :—

Carbon  $\cdot 735$  part in 100,000 of water.

Nitrogen  $\cdot 122$            "           "

The analysis of the gases expelled from waters by ebullition in vacuo\* is performed with equal facility with this apparatus. In all but extremely rare cases these gases consist only of carbonic anhydride, oxygen, and nitrogen. The carbonic anhydride is absorbed by a few drops of concentrated potash solution, as before described, and the remaining oxygen and nitrogen gases are then separated by means of pyrogallic acid. In this case the results are usually expressed in cubic centimetres at 0° C. and 760 mm. pressure. The volumes actually read off are reduced to this standard by the following formula :—

$$\frac{AB}{(1 + \cdot 003665 t) 760}$$

in which A = the observed volume of gas in cubic centimetres, B = the pressure upon the dry gas, and  $t$  = the temperature at the time the volume was measured. A table is given below, showing the log. of  $(1 + \cdot 003665t) 760$  for each 0°·1 C. from 0° to 30°.

\* An improved method for extracting the gases from waters in vacuo, will be shortly laid before the Society, by Mr. McLeod, Demonstrator in the Royal College of Chemistry.

Table for the Reduction of Cubic Centimetres of Nitrogen to Grams.

Log.  $\frac{.0012562}{(1 + .00867t)760}$  for each tenth of a degree from 0° to 30°C.

t.°C.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0°	—6,21824	808	793	777	761	745	729	713	697	681
1	665	649	633	617	601	586	570	554	538	522
2	507	491	475	459	443	427	412	396	380	364
3	349	333	318	302	286	270	255	239	223	208
4	192	177	161	145	130	114	098	083	067	051
5	085	020	004	*989	*973	*957	*942	*926	*911	*895
6	—6,20879	864	848	833	817	801	786	770	755	739
7	723	708	692	676	661	645	629	614	598	583
8	567	552	536	521	505	490	474	459	443	428
9	413	397	382	366	351	335	320	304	289	274
10	259	244	228	213	198	182	167	151	136	121
11	106	090	075	060	045	029	014	*999	*984	*969
12	—6,19953	938	923	907	892	877	862	846	831	816
13	800	785	770	755	740	724	709	694	679	664
14	648	633	618	603	588	573	558	543	528	513
15	497	482	467	452	437	422	407	392	377	362
16	346	331	316	301	286	271	256	241	226	211
17	196	181	166	151	136	121	106	091	076	061
18	046	031	016	001	*986	*971	*956	*941	*926	*911
19	—6,18897	882	867	852	837	822	807	792	777	762
20	748	733	718	703	688	673	659	644	629	614
21	600	585	570	555	540	526	511	496	481	466
22	452	437	422	408	393	378	363	349	334	319
23	305	290	275	261	246	231	216	202	187	172
24	158	143	128	114	099	084	070	055	041	026
25	012	*997	*982	*968	*953	*938	*924	*909	*895	*880
26	—6,17866	851	837	822	808	793	779	764	750	735
27	721	706	692	677	663	648	634	619	605	590
28	576	561	547	532	518	503	489	475	460	446
29	432	417	403	388	374	360	345	331	316	302

Table of the Elasticity of Aqueous Vapour for each  $\frac{1}{10}$ th degree centigrade from  $0^{\circ}$  to  $30^{\circ}$  (Regnault).

Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.
0	4.6	.2	6.6	.4	9.4	.6	13.2	.8	18.8
.1	4.6	.3	6.7	.5	9.5	.7	13.3	.9	18.4
.2	4.7	.4	6.7	.6	9.5	.8	13.4	21.0	18.5
.3	4.7	.5	6.8	.7	9.6	.9	13.5	.1	18.6
.4	4.7	.6	6.8	.8	9.7	16.0	13.5	.2	18.7
.5	4.8	.7	6.9	.9	9.7	.1	13.6	.3	18.8
.6	4.8	.8	6.9	11.0	9.8	.2	13.7	.4	19.0
.7	4.8	.9	7.0	.1	9.9	.3	13.8	.5	19.1
.8	4.9	6.0	7.0	.2	9.9	.4	13.9	.6	19.2
.9	4.9	.1	7.0	.3	10.0	.5	14.0	.7	19.3
1.0	4.9	.2	7.1	.4	10.1	.6	14.1	.8	19.4
.1	5.0	.3	7.1	.5	10.1	.7	14.2	.9	19.5
.2	5.0	.4	7.2	.6	10.2	.8	14.2	22.0	19.7
.3	5.0	.5	7.2	.7	10.3	.9	14.3	.1	19.8
.4	5.1	.6	7.3	.8	10.3	17.0	14.4	.2	19.9
.5	5.1	.7	7.3	.9	10.4	.1	14.5	.3	20.0
.6	5.2	.8	7.4	12.0	10.5	.2	14.6	.4	20.1
.7	5.2	.9	7.4	.1	10.5	.3	14.7	.5	20.3
.8	5.2	7.0	7.5	.2	10.6	.4	14.8	.6	20.4
.9	5.3	.1	7.5	.3	10.7	.5	14.9	.7	20.5
2.0	5.3	.2	7.6	.4	10.7	.6	15.0	.8	20.6
.1	5.3	.3	7.6	.5	10.8	.7	15.1	.9	20.8
.2	5.4	.4	7.7	.6	10.9	.8	15.2	23.0	20.9
.3	5.4	.5	7.8	.7	10.9	.9	15.3	.1	21.0
.4	5.5	.6	7.8	.8	11.0	18.0	15.4	.2	21.1
.5	5.5	.7	7.9	.9	11.1	.1	15.5	.3	21.3
.6	5.5	.8	7.9	13.0	11.2	.2	15.6	.4	21.4
.7	5.6	.9	8.0	.1	11.2	.3	15.7	.5	21.5
.8	5.6	8.0	8.0	.2	11.3	.4	15.7	.6	21.7
.9	5.6	.1	8.1	.3	11.4	.5	15.8	.7	21.8
3.0	5.7	.2	8.1	.4	11.5	.6	15.9	.8	21.9
.1	5.7	.3	8.2	.5	11.5	.7	16.0	.9	22.1
.2	5.8	.4	8.2	.6	11.6	.8	16.1	24.0	22.2
.3	5.8	.5	8.3	.7	11.7	.9	16.2	.1	22.3
.4	5.8	.6	8.3	.8	11.8	19.0	16.3	.2	22.5
.5	5.9	.7	8.4	.9	11.8	.1	16.4	.3	22.6
.6	5.9	.8	8.5	14.0	11.9	.2	16.6	.4	22.7
.7	6.0	.9	8.5	.1	12.0	.3	16.7	.5	22.9
.8	6.0	9.0	8.6	.2	12.1	.4	16.8	.6	23.0
.9	6.1	.1	8.6	.3	12.1	.5	16.9	.7	23.1
4.0	6.1	.2	8.7	.4	12.2	.6	17.0	.8	23.3
.1	6.1	.3	8.7	.5	12.3	.7	17.1	.9	23.4
.2	6.2	.4	8.8	.6	12.4	.8	17.2	25.0	23.5
.3	6.2	.5	8.9	.7	12.5	.9	17.3	.1	23.7
.4	6.3	.6	8.9	.8	12.5	20.0	17.4	.2	23.8
.5	6.3	.7	9.0	.9	12.6	.1	17.5	.3	24.0
.6	6.4	.8	9.0	15.0	12.7	.2	17.6	.4	24.1
.7	6.4	.9	9.1	.1	12.8	.3	17.7	.5	24.3
.8	6.4	10.0	9.2	.2	12.9	.4	17.8	.6	24.4
.9	6.5	.1	9.2	.3	12.9	.5	17.9	.7	24.6
5.0	6.5	.2	9.3	.4	13.0	.6	18.0	.8	24.7
.1	6.6	.3	9.3	.5	13.1	.7	18.2	.9	24.8

TABLE—(continued).

Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.
26·0	25·0	·8	26·2	·6	27·5	·4	28·8	·2	30·1
·1	25·1	·9	26·4	·7	27·6	·5	28·9	·3	30·3
·2	25·3	27·0	26·5	·8	27·8	·6	29·1	·4	30·5
·3	25·4	·1	26·7	·9	27·9	·7	29·3	·5	30·7
·4	25·6	·2	26·8	28·0	28·1	·8	29·4	·6	30·8
·5	25·7	·3	27·0	·1	28·3	·9	29·6	·7	31·0
·6	25·9	·4	27·1	·2	28·4	29·0	29·8	·8	31·2
·7	26·0	·5	27·3	·3	28·6	·1	30·0	·9	31·4

Table of log.  $(1 + \cdot 003665 t)$  760 for each  $\frac{1}{10}$ th of a degree from  $0^\circ$  C. to  $30^\circ$  C.

t°.	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0°	2,88081	097	113	129	144	160	176	192	208	224
1	240	256	272	288	304	319	335	351	367	383
2	399	415	431	447	462	478	494	510	526	542
3	557	573	589	604	620	636	651	667	683	699
4	714	730	746	761	777	793	809	824	840	856
5	871	887	903	918	934	950	965	981	996	*012
6	2,89027	048	058	074	089	105	120	136	151	167
7	182	198	213	229	244	260	275	291	306	322
8	337	353	368	384	399	415	430	445	461	476
9	491	507	522	538	553	569	584	599	615	630
10	645	661	676	691	707	722	738	753	768	783
11	798	814	829	844	860	875	890	906	921	936
12	951	967	982	997	*012	*028	*043	*058	*073	*088
13	2,90103	119	134	149	164	179	194	209	224	239
14	255	270	285	300	315	330	345	360	375	390
15	406	421	436	451	466	481	496	511	526	541
16	557	572	587	602	617	632	647	662	677	692
17	707	722	737	752	767	782	797	812	827	842
18	857	872	887	902	917	932	947	962	977	992
19	2,91006	021	036	051	066	081	096	111	126	141
20	155	170	185	200	215	229	244	259	274	289
21	308	318	333	343	363	377	392	407	422	437
22	451	466	481	495	510	525	540	554	569	584
23	598	613	628	642	657	672	687	701	716	731
24	745	760	775	790	804	819	834	848	863	878
25	892	907	922	936	951	965	980	994	*009	*024
26	2,92088	058	068	082	097	112	126	141	155	170
27	184	199	213	228	242	257	271	286	300	315
28	329	344	358	373	387	402	416	431	445	460
29	474	489	503	518	532	547	561	575	590	604
30	618	633	647	661	676	690	704	719	733	747

XIII.—*Reduction of Carbonic Acid to Oxalic Acid.*

By Dr. E. DRECHSEL.

(Communicated by H. KOLBE.)

AFTER many unsuccessful experiments, made during several years in my laboratory, with the view of directly reducing carbonic to oxalic acid—by a method similar to that by which Dr. R. Schmitt and I had effected its transformation seven years ago—my assistant, Dr. Drechsel, has at length succeeded in solving this problem by very simple means.

When a mixture of pure sodium and recently ignited dry sand is heated in a flask imbedded in a small sand-bath to the temperature of boiling mercury, while a rapid stream of dry carbonic acid gas is continually passed through the vessel, the pulpy mixture of sodium and sand, which has at first a silvery lustre, soon turns red, and in a few hours the whole becomes converted into a dark-coloured pulverulent mass. Towards the end of the operation, care must be taken not to heat the mixture too strongly, as in that case the product is apt to decompose with a glimmering light.

The cooled mass is spread out on shallow dishes to facilitate the oxidation of the free sodium, then exhausted with water, and supersaturated with acetic acid; and the oxalic acid is precipitated from the filtrate by chloride of calcium. The precipitate is usually brownish; but by dissolving it in hydrochloric acid, and neutralizing the filtered solution with ammonia, the salt is obtained in the form of a snow-white powder.

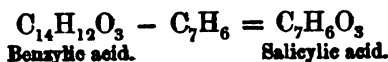
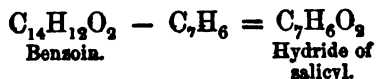
60 grms. of sodium thus treated yielded 6 grms. of calcic oxalate.

Dr. Drechsel has subsequently found that potassium-amalgam containing 2 p. c. potassium, heated in carbonic acid gas to the boiling point of mercury, absorbs the carbonic acid abundantly, and yields a somewhat considerable quantity of oxalic acid.

XIV.—*On some new Benzyllic Derivatives of the Salicyl Series.*

By W. H. PERKIN, F.R.S.

ON comparing the formulæ of benzoin and benzylic acid with those of the hydride of salicyl and salicylic acid, it will be observed that there exists a difference of  $C_7H_6$  in their composition:—



If, therefore, an equivalent of hydrogen could be replaced by benzyl ( $C_7H_7$ ) in the salicylic aldehyde and acid, isomers of these substances would be produced.

The following is an account of some experiments which I have made in this direction, and now beg leave to lay before the Society:—

*Action of Chloride of Benzyl upon the Hydride of Sodium-salicyl.*

On heating a mixture of equivalent quantities of the hydride of sodium-salicyl (salicylite of sodium) and chloride of benzyl with several times its volume of alcohol, for three or four hours, to a temperature of  $120^\circ$  to  $140^\circ$  C., in a sealed tube, chemical action, takes place, with formation of chloride of sodium.

After filtering off this salt, and separating the excess of alcohol by evaporation, a thick oily substance is obtained, which, when distilled, yields only a small quantity of product below  $320^\circ$  C., by far the larger quantity coming over as a thick yellow oil above the range of the mercurial thermometer. To purify this oily distillate, it is first agitated with a solution of hydrate of potassium, and then with a strong solution of bisulphite of sodium, with which it slowly combines. It should be kept in contact with this reagent for two or three days, with frequent agitation or stirring, otherwise a quantity of product may remain uncombined, and be lost. The crystalline com-



pound thus obtained is collected upon a cloth filter, drained, well squeezed from the excess of bisulphite of sodium, and afterwards dissolved in very cold water. Ether is then added to remove oily impurities, and the clear aqueous solution rendered alkaline with carbonate of sodium. The new body which has been liberated by this reagent is taken up with ether, and, upon evaporating, this ethereal solution is obtained as a colourless viscid oil, remaining fluid for days if left undisturbed, but gradually solidifying if agitated. It may then be rendered perfectly pure by recrystallisation from alcohol. The following combustions of this substance were made:—

- I. 1832 of substance gave  
 5331 of  $\text{CO}_2$ , and  
 0976 of  $\text{H}_2\text{O}$ .
- II. 2661 of substance gave  
 7706 of  $\text{CO}_2$ , and  
 1425 of  $\text{H}_2\text{O}$ .
- III. 2437 of substance gave  
 7062 of  $\text{CO}_2$ , and  
 1253 of  $\text{H}_2\text{O}$ .

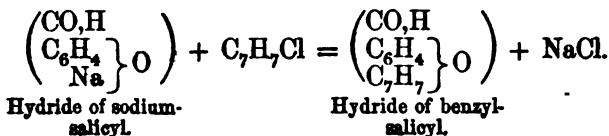
These numbers give percentages agreeing with the formula—



as the following comparisons will show:—

	Theory.		Experiment.		
	I.	II.	I.	II.	III.
$\text{C}_{14}$ . . . .	168	79.24	79.31	78.97	79.03
$\text{H}_{12}$ . . . .	12	5.66	5.91	5.95	5.71
$\text{O}_2$ . . . . .	32	15.10	—	—	—
	<hr/>	<hr/>			
	212	100.00			

This substance represents the hydride of salicyl with its phenolic hydrogen replaced by benzyl. I, therefore, propose to call it the *hydride of benzyl-salicyl*. Its formation may be expressed thus:—



As anticipated, the hydride of benzyl-salicyl is not identical with benzoin, but only isomeric. It melts at  $46^{\circ}\text{C}$ ., benzoin melting at  $120^{\circ}\text{C}$ . With concentrated sulphuric acid it forms a yellow solution, benzoin, under the same circumstances, producing a crimson one. With alcoholic hydrate of potassium it yields a yellow liquid, benzoin giving a violet-coloured reaction.

The hydride of benzyl-salicyl boils at a temperature above the range of the mercurial thermometer. When cold, it possesses a slightly aromatic odour, somewhat similar to that of cloves; but when heated, its vapour is both irritating and suffocating. It is easily soluble in ether, tetrachloride of carbon, benzol, and likewise in boiling alcohol, from which it crystallises on cooling in splendid transparent, flat, oblique prisms. In boiling water it dissolves to a small extent, the solution becoming turbid on cooling, and, after standing, depositing a small quantity of the aldehyde in crystals.

Bromine and also nitric acid attack the hydride of benzyl-salicyl, but the derivatives appear to be uncrystallisable bodies.

As already seen, this body is an aldehyde, and combines with bisulphites. These combinations, however, do not form very easily when pure hydride of benzyl-salicyl is employed, apparently on account of its solid condition, and the insolubility of the resulting compounds in solution of the bisulphites; therefore, it is better to employ the crude oily aldehyde in their preparation. The compound with bisulphite of sodium, when crystallised over sulphuric acid, forms beautiful small micaceous crystals, possessing a very burning taste.

When heated in a sealed tube with acetic anhydride to a temperature of  $150^{\circ}\text{C}$ . for three or four hours, the hydride of benzyl yields an oily product, apparently a direct combination. This compound, if heated with water to  $150^{\circ}\text{C}$ ., decomposes with formation of acetic acid.

#### *Action of Chloride of Benzyl upon Gaultherate of Sodium.*

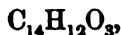
Chloride of benzyl acts easily upon the gaultherate of sodium when heated with alcohol in a sealed tube of  $100^{\circ}\text{C}$ .; four or five hours' digestion being generally sufficient to complete the

reaction. The product on being filtered off from the chloride of sodium which has formed, and evaporated on the water-bath to remove alcohol, yields a rather viscid oil, which, when rectified, gives a considerable quantity of distillate, boiling above  $320^{\circ}$  C.; this consists of crude benzyl-salicylate of methyl.

To obtain the acid from this product, it is decomposed by boiling with alcoholic hydrate of potassium. On separating the alcohol by evaporation, a crude pasty potassium salt is obtained, floating upon the excess of hydrate of potassium, which remains as a clear fluid, and may be poured away. The potassium salt is then dissolved in water and agitated with ether to remove oily impurities, and the clear aqueous solution decomposed with hydrochloric acid; this causes the new acid to separate as an oil, which solidifies in the course of twenty-four hours. It is then crystallised from alcohol once or twice, or preferably from tetrachloride of carbon. Two combustions of this acid gave the following numbers:—

- I. .2570 of substance gave  
 .6929 of  $\text{CO}_2$  and  
 .1234 of  $\text{H}_2\text{O}$ .
- II. .2452 of substance gave  
 .6627 of  $\text{CO}_2$  and  
 .1224 of  $\text{H}_2\text{O}$ .

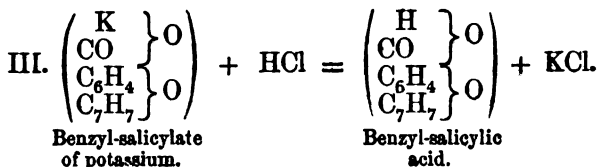
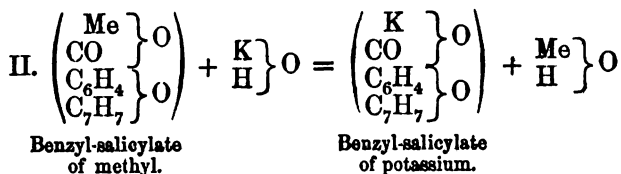
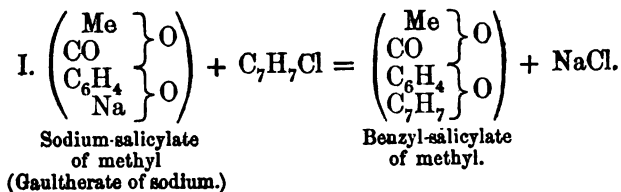
These numbers give per centages agreeing with those required by the formula



as the following comparisons will show:

	Theory.		Experiment.	
			I.	II.
$\text{C}_{14}$ .....	168	73·68	73·53	73·70
$\text{H}_{12}$ ....	12	5·27	5·33	5·54
$\text{O}_3$ .....	48	21·05	—	—
	<hr/>	<hr/>		
	228	100·00		

This substance represents salicylic acid, in which the phenolic hydrogen is replaced by benzyl. I therefore propose to call it *benzyl-salicylic acid*. Its formation may be expressed thus:—



Benzyl-salicylic acid melts at 75° C., and on cooling forms a viscid oil, which crystallises in a confused manner when rubbed with a glass rod. It is extremely soluble in boiling, and easily so in cold alcohol; it crystallises from this solvent in minute plates. In one experiment a portion of crude acid, dissolved in slightly diluted alcohol, at first deposited an oil, but after standing for about twenty-four hours, beautiful transparent plates of the pure acid, an eighth of an inch in diameter, filled the oily deposit and jutted out into the clear solution. If boiled with water, this acid dissolves to a small extent, and the solution on cooling becomes milky, and, after standing some time, deposits the acid in thin brilliant plates.

Benzyl-salicylic acid is isomeric with benzylic acid, but does not give its coloured reactions, neither does it give the violet coloration of salicylic acid with persalts of iron.

*Benzyl-salicylate of Ammonium.*—Benzyl-salicylic acid dissolves freely in ammonia, and on boiling off the excess of alkali, a clear solution is obtained, but this, if evaporated to dryness, decomposes with separation of the acid.

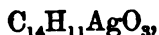
*Benzyl-salicylate of Silver.*—This body is obtained by the addition of nitrate of silver to the ammonium salt. It is

thrown down as a pure white precipitate slightly soluble in water.

As a small quantity of benzyl-salicylic acid is often carried down with this compound, especially if the ammonium salt employed in its preparation has been boiled rather too much, it should be washed with alcohol as well as with water. It must be dried in vacuo, as it fuses if heated in the water oven. A combustion and silver determinations gave the following results:—

- I. ·1979 of substance gave  
·3643 of CO<sub>2</sub> and  
·0635 of H<sub>2</sub>O.
- II. ·2194 of substance gave  
·0694 of silver.
- III. ·1597 of substance gave  
·0508 of silver.

These numbers give per centages agreeing with the formula,



as the following comparisons will show:—

	Theory.		Experiment.		
			I.	II.	III.
C <sub>14</sub> ....	168	50·15	50·20	—	—
H <sub>11</sub> ....	11	3·28	3·56	—	—
Ag ....	108	32·23	—	31·63	31·80
O <sub>3</sub> .....	48	14·34	—	—	—
	<hr/>	<hr/>			
	385	100·00			

*Benzyl-salicylate of Lead.*—The addition of acetate of lead, to a solution of benzyl-salicylate of ammonium, causes the salt to form as a white curdy precipitate.

*Benzyl-salicylate of Mercury* is a white precipitate.

*Benzyl-salicylate of Copper* is a pale apple-green precipitate.

XV.—*On Gas Analysis.*

By W. J. RUSSELL, Ph.D.

THE method of gas analysis proposed by Bunsen has this great advantage, that it requires no complicated apparatus; a graduated glass tube, with the means of holding it vertically in a mercury trough, may be said to be all the special apparatus required. The reagent is used in the solid state and introduced into the eudiometer. The defect of this method, as is well known, is that the absorptions take place but slowly, and that after touching the eudiometer it takes a considerable length of time to regain the temperature of the surrounding air, so that several hours are required to complete an analysis by this method.

These defects are obviated in the methods proposed by Regnault and Reiset and by Frankland. These chemists use the reagent in the liquid state, and surround the eudiometer with water. To do this it was, however, found necessary to have a more complicated form of apparatus; the liquid reagent was not allowed to enter the eudiometer, but was introduced into another tube termed the *laboratory tube*, and the gas had by suitable means to be passed backwards and forwards between the eudiometer and this laboratory tube. In the apparatus which Dr. Williamson and I described in 1864\* this transference of the gas was effected by a simple means free from any chance of loss or leakage. In all these forms of apparatus it is then principally the necessity of having a separate tube for the reagent, which has rendered them so much more complicated than the apparatus of Bunsen.

My object now is to describe a method by which the liquid reagent can be introduced and removed from the eudiometer itself, thus avoiding the necessity of a laboratory tube, and the sluggish action of solid reagents.

In what follows, the process is applied to the method of Williamson and Russell above alluded to.

The mercury trough is made of gutta-percha, the form of it

\* Chem. Soc. Journ. xvii, 238.

is shown in figs. 1 and 2. Fig. 1 is a horizontal section, and fig. 2 a section through A B. The larger part of the trough is circular; in this part stands the glass cylinder which contains

FIG. 1.

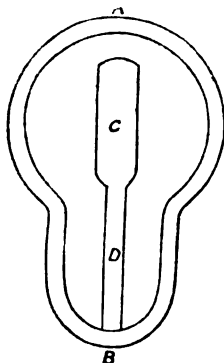
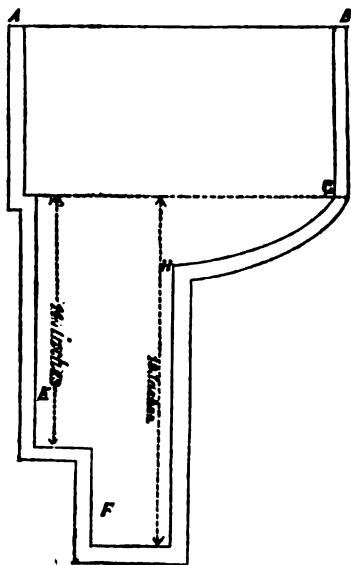


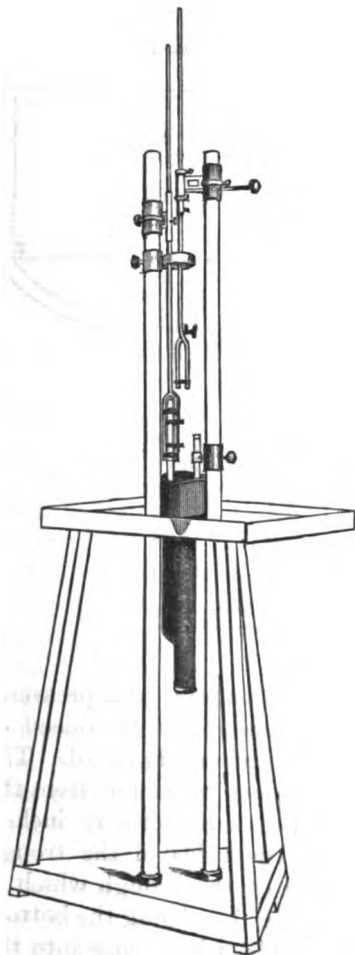
FIG. 2.



the water, and in the centre are the eudiometer and pressure-tube. The form of the well in which these tubes are raised or lowered is represented at C; it is  $2\frac{1}{2}$  inches long,  $1\frac{1}{8}$  broad. The well for the pressure-tube is 14 inches deep measured from the bottom of the trough, and that for the eudiometer 19 inches. These are shown in fig. 2 E and F. The sides of the trough are  $3\frac{1}{2}$  inches high. The smaller part of the trough which is without the glass cylinder is shown in fig. 1. Along the bottom of this part there is a channel  $\frac{1}{2}$  inch wide, which runs into the well. The depth of this channel starting from the end of the bottom of the trough at B gradually increases till it reaches the well, where it is  $1\frac{1}{2}$  inches deep, G H, fig. 2. The circular part of the trough is  $3\frac{1}{2}$  inches in diameter, and the total length through A B  $6\frac{1}{2}$  inches. The above dimensions are all inside measurements. The thickness of the gutta-percha is half an inch.

The pressure tube now used is simply a straight piece of tubing of about the same diameter as the eudiometer; this

FIG. 3.



simple form is more convenient than the one which was formerly proposed. The paper screen between the apparatus and the light is conveniently replaced by a strip of tissue-paper gummed on to the glass cylinder. Figure 3 represents the whole apparatus. The glass cylinder is omitted for the sake of clearness, also the eudiometer, but the clamp intended to hold it is very evident.

The liquid reagent is introduced into the eudiometer by means of a small syringe, readily made from a piece of tubing about 8 or 9 inches long, and  $\frac{1}{4}$ th inch internal diameter; one end of it is bent round so as to give it the form of a hook, and drawn out; into the other end a piston fits, made from a piece of stout steel wire, one end of it roughened or a screw turned on it, and round this cotton wool is tightly wrapped till it just fits the tube. In order to have a measure of the quantity of liquid to be introduced into the eudiometer, it is convenient to make five or six marks on the straight end of the syringe with a file,

a quarter of an inch apart. When the liquid is to be introduced, a dot with a piece of chalk is made on the piston, and it is then pushed down till this chalk dot reaches the mark corresponding to the volume of liquid to be injected.

We now come to the question of how this liquid reagent is to be withdrawn without altering the bulk of gas in the



eudiometer. Several different processes were tried, but it is only necessary to describe the one found to answer by far the best. The problem evidently was to find some body which could absorb a certain amount of liquid, but which would not carry air with it when introduced into the eudiometer, or abstract gas on being withdrawn.

The following experiments will show that wet cotton wool has the required properties. It is used in this way: a piece of steel wire, size No. 9 or 10, has one end bent into a loop, and some cotton wool is twisted tightly round it; this mass of wool should be about  $\frac{1}{4}$  inch in diameter and  $\frac{3}{4}$  inch long. It is placed in a basin of water, and thoroughly kneaded and squeezed for some time; this treatment wets the whole mass of cotton wool and expels all the air adhering to it.

This ball of cotton on the steel wire might of course be introduced into the eudiometer in the same way as Bunsen introduces his solid reagents; but it is found much more convenient, especially where it is important to have the mercury trough small, to use what may be called a guide tube. This is merely a piece of fine glass tubing about 8 or 9 inches in length, and bent into a curve at one end. The steel wire is introduced at this end and pulled through till the cotton ball prevents its going further. Held in this way the ball is easily introduced or withdrawn from the eudiometer, and that without dipping the fingers into the mercury. The ball being now held in the tube and thoroughly saturated with water, is lifted from the basin and plunged below the surface of the mercury in the trough; it is then squeezed between the finger and thumb, so as to expel a considerable portion of water, but still to leave it very wet. The guide tube is now introduced into the canal D, fig. 1, of the trough, and pushed down it so that the curved end with the ball comes within the tall glass cylinder. In order to introduce the ball into the eudiometer, the eudiometer is raised so that the open end of it is a little above the well in the trough, a mark on the cylinder, or on one of the supports will indicate the point to which the top of the eudiometer must be raised in order that the open end of it may be in the right position. Thus raised it is easy to hook the cotton ball projecting from the guide-tube into the eudiometer; then by pushing the wire the ball rises in the tube and is completely under control. It is well to apply a very little grease to the wire, and if by any

chance it should become bent, it must of course be discarded. To withdraw the reagent, the eudiometer is raised and the cotton ball introduced as above described; it is pushed up till the top of it comes in contact with the reagent, which is then quickly taken up by the cotton-wool and the meniscus left free from liquid. The ball is now pulled below the surface of the mercury; this should be done with a jerk, to prevent any gas adhering to it, and withdrawn from the trough.

The following consecutive experiments will show with what great accuracy this removal of the reagent may be effected by this process. The experiments were the first ones made to test the accuracy of the process. Instead of using a reagent, water was introduced into the eudiometer by means, of course, of the syringe. The numbers indicate the volume of liquid used; for instance six of water means that six quarter-inches of this syringe-tube,  $\frac{1}{4}$ -inch diameter full of water, were used in that experiment.

Volume of air taken .....	300.4
Do. after withdrawing 6 of water ....	300.5
Do. do. ....	300.5
Do. do. ....	300.5
Do. do. ....	300.5
 Volume of air taken .....	 300.0
Do. after withdrawing 6 of water another ball of cotton used .....	 300.0
 Volume of air taken .....	 366.3
Do. after withdrawing 6 of water ....	366.2
Do. do. ....	366.2
Do. do. ....	366.2
(another and larger ball used) ....	366.1
Do. do. ....	366.1
 Volume of air taken .....	 88.7
Do. after withdrawing 6 of water ....	88.7
Do. do. ....	88.6
Do. do. ....	88.7

In this case the gas was very much expanded, there being

when the bulk was introduced, a column of mercury 18 inches high in the eudiometer.

Volume of air taken .....	89·0
Do. after withdrawing 6 of water .....	89·0
Do. after adding carbonic acid .....	111·3
Do. after withdrawing 6 of potash .....	89·0
Do. do. ....	89·0
Volume of air taken .....	169·5
After withdrawing 7 of potash.....	169·4
Do. 6 of potash.....	169·4
Do. do. ....	169·4
Volume of air taken .....	116·5
Do. after adding carbonic acid .....	141·0
After withdrawing 6 of potash.....	116·6
Do. do. ....	116·4
Volume after adding carbonic acid .....	167·0
After withdrawing 8 of potash.....	116·4
Volume after adding carbonic acid .....	210·0
After withdrawing 6 of potash.....	148·0
Do. do. ....	116·4
Volume after adding carbonic acid .....	225·0
After withdrawing 10 of potash .....	139·0
Do. 6 of potash .....	116·3 to 4
Volume of air taken .....	133·6
After withdrawing 3 of water .....	133·6
Do. do. ....	133·6
After withdrawing 2 of water .....	133·6
Do. do. ....	133·6
Do. 6 of water .....	133·6
Do. 2 of potash.....	133·6
Do. do. ....	133·6
Do. 6 of potash, new ball used, ball up twice .....	133·5
Do. 6 of potash, repeated 3 times .....	133·5

These experiments will be sufficient to show the general

accuracy of the process. Connected with the use of each of the ordinary reagents, there are some points it will be necessary to allude to.

*Absorption of Carbonic Acid.*—The following experiments were made with air and known quantities of carbonic acid, to test the accuracy of the method:—

Volume of air taken .....	189·0
After adding carbonic acid ..	204·0
The gas absorbed, no reading made.	
After adding carbonic acid .....	209·0
The gas absorbed, no reading made.	
After adding carbonic acid .....	211·0
The gas absorbed .....	189·0

To absorb the gas in each case, six of potash were used, and allowed to remain in the eudiometer ten minutes. The potash solution was made from a saturated solution of caustic potash, diluted with twice its bulk of water. In the following experiments when the term potash is used, a solution of this strength is always meant:—

Volume of air taken .....	278·4
After adding carbonic acid .....	305·6
After 5 potash, up 15 minutes .....	278·3
Volume of air taken .....	340·9
After adding carbonic acid .....	380·1
After 5 potash, up 18 hours .....	340·8
Volume of air taken .....	325·2
After adding carbonic acid .....	338·3
After 5 potash, up 20 minutes .....	325·1
Volume of air taken .....	326·3
After adding carbonic acid .....	335·9
After 5 potash, up 20 minutes .....	326·3
Volume of air taken .....	333·1
After adding carbonic acid .....	345·0
After 5 potash, up 20 minutes .....	333·0

Volume of air taken .....	327.1
After adding carbonic acid .....	332.8
After 5 potash, up 20 minutes .....	327.0

The foregoing series of experiments are sufficient to show the accuracy with which this absorption of carbonic acid may be made. Although these results are satisfactory, it was still a question whether, under other circumstances, the introduction of a certain amount of caustic potash might not alter the tension of the gas even in a wet eudiometer. To investigate this point, moist air free from carbonic acid was first taken, and potash brought in contact with it in the eudiometer.

Volume of air taken .....	341.8
After 5 potash, up 20 minutes .....	341.5

Volume of air taken .....	333.7
After 5 potash .....	333.7

Volume of air taken .....	327.9
After 5 potash, up 15 minutes .....	327.5

Volume of air taken .....	140.7
After 8 potash, up all night .....	140.0

Volume of air taken .....	191.2
After 5 potash, up 5 minutes .....	190.9
Do. 10 minutes .....	190.8
Do. do. ....	190.8
Do. do. ....	190.7

Volume of air taken .....	169.9
After 5 potash, up 10 minutes .....	169.6
Do. do. ....	169.6

The introduction of five of potash into a gas containing no carbonic acid causes a slight diminution of tension. By means of the syringe, a bubble of water is easily introduced into the gas, after the removal of the potash; but unless comparatively large quantities of water are used, which of course would be inadmissible, the original tension of the gas is not generally restored.

Volume of air taken .....	204·7
After 5 potash, up 10 minutes .....	204·5
" 5 water, up 10 minutes .....	204·5
" 5 water, up all night .....	204·45
" 5 potash, up 10 minutes .....	204·4
" 5 strong potash, up 10 minutes .....	204·1
" 5 water .....	204·45

The strong potash consisted of 2 parts of a saturated solution of caustic potash 1 part of water.

Volume of air taken .....	318·4
After 3 potash, up 15 minutes, tube lowered 3 times .....	318·0
After 4 water, up 10 minutes, tube lowered 2 times .....	318·3
After 3 potash, up 10 minutes, tube lowered 3 times .....	318·0
After 3 water, up 10 minutes, tube lowered 3 times .....	318·3
After 3 potash, up 10 minutes, tube lowered 3 times .....	318·0
Volume of air taken .....	315·2
After 6 potash, up 15 minutes .....	314·8
" 5 " 10 minutes .....	314·8
" 5 " all night .....	314·6
" 5 water up .....	314·7
" " .....	314·8
Volume of air taken .....	121·9
After 6 potash, up all night .....	121·4
" water up .....	121·6

These experiments, and many others which have been made, show that, under certain circumstances, a very appreciable error may be made by the potash altering the tension of the aqueous vapour. It appears, however, that when a considerable quantity of carbonic acid is present, some twenty or more millimetres of that gas, this diminution of tension does not take place, as is seen in some of the analyses already quoted, and, in some

cases, with even a much less quantity of carbonic acid, it does not take place.

This source of error is, however, easily avoided by using a much weaker solution of potash; one made by diluting 1 pt. of a saturated solution of potash with 5 pts. of water answers very well. In the following experiments a solution of this degree of dilution is termed "weak potash." If 5 pts. of this solution are introduced into a moist gas, even entirely free from carbonic acid, it will produce no appreciable alteration in the tension of the aqueous vapour, as shown by the following experiments:—

Volume of air taken .....	321·6
After 5 weak potash, up 15 minutes .....	321·6
Volume of air taken .....	338·1
After 5 weak potash, up 45 minutes .....	337·95
Volume of air taken .....	281·1
After 5 weak potash, up 15 minutes .....	281·1

In the following experiments carbonic acid was present.

Volume of air taken .....	188·6
After adding carbonic acid.....	190·0
„ 2 weak potash, up 20 minutes.....	188·5
Volume of air taken .....	243·6
Do. after adding carbonic acid .....	313·4
After 5 potash, up 2 hours.....	244·9
„ 3 weak potash, up 10 minutes.....	243·5
„ adding carbonic acid.....	255·3
„ 5 potash, up 30 minutes .....	243·5
Volume of air taken .....	339·4
After adding carbonic acid.....	340·3
„ 5 weak potash, up 15 minutes.....	339·4

The absorption of carbonic acid by this process is then perfectly simple and accurate; the only precaution to be taken is when only testing for the presence of the gas, or absorbing very small quantities to use a dilute solution, in other cases it is

better to use a stronger one. The 5 of potash used in most of the foregoing experiments would absorb about 80 millimetres of carbonic acid, measured in a eudiometer about  $\frac{1}{8}$ th inch in diameter, and under a pressure of about 8 inches less than the ordinary barometric pressure. The weak potash contains only half the amount of potash which the stronger does. In some cases it is convenient to use even a still stronger solution—one containing 2 pts. of saturated potash to one of water.

In all the absorptions of carbonic acid, after introducing the caustic potash, the eudiometer was lowered so as to wet with the solution a considerable portion of the tube, and thus expose a large surface of the solution to the gas. This raising and lowering of the tube should be repeated; the absorption then takes place very rapidly. The time required to absorb the whole of the carbonic acid depends on the absolute and relative amount of the gas present, and on the amount of potash solution used. Generally about ten minutes is ample time. A rapid observation of the height of the mercury in the eudiometer with the telescope will show whether any further absorption is taking place.

In the experiments, when a diminution of tension was produced by introducing potash into moist air, a few drops of water were of course, as in other cases, first placed at the closed end of the eudiometer; it was then filled with mercury, and the air introduced, the upper part of the tube thus becoming moistened all over, and covered with visible drops of water; in raising and lowering the tube, the potash did not come within three or four inches of the top of the eudiometer, so that, although the tension of the aqueous vapour diminished, there was still an abundance of water in the top of the tube, so much as to be perfectly visible to the naked eye. It appears then that in the upper part of the tube the original full tension of the aqueous vapour must have continued; but below, where some of the potash would be still sticking to the sides of the tube, a diminution of tension was produced. A continual evaporating of the water at the top and diluting of the potash below is going on, but is not sufficient in amount and rapidity to restore the original tension.

Volume of air taken .....	330·7
After 5 potash, up 10 minutes .....	380·2



When this reading was made, the upper part of the eudiometer in fact nearly 5 inches from the top, was covered with small drops of water. The eudiometer was allowed to stand for 50 hours, and the bulk of gas then read off it, was 330.3.

The top of the tube now looked perfectly dry.\*

*Absorption of Oxygen.*—This gas is absorbed by first putting up into the eudiometer some potash, and then, with another syringe, adding a little of a strong solution of pyrogallic acid to it. The quantities must of course depend on the amount of oxygen present. To test the process some air was taken which, containing so large an amount of oxygen, would show any defects in the process. The following are the results obtained, the quantities of the reagents used, and the time they were allowed to act:—

		Corrected vol.
Volume of air taken .....	130.3	132.15
4 potash and 3 pyrogallic acid solution, left up half hour ....	103.5	104.46
2 potash and 2 pyrogallic acid solution, left up half hour ....	103.5	
Oxygen .....	20.953 per cent.	
Volume of air taken .....	129.0	130.80
4 potash and 3 pyrogallic acid solution, left up 20 minutes ..	103.3	104.26
3 potash and 2 pyrogallic acid solution, left up 15 minutes ..	102.6	103.53
Oxygen .....	20.848 per cent.	
Volume of air taken .....	135.4	137.44

\* The following experiment may also be cited as illustrating in a different way the absorption of aqueous vapour. Three portions of calcic chloride, of about 10 grms. each, were taken; one portion placed in a watch-glass, another at the bottom of a glass cylinder,  $4\frac{1}{2}$ -in. high and  $1\frac{1}{2}$ -in. in diameter, and the third at the bottom of a cylinder,  $8\frac{1}{2}$ -in. high and  $1\frac{1}{2}$ -in. in diameter; all these glasses were placed close together on a shelf and left uncovered. On the next day the calcic chloride in the watch-glass was liquid; on the thirteenth day that in the shorter cylinder was liquid, but it was not till the twenty-first day that the chloride in the tallest cylinder was liquid.

		Corrected vol.
4 potash and 3 pyrogallic acid		
solution, left up half hour . . . .	107·7	108·79
Oxygen . . . . .	20·845	per cent.

*Absorption of Olefiant Gas.*—This gas is absorbed in the ordinary way, with fuming sulphuric acid; the only question was whether the acid should be introduced by means of a syringe, or by a coke ball. The latter process is perhaps the best. The coke ball is fastened on a platinum wire, and with the guide tube is very easily introduced into the eudiometer. The same ball may be used a great number of times. After the ball has absorbed all the olefiant gas (it will generally take from half-an-hour to an hour to do this), a little water is introduced into the tube, this withdrawn, and then some dilute potash.

The following are some instances of the absorption of carbonic acid and olefiant gas in coal gas; the specimens operated on were from the same works, but not collected at the same time:—

		Corrected vol.
Volume of gas taken . . . . .	217·8	229·11
After 5 weak potash . . . . .	214·7	225·82
After coke ball and absorption of acid fumes . . . . .	202·8	213·21
CO <sub>2</sub> . . . .	1·950	p. c.
C <sub>n</sub> H <sub>2m</sub> ..	5·504	„
Volume of gas taken . . . . .	214·2	225·29
After 5 weak potash . . . . .	211·0	221·90
After coke ball and absorption of acid fumes . . . . .	200·0	210·25
CO <sub>2</sub> . . . .	1·505	p. c.
C <sub>n</sub> H <sub>2m</sub> ..	5·171	„

In the following analysis no coke ball was used, the acid being introduced by means of a syringe. The carbonic acid and acid fumes were absorbed at one operation.

		Corrected vol.
Volume of gas taken . . . . .	166·4	174·79

		Corrected vol.
4 fuming acid up, afterwards phosphate of soda, and then potash	155·4	163·34
CO <sub>2</sub> and C <sub>2</sub> H <sub>2m</sub>	6·551 p. c.	

The following is a complete analysis of a specimen of coal gas:—

Volume of gas taken .....	229·11
After 5 weak potash.....	225·82
„ coke ball .....	213·21
„ 4 potash and 2 pyrogallic acid	202·5
Volume of combustible gases taken	51·82
After adding oxygen .....	171·04
„ explosion .....	85·38
„ potash .....	60·08
„ adding hydrogen.....	411·40
„ explosion .....	249·47

This gives the following percentage composition for the gas:—

Carbonic acid.....	1·950
Olefiant gas, &c.....	5·504
Oxygen .....	0·139
Hydrogen .....	45·847
Light carburetted hydrogen .....	40·948
Carbonic oxide .....	4·167
Nitrogen.....	1·445
	<hr/>
	100·000

### XVI.—On Chloranil. No. I.

By JOHN STENHOUSE, LL.D., F.R.S., &c

#### *Preparation of Chloranil.*

THE best process for the preparation of chloranil hitherto published is that of Dr. Hofmann,\* which consists in digesting

\* *Ann. Pharm.* liii, 55.

a boiling saturated aqueous solution of phenol, with a mixture of chlorate of potassium and hydrochloric acid.

When chlorate of potassium and phenol are dissolved in hot water, and a sufficient quantity of hydrochloric acid is added, the solution becomes dark-coloured and turbid, and after the lapse of a few minutes, a strong reaction sets in, with evolution of pungent vapours and separation of yellow crystalline scales, which are, however, contaminated with a considerable quantity of a dark red oil. This mass, when cold, is freed as much as possible from water, and extracted with hot spirit to get rid of the red oil. The pale yellow crystalline scales thus obtained consist of terchlorquinone, mixed with from 20—50 per cent. of chloranil. By repeated treatment with boiling spirit, the terchlorquinone, as it is rather soluble in that menstruum, may be removed and the chloranil obtained in a state of tolerable purity. The terchlorquinone thus extracted contains chloranil, and although I have operated upon very large quantities, I have never been able to obtain it free from adhering traces of the latter substance, either by sublimation, or by crystallisation from spirit or benzol; but as will presently be seen, I have been able to obtain it pure indirectly.

After making numerous experiments to determine the most advantageous proportions for preparing chloranil according to the above method, the following was found to be the best process:—3 parts chlorate of potassium were dissolved in 70 parts boiling water, and 1 part phenol added. This mixture, when poured into an earthenware vessel capable of containing about twice the volume of the liquid, had a temperature of 90° C.; 14 parts hydrochloric acid of sp. gr. 1.16 were then added at once, and the whole was well agitated. In a few minutes the clear, brownish-red liquid became opaque and very hot, chlorine and a pungent vapour of very disagreeable and persistent odour were given off with violent effervescence, and chloranil was deposited in yellow scales, contaminated with the before-mentioned red oil.

On extracting this with a large quantity of boiling spirit, chloranil is left undissolved, but even when a great excess of chlorate of potassium and hydrochloric acid was used, I never succeeded in obtaining more than 40 parts of chloranil from 100 of phenol. It seemed to me, however, that the terchlorquinone and chlorinated oil, holding as they do an intermediate

position between phenol and chloranil, might be converted into the latter by proper treatment; and finding from a preliminary experiment that chloride of iodine rapidly converted both of them into chloranil, I resolved to utilize this reaction for the preparation of that substance.

The above-mentioned mixture of crude chloranil, tetrachloroquinone and red oil, obtained from phenol by chlorate of potassium and hydrochloric acid, after standing from 12—24 hours, was collected on a cloth filter, freed as much as possible from water by pressure, and introduced into a flask with an equal weight of water and about half its weight of iodine. This flask was furnished with two tubes, one serving as a condenser, and the other for passing a current of chlorine into the mixture, whilst heat was applied by means of a paraffin bath. The current of chlorine, which was at first very rapidly absorbed, was so adjusted that there was always a slight excess of iodine. This was readily ascertained by the violet colour of the vapour in the flask. After 10 or 12 hours, when the absorption of chlorine became very slow, the digestion was stopped, a bent tube fitted to the flask in place of the condenser, and the chloride of iodine solution distilled off as far as possible, a gentle current of chlorine being passed through the apparatus during the latter part of the operation. When cold, the residue was boiled up with water, and the yellow scales, which were now almost free from oily matter, well washed with cold water, pressed, and extracted several times with small quantities of spirit. It now presented the appearance of brownish-yellow scales, and was tolerably pure chloranil, considerably more than equal in weight (1.25) to the phenol originally employed.

Attempts were also made to convert both the red oil and tetrachloroquinone into chloranil, by treating them with chlorate of potassium and hydrochloric acid, also by digestion with pentachloride of antimony and sesquichloride of iron in a current of chlorine, but these methods gave very unsatisfactory results, as did also passing chlorine through the solution of the substances in tetrachloride of carbon, either with water or without.

In order to purify the chloranil obtained by the above method, one part of it was dissolved in 20 parts of hot benzol, filtered, and the excess of benzol distilled off, until scales began to deposit in the hot solution; the distillation was then discontinued, and when cold, the chloranil was collected on a cloth

and strongly pressed. One or two crystallisations thus rendered it perfectly pure. It is necessary that the benzol should be purified by sulphuric acid,\* as otherwise the chloranil becomes contaminated with a large quantity of black resinous substance. This is a better method of treating the chloranil than crystallisation from boiling alcohol, as it is but slightly soluble in that liquid.

*Analyses of Chloranil.*

- I. .245 grm. substance gave .571 grm. argentic chloride.  
 II. .294 grm. substance gave .686 grm. argentic chloride.

			I.	II.
C <sub>6</sub>	= 72	29.26	—	—
Cl <sub>4</sub>	= 142	57.73	57.65	57.73
O <sub>2</sub>	= 32	13.01	—	—
	246	100.00		

I. was obtained by the action of chloride of iodine on the dark red oil, and II. from terchlorquinone containing traces of chloranil, by the same method.

When phenol previously combined with sulphuric acid (equal measures), was dissolved in a large quantity of hot water, and submitted to the action of chlorate of potassium and hydrochloric acid, no red oil was formed, but the amount of chloranil and terchlorquinone was less than that obtained by acting on a solution of pure phenol in water.

*Preparation of Chloranil from Picric Acid.*

On dissolving equal parts of picric acid and chlorate of potassium in 30 parts boiling water, a considerable quantity of the difficultly soluble picrate of potassium was formed, and the addition of hydrochloric acid (7 parts) caused a violent reaction; chloropicrin distilled over, and chloranil remained in the retort, equal to about one-twelfth the weight of the picric acid originally employed, being only 12 per cent. of the theoretical

\* Proc. Roy. Soc. xiv, 351.

quantity. This, therefore, is not by any means an advantageous process. Chloranil is but slightly soluble in bisulphide of carbon, tetrachloride of carbon, ether, chloroform, or petroleum oil.

### *Chlorhydranil.*

Städeler, in 1849,\* prepared chlorhydranil by digesting chloranil with boiling aqueous sulphurous acid until it exhibited no further change of colour. He believed that chlorhydranil was the only product formed by this reaction. This however was a mistake, as I found, on carefully repeating his process, that 100 parts chloranil gave only 70 chlorhydranil, instead of 101, and that the crude chlorhydranil thus obtained had a brown colour which is very difficult to remove. A much better method, which gave the theoretical quantity of colourless chlorhydranil at one operation, consisted in digesting finely powdered pure chloranil, with moderately strong hydriodic acid, and about one-tenth its weight of ordinary phosphorus for 30—40 minutes, washing well with cold water, and crystallising from boiling alcohol (5 parts). The product thus obtained was quite colourless, and of a high lustre. It was however contaminated with traces of phosphorus, which soon became oxidised on exposure to the air, and the resulting phosphorous acid was removed by washing with cold water. This impurity can also be got rid of by boiling with aqueous cupric sulphate and recrystallising. The substitution of amorphous for ordinary phosphorus in the above process, is not advisable, as the crystals are then slightly coloured.

Chlorhydranil,  $C_6Cl_4O_2H_2$ , is almost insoluble in bisulphide of carbon, tetrachloride of carbon, and benzol, but very soluble in ether. It dissolves in carbonate of sodium solution with a beautiful green colour, which rapidly changes into brown, and at the same time a few green needles are deposited. By heating with strong nitric acid, or better still, a mixture of nitric and sulphuric acids, it is easily reconverted into chloranil. This method may be employed for the purification of crude chloranil, instead of crystallisation from benzol.

\* Ann. Ch. Pharm. lxi, 327.

*Action of Sulphurous Acid on Chloranil. Terchlorhydroquinone.*

Although chlorhydranil was the principal product obtained by passing a current of sulphurous acid through boiling water holding chloranil in suspension, yet as I have mentioned above, about 30 per cent. of it was converted into other compounds, which remained in the aqueous solution, contaminated with sulphuric and hydrochloric acids.

This solution was neutralized with carbonate of lead (previously made into a cream with water), and filtered. The sulphuric acid was thus removed as sulphate of lead, whilst plumbic chloride remained in solution together with an organic lead salt. The lead was precipitated from this solution by sulphuretted hydrogen, the clear liquor evaporated to dryness on the water-bath, and the residue, consisting of an organic acid, submitted to sublimation, which was best effected by placing it in a covered beaker heated by means of a paraffin bath to 120°—130° C., white lustrous crystals were thus obtained. These were purified from adhering hydrochloric acid by one or two resublimations, or by recrystallising from bisulphide of carbon, and then subliming them. The residue in the subliming vessel contained free sulphuric acid. The crystals are moderately soluble in hot water, alcohol, bisulphide, and tetrachloride of carbon, and very soluble in ether. When subjected to analysis they gave the following results:—

I. .229 grm. substance gave .282 grm. carbonic acid, and .030 grm. water.

II. .276 grm. substance gave .341 grm. carbonic acid, and .036 grm. water.

III. .180 grm. substance gave .362 grm. argentic chloride.

			I.	II.	III.
C <sub>6</sub>	= 72	33.72	33.59 p.c.	33.70 p.c.	—
Cl <sub>2</sub>	= 106.5	49.89	—	—	49.75 p.c.
H <sub>2</sub>	= 3	1.41	1.45	1.45	—
O <sub>2</sub>	= 32	14.98	—	—	—
	<hr/>	<hr/>			
	213.5	100.00			

It will be seen from these results that the crystalline subli-



mate had the composition of terchlorhydroquinone  $C_6Cl_3H_3O_2$ . Its properties also agreed with those ascribed to that substance by Städeler.\*

On adding nitrate of silver to a warm solution of the crystals, a white precipitate was produced containing 50 per cent. of silver. It appears however to be a mixture of a silver compound with terchlorquinone.

Nitric acid acted strongly on terchlorhydroquinone, red fumes were evolved, chloropicrin distilled over, and the solution on cooling deposited yellow crystals, a further quantity being obtained on the addition of water. They were well washed with cold water and crystallised from alcohol. As might be expected, the analysis of the substance proved it to be terchlorquinone  $C_6Cl_3HO_2$ .

I. .281 grm. substance gave .349 grm. carbonic acid, and .014 grm. water.

			I.
$C_6$	=	72	33.88 p.c.
$Cl_3$	=	106.5	—
H	=	1	.55
$O_2$	=	32	—
		<hr style="width: 50px; margin: 0 auto;"/>	
		211.5	100.00

The removal of chlorine from chloranil by sulphurous acid, and formation of terchlorquinone from the resulting products is very interesting, as it will probably afford a method of obtaining bichlorquinone and chlorquinone, in a state of absolute purity, which Städeler was unable to effect by the means he employed, viz., fractional crystallisation.

The substance from which the terchlorhydroquinone was obtained by sublimation seems to be a conjugate acid, but hitherto I have not been able to obtain either it, or any of its salts in a state sufficiently pure for analysis. It is exceedingly soluble in water, alcohol, and ether, and crystallises from the latter in large prisms.

#### *Terchlorquinone.*

Although, as I have already stated, I was unable to obtain terchlorquinone free from chloranil, either by crystallisation or

\* Ann. Ch. Pharm. lxi, 322.

sublimation, yet, as I found that their hydrogen compounds admit of being readily separated, it offered a method of obtaining large quantities of terchlorquinone in a pure state. This is the more important, as Städeler, who discovered this body, did not get it in sufficient quantity for analysis.

The crude mass obtained in the preparation of chloranil by the process described in the first part of this paper, was treated three or four times with small quantities of boiling alcohol to remove the red oil, and then extracted with a considerable quantity (six times its weight) of the same solvent, filtering whilst hot. On cooling, the impure terchlorquinone which crystallised out was collected, and the mother-liquor again boiled up with the undissolved portion left on the filter. By this means the original mixture was separated into three portions—

I. The red oil which could be converted into chloranil by treatment with chloride of iodine solution.

II. The portion almost insoluble in spirit, consisting of nearly pure chloranil; and

III. The crude terchlorquinone, still retaining, however, a considerable quantity of chloranil.

In order to effect the separation of these two substances, this portion (III) was added by small quantities at a time to moderately strong boiling hydriodic acid, containing a few pieces of phosphorus. The chloranil and terchlorquinone were thus converted into chlorhydranil and terchlorhydroquinone, which sank to the bottom as an oil, and on cooling, a large quantity more of the terchlorhydroquinone crystallised out. This was then collected, washed slightly with cold water, boiled with spirit, and filtered from the undissolved phosphorus. The solution after evaporation to dryness at a gentle heat, was exposed to the air until the phosphorus it contained had oxidised.

The white crystalline mass was then powdered and submitted to sublimation in a glass vessel heated to  $120^{\circ}$ — $130^{\circ}$  in a paraffin bath. The terchlorhydroquinone sublimed in brilliant plates, leaving behind the chlorhydranil, which is not volatile at that temperature. After one or two crystallisations from hot water (10 parts), it was found to be perfectly pure, as may be seen from the results of the subjoined analysis:—

I. .326 grm. substance gave .404 grm. carbonic acid and .050 grm. water.

			I.
$C_6$	= 72	33·72	33·81 p.c.
$Cl_3$	= 106·5	49·89	—
$H_3$	= 3·4	1·41	1·70
$O_2$	= 32	14·89	—
	<hr/>	<hr/>	
	213·5	100·00	

Sometimes the aqueous solution did not crystallise out for days, but the addition of a few crystals, or immersing the beaker in a freezing mixture caused it to solidify to a mass of fine needles. It requires 160 parts of water at 15° C. to dissolve it.

As terchlorquinone when digested with strong nitric acid was slowly decomposed, with formation of chloropicrin and evolution of carbonic anhydride and nitrous fumes, I found it advisable to effect the conversion of terchlorhydroquinone into terchlorquinone by dissolving it in hot water strongly acidulated with sulphuric acid, and then adding a solution of acid chromate of potassium, when the terchlorquinone was precipitated in the crystalline state.

#### *Terchlorbromquinone.*

When terchlorquinone and bromine were digested together for some hours in a sealed tube at 120°—130° C., on opening the tube a considerable quantity of hydrobromic acid escaped, and the residue, after being washed with water, was found to be very slightly soluble in hot alcohol, from which it crystallised in yellow plates resembling chloranil. It contained bromine and when dried at 100° and analysed it proved to be terchlorbromquinone,  $C_6Cl_3BrO_2$ .

·350 grms. substance gave ·317 grm. carbonic anhydride, and ·004 grms. water.

This corresponds to 24·71 per cent. carbon, whilst the formula  $C_6Cl_3BrO_2$  requires 24·78 per cent.

#### *Terchlorbromhydroquinone, $C_6Cl_3BrO_2H_2$ .*

When the terchlorbromquinone was digested with hydriodic acid and phosphorus, as in the preparation of chlorhydranil from chloranil, terchlorbromhydroquinone was formed. It was

very soluble in alcohol, from which it crystallised in long prisms and was readily reconverted into terchlorobromquinone by boiling with nitric acid.

The analyses in this paper were made for me by my assistant Mr. Charles E. Groves.

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XVII.—*Action of Nitric Acid on Picramic Acid.*

By JOHN STENHOUSE, LL.D., F.R.S., &c.

FROM the conflicting statements that have been published regarding the products of the action of nitric acid on picramic acid, I was led to examine into the nature of this reaction. Girard and Pugh\* state that when picramic acid is treated with strong nitric acid it is converted into picric acid. Wöhler and Carey Lea,† on the contrary, state that picramic acid is not converted into picric acid by the action of nitric acid.

Three parts by weight of boiling nitric acid, sp. gr. 1·45, were poured on one part of picramic acid, which it readily dissolved, and after a few minutes a violent reaction ensued, and nitrous fumes were evolved with almost explosive violence. When the action had somewhat moderated, heat was applied to the mixture, and after continuing the digestion for about ten minutes the liquid was allowed to cool. This, on standing some time, deposited a crystalline substance in such large quantity that it became semi-solid.

The crystals were drained from the acid mother-liquor on a funnel, plugged with gun-cotton, dried on a porous tile, and after being crystallised two or three times from spirit were analysed, with the following results.

I. ·228 grm. substance gave ·286 grm. carbonic acid and ·028 grm. water.

II. ·416 grm. substance gave ·524 grm. carbonic acid and ·049 grm. water.

\* Girard, *Compt. Rend.*, 86, 421; Pugh, *Ann.*, *Ch. Pharm.* 96, 83.

† Wöhler, *Pogg. Ann.*, 13, 488; Carey Lea, *Sill. Am. J.* [2], 26, 279.

		Theory.	I.	II.	Mean.
C <sub>6</sub>	= 72	34.28	34.22	34.36	34.29
H <sub>2</sub>	= 2	0.95	1.36	1.31	1.33
N <sub>4</sub>	= 56	26.67	—	—	—
O <sub>5</sub>	= 80	38.10	—	—	—
	<hr/>	<hr/>			
	210	100.00			

From the analysis it will be seen that the crystalline compound above-mentioned is identical in composition with the *diazodinitrophenol* C<sub>6</sub>H<sub>2</sub>N<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>O of Griess,\* with which its physical properties also correspond.

The mother-liquors from which the *diazodinitrophenol* had separated after concentration, yielded crystals, which, when purified by repeated crystallisation from water, were found to have the composition and all the physical properties of picric acid. Subjoined is the analysis:—

I. .478 grm. crystals gave .556 grm. carbonic acid and .074 grm. water.

II. .388 grm. crystals gave .453 grm. carbonic acid and .056 grm. water.

		Theory.	I.	II.	Mean.
C <sub>5</sub>	= 72	31.44	31.74	31.85	31.80
H <sub>3</sub>	= 3	1.31	1.72	1.61	1.66
N <sub>3</sub>	= 42	18.34	—	—	—
O <sub>7</sub>	= 112	48.91	—	—	—
	<hr/>	<hr/>			
	229	100.00			

The silver salt was also prepared by neutralising the acid with argentic carbonate and recrystallising. On analysis .775 grm. of the salt gave .330 grm. of argentic chloride = 32.05 per cent. of silver. Theory C<sub>6</sub>H<sub>2</sub>Ag(NO<sub>2</sub>)<sub>3</sub>O requires 32.15 per cent.

In most of the experiments which I made much *diazodinitrophenol* was produced, and comparatively little picric acid. In one instance, however, this result was entirely reversed; scarcely any nitrous fumes were given off, and picric acid was the chief product. The effect of the action of nitric acid on picramic acid is therefore the production of *diazodinitrophenol* and picric acid in variable proportions, probably dependent on temperature and the strength of the nitric acid employed, a circumstance which readily explains the discordant results of previous experimenters.

\* Griess, Ann. Ch. Pharm., 113, 205.

XVIII.—*Note on Frankland and Armstrong's Memoir on the Analysis of Potable Waters.*

By J. ALFRED WANKLYN, E. T. CHAPMAN, and MILES H. SMITH.

IN the memoir lately published\* by Frankland and Armstrong describing the method by which they propose to conduct the examination of waters as regards organic substance, objections are raised to the method we have recommended for determining the relative quality of water by means of the albuminoid ammonia it yields by treatment with alkaline solution of permanganate of potash. Those objections are, to a great extent, based upon a comparison of the results obtained in this way with the results obtained by Frankland and Armstrong's method. We have, therefore, made a careful inquiry into the conditions to which the difference between the results furnished by the two methods may be referred, and into the accuracy of Frankland and Armstrong's method to be applied as a test of the results furnished by our method.

In placing before the Society the conclusions at which we have arrived, we must, in the first place, premise,† as before stated, that we do not consider the complete conversion of organic nitrogen into ammonia by our method as being essential to its applicability for determining the relative quality of water, and that we rely simply upon the constancy of the ratio between the amount of albuminoid substance in the water and the quantity of ammonia produced.

The next point which we have to consider is the degree of accuracy attainable in estimating the carbon and nitrogen in the water-residue according to Frankland and Armstrong's method. In order to enable a judgment to be formed on this point, the authors gave ten examples, in which known weights of known substances were dissolved in distilled water with some carbonate of soda, or carbonate of lime, and the residues obtained, after treatment with  $\text{SO}_2$  and evaporation, were burnt with chromate of lead. In the following tables we give

\* Chem. Soc. Journal (March, 1868.)

† Chem. Soc. Journal (December, 1867.)

the amounts of carbon taken, and the amounts obtained, also the amounts of nitrogen taken and obtained, and the errors applying to each experiment:—

	Substance taken.	Carbon taken.	Error.	Carbon obtained.
	milligram.	milligram.	milligram.	milligram.
I..	35·2 Sugar	14·82	— 0·19	14·63
II..	34·7 „	14·60	— 0·74	13·86
III..	11·4 „	4·80	— 0·40	4·40
IV..	12·2 „	5·14	+ 0·16	5·30
V..	11·5 „	4·84	— 0·50	4·34
VI..	10· Urea	2·00	— 0·23	1·77
VII..	10·25 „	2·05	+ 0·06	2·11
VIII..	10·4 „	2·08	+ 0·31	2·39
IX..	20·2 „	4·04	+ 0·48	4·52
X..	25· Hippuric acid	15·08	— 1·22	13·86

	Nitrogen taken.	Error.	Nitrogen obtained.
	Milligramme.		Milligramme.
V.....	2·46	+ 0·08	2·54
VI.....	4·66	— 0·03	4·63
VII.....	4·78	— 1·21	3·57
VIII.....	4·84	— 0·16	4·68
IX.....	9·42	— 0·55	8·87
X.....	1·95	+ 0·08	2·03

From these tables it will be seen that there is a deficit of carbon in six out of the ten determinations, and an excess in four of them. The greatest error in deficit is 1·22 milligram.; the least error in deficit is 0·19 milligram.; the mean error on the six determinations being 0·49 milligrams. In ordinary organic analyses, wherein 200 or 300 milligrams of a substance such as sugar is taken, it is possible to obtain results which are accurate to within about one-tenth per cent., equal to an absolute error of 0·2 milligram. of carbon. When smaller quantities of substance are analysed in the ordinary way, it is admitted that the degree of *percentage accuracy* attainable is inferior.

The quantities of organic substance to which the results given by Frankland and Armstrong refer are from 10 to 35 milligrams., being about one-tenth as much as would be operated

upon in an ordinary organic analysis. But the absolute error, as shown in the tables above, is from 0.2 to 1.2 milligram of carbon, so that while operating on smaller quantities there is no corresponding reduction of *absolute* error, and consequently Frankland and Armstrong's method, as exhibited by their own experiments, does not attain to a higher degree of accuracy than would be reached by ordinary organic analysis applied to very small quantities of organic substance.

The importance of this circumstance as regards the estimation of organic substance in a water will be appreciated when it is considered that the quantity of organic substance in a litre of water is seldom anything like so much as the quantities of sugar, &c., operated upon in the experiments given as indicative of the degree of accuracy attainable by Frankland and Armstrong's method.

From the results obtained for nitrogen it will be seen that out of the six experiments the results of four are in deficit, and those of two are in excess. These results apply to quantities of nitrogenous substance fully ten-fold as large as those likely to be present in a litre of ordinary water. It, therefore, appears to us that taking these data as representing the extent to which this method can be depended on for the determination of the minute quantities of carbon and nitrogen in a water-residue, it does not estimate quantities of nitrogen which fall short of half a milligramme. Now, on turning to the table of analyses at the end of the memoir,\* it will be seen that the quantity of organic nitrogen per litre (and a litre is the quantity of water upon which the determinations were made) is represented as ranging from 0.00 through all varieties of intermediate value to 0.56 milligram. These quantities of nitrogen are, however, within the limits of error indicated by the experiments above referred to; consequently, we cannot regard these results as representing differences of quality in the different kinds of water.

Having thus considered what are the capabilities of the method proposed by Frankland and Armstrong we will now proceed to discuss the comparison which they institute between the results furnished by our method and those obtained by their own. In the first place it will be seen that the differences

\* Chem. Soc. Journal, March, 1868, p. 108.



between the results of the two methods observed by Frankland and Armstrong, range from + 0.05 to - 0.52 of a milligramme, amounts which, as we have already shown, lie within the limits of experimental error.

From these differences, therefore, no conclusion of any kind can be drawn, and we consider it to be sufficiently evident that Frankland and Armstrong's method is incapable of testing the accuracy of the results obtained by our method as stated below.

	Milligramme per litre.	
	Albuminoid NH <sub>3</sub> , Wanklyn, Chapman, and Smith.	Organic Nitrogen. Frankland and Armstrong.
Bala Lake water .....	0.25	0.01
Loch Katrine water .....	0.13	0.08
Manchester water .....	0.07	0.26
Thames water as delivered in London by the different com- panies at different dates .....	0.06 0.15 0.12 0.14 0.20	0.48 — — — —
New River water ....	0.084 0.09	0.14 —
East London Water Company....	0.09	0.24
Caterham water.....	0.00	0.07

On general grounds we are disposed to consider that the circumstance of Frankland and Armstrong's method being applicable only to the residue obtained by evaporation of a water, is a disadvantage, both as regards the time requisite for making an experiment, and on account of the probability of loss of organic substance. But, in our opinion the preliminary treatment of the water with SO<sub>2</sub> in order to eliminate nitrogen existing as nitrates and nitrites comprises a source of error of a far more serious character. There can be no question as to the complete expulsion of CO<sub>2</sub> by this treatment, and we therefore pass over that part of the subject. But as the nitrogen existing as nitrates in some kinds of water is often much more than ten times as much as the nitrogen existing in organic states of combination, it will be manifest that the estimation of organic nitrogen by Frankland and Armstrong's method,

would become illusory, if only a small portion of the nitrates were to escape decomposition.

On referring to Frankland and Armstrong's paper it will be seen that, the process for the destruction of the nitrates and nitrites is as follows:—"2 litres are poured into a convenient stoppered bottle, and 60 c.c. of a recently prepared saturated solution of sulphurous acid are added." . . . "One half of this sulphurized water is now boiled for two or three minutes, and unless it contained a considerable amount of carbonates, 0.2 gm. of sodic sulphite is to be added during the boiling, so as to secure the saturation of the sulphuric acid formed during the subsequent evaporation." The addition of "a couple of drops" of solution of ferrous or ferric chloride is also recommended, and the water is subsequently to be evaporated to dryness upon a steam or water-bath.

The authors remark further on, that "such an expulsion of the nitrogen of nitrates and nitrites is a remarkable reaction, and could scarcely have been predicted; indeed it takes place to a very partial extent only when a nitrate is dissolved in water, and evaporated with excess of sulphurous acid in imitation of a natural water; neither is the result very different when sodic chloride, or calcic or magnesian carbonate is added."

We agree with the authors in looking upon a total decomposition of a *nitrate* by a few minutes' boiling with a solution of sulphurous acid as remarkable. On the other hand a decomposition of free *nitric acid* by sulphurous acid is what we should be quite prepared to expect.

When it is considered that a litre of many waters contains in solution sufficient free oxygen to generate 0.06 gm. of sulphuric acid by oxidation of the sulphurous acid, it will become obvious that, notwithstanding the addition of the 0.2 gm. of sodic sulphite, which is recommended in the case of those waters containing no considerable amount of carbonates, there will always be great danger of the water becoming strongly acid. The probability of the 30 c.c. of saturated solution of sulphurous acid containing sulphuric acid is also great; there is, moreover, the risk of absorption of oxygen, and consequent formation of sulphuric acid during the standing in the bottle, and during the boiling in the flask.

It is worthy of note, that the addition of the "couple of drops" of solution of ferric chloride, which the authors find

to be so efficacious in rendering the decomposition of the nitrate complete, is equivalent to an addition of so much free acid.

Of the six experiments given by Frankland and Armstrong to illustrate the *complete* decomposition of the nitrates (pp. 96 and 97), the first one, the third and fourth, are instances in which, from the absence of any alkaline or earthy sulphite to take up the sulphuric acid, there must necessarily have been free nitric acid from the very beginning of the reaction. In the second of these experiments, 10 c.c. of a solution of sodic sulphite (strength unknown) were added. In the fifth experiment a natural water was taken, but no mention is made of the amount of carbonate of lime in it. Only the sixth admits of discussion as a possible example of a complete reduction of nitrates without the charging of the water with free sulphuric acid. In this experiment, 0.1 grm. magnesia, 0.1 grm. calcic carbonate, 0.1 grm. sodic chloride, 0.01 grm. potassic chloride, 1 drop of solution of ferric chloride, 2 drops of solution of hydric sodic phosphate, 0.1 grm. potassic nitrate, and 15 c.c. of sulphurous acid solution were taken, and complete destruction of the nitrate was the result.

By calculation, it will be seen that the 10 milligrammes of magnesia and 100 milligrammes of carbonate of lime are equivalent to 122.5 milligrammes of sulphuric acid. Now the oxygen dissolved in the water cannot have been less than would suffice to form about 60 milligrammes of sulphuric acid, whilst 97 milligrammes of sulphuric acid would be set free by the reduction of the 100 milligrammes of nitrate of potash. Thus we should have about 34.5 milligrammes of free sulphuric acid as the final result of the reaction.

It would, therefore, appear that in Frankland and Armstrong's test-experiments, in which there was complete reduction of the nitrates, the circumstances were such as to give rise to free sulphuric acid as a final product.

We have made experiments in which care was taken to avoid the production of this acid as an ultimate product of the reaction, and have never succeeded, under such circumstances, in effecting a *complete* destruction of the nitrates. In some instances, iron and phosphates were present in the *natural waters* experimented upon; but still the destruction of the nitrates was incomplete.

The following experiments may be cited:—Water from a pump in Great Portland Street: 1 litre taken, 30 c.c. of a saturated solution of sulphurous acid was added, and then boiled for two minutes; evaporated on the steam-bath (one or two c.c. of a saturated solution of sulphurous acid being added four times during the evaporation). Result: 14 milligrammes of  $\text{HNO}_3$  were left in the residue. It is to be observed that this water contains both iron and phosphates. The water from a pump in Bartholomew Lane gave a similar result.

To another well-water a quantity of sulphite of protoxide of iron was added before submitting it to the action of sulphurous acid, and yet the residue contained much unreduced nitrates.

In another instance, 100 milligrammes  $\text{HNO}_3$  (in the state of nitrate of potash), 300 milligrammes  $\text{Ca}_2\text{O}\cdot\text{CO}_2$ , 100 milligrammes  $\text{KCl}$ , and about 400 milligrammes of phosphate of lime were put into half a litre of distilled water, boiled with 30 c.c. saturated solution of sulphurous acid, and evaporated to dryness. Result: 55 milligrammes of  $\text{HNO}_3$  left undecomposed in the residue.

On repeating this experiment and substituting sulphite of protoxide of iron for the phosphate of lime, 69.5 milligrammes of  $\text{HNO}_3$  was left undecomposed.

In another experiment half-litre of New River water was taken, saturated with carbonic acid, and then boiled, cooled in an atmosphere of that gas, and again boiled and cooled in carbonic acid; in this way it was insured that the water should be free from dissolved oxygen. 15 c.c. of a saturated solution of sulphurous acid, free from sulphuric acid, was then added, and the whole mixture boiled for 2½ minutes and evaporated to dryness. The residue was found to contain much nitric acid. (These determinations of nitric acid were made by a modification of Schulze's aluminium-process, a description of which has been laid before the Chemical Society.)

From all these experiments two facts are very apparent. First, the operation of destroying the nitrates in water by means of sulphurous acid is a very uncertain one. Secondly, the operation, as practised by Frankland and Armstrong, gives rise to free sulphuric acid in the residue. We need hardly add that few organic substances will bear being heated to  $100^\circ\text{C}$ ., with their own weight of sulphuric acid, without undergoing great decomposition.

We must here call attention to the circumstance that in the experiments made to determine the degree of accuracy attainable by Frankland and Armstrong's method of estimating carbon and nitrogen, no nitrates were added to the water, and as there was in all cases sufficient alkaline or calcareous sulphite to take up any sulphuric acid produced by oxidation of sulphurous acid by the oxygen dissolved in the water, there was no charring of the residue by sulphuric acid. In this very material condition, therefore, the trial experiments differ from those made to prove complete destruction of nitrates, and from operations on natural water.

In the case of water containing large quantities of organic nitrogen, as for example actual sewage in which the amount of nitrogen would be capable of estimation by Frankland and Armstrong's method, we encounter another difficulty, due to the presence of ammonia in the water residue.

In order to arrive at the organic nitrogen, it would then be necessary to make a determination of the free ammonia in the water, and to deduct the nitrogen corresponding to it from the total nitrogen of the residue. Owing, however, to the circumstance that ammonia would be lost by diffusion during the evaporation (even in presence of an acid), the water-residue will contain only a part of the original ammonia, and consequently an error would arise in deducting the amount of nitrogen corresponding to the original ammonia, from the total nitrogen of the residue.

This source of error would, of course, affect to some extent all determinations of organic nitrogen in waters containing free ammonia, but it would become important in the case of such waters as London well water, which often contains a considerable quantity of free ammonia.

We will conclude by giving in a tabular form a number of analyses made by our ammonia-method, showing the extreme constancy of the results. Each of the first five sets of analyses bracketed together was made on the same day, on the same sample of water.

Name of Water.	Quantity operated upon. Litres.	Milligrammes of Albuminoid Ammonia per litre of the water.
West Middlesex water ..	1	0.070
	1	0.065
	1½	0.07
Southwark and Vauxhall..	1	0.20
	1	0.205
	½	0.19
	¼	0.18
	1½	0.21
Well at Wimbledon ..	1	0.15
	½	0.16
Bishopsgate-street pump..	1	0.24
Mixed with equal volume of distilled water ..	½	0.255
	½ (= 1 litre of mixture).	0.26
Thames water above Hampton ..	½	0.21
	1	0.21
	1½	0.205
Manchester water all taken at same date, but from different parts of the town	½	0.06
	½	0.07
	½	0.07
Edinburgh water taken from a tap at the University on 18th and 19th Sept., 1867	1	0.075
	1½	0.063
	1	0.070

London Institution.

XIX.—*On the Action of Oxidizing Agents on Organic Compounds in presence of excess of Alkali.*

By J. ALFRED WANKLYN, Professor of Chemistry in the London Institution, and E. THEOPHRON CHAPMAN.

PART I. *Ammonia evolved by Alkaline Permanganate acting on Organic Nitrogenous Compounds.*

It has been observed that albumin evolves ammonia when submitted to the action of permanganate of potash in strongly alkaline solutions.\* Furthermore, that this ammonia is perfectly constant in quantity, being strictly proportional to the amount of albumin employed, and that it is not the whole, but only a fraction of the total ammonia which the total nitrogen of the albumin is capable of furnishing.†

On extending this enquiry to organic nitrogenous substances in general, we find the action of strongly alkaline permanganate to be perfectly definite, as will be apparent from the results to be given further on.

We shall confine ourselves, in this paper, to a consideration of the ammonia evolved, and in subsequent papers, in continuation of the subject, hope to render account of the residual nitrogen (when there is any) and of the other complementary products of the oxidation.

We will first describe the mode of conducting the experiments.

The ammonia evolved during the reaction was (as in the papers just referred to) measured by means of the Nessler test, and inasmuch as this test is used with very small quantities of ammonia, it was convenient to operate on very small quantities of organic matter.

In order to measure these small quantities with the necessary degree of precision the following plan was usually adopted.

\* Wanklyn, Chapman, and Smith, *Journal of the Chem. Soc.* (1867), vol. v [Ser. 2], 445.

† *Ibid.* Wanklyn (1867), vol. v [Ser. 2], 591.

100 milligrams of the substance to be oxidized were weighed out and dissolved in 100 c.c. of water, thus giving a solution containing one milligram in a cubic centimetre of the solution. By measuring this solution in an accurate burette divided into tenths of a cub. cent., or by weighing out, there was obtained the requisite quantity of the organic substance measured with the requisite degree of accuracy.

The oxidation was usually effected as follows:—Half a litre of freshly distilled water was put into a retort, then 50 c.c. of a solution of potash (equal to 10 grams of solid potash) were added.

Then about 100 c.c. were distilled over and usually found to be ammoniacal. This having been done, the further distillate was generally found to be ammonia-free.

Next some permanganate of potash (from 0·1 to 0·5 grm.) was added, also a few fragments of freshly ignited tobacco pipe (Mr. Duppa's device to avoid bumping and violent boiling).

Then the weighed, or measured liquid containing the substance to be oxidized was put into the retort, and the distillation proceeded with.

The distillation was continued until the evolution of ammonia ceased or became very trifling.

Blank trials having been made with the distilled water and reagents, the following substances were investigated:—

I. *Asparagine*,  $C_4H_8N_2O_3 + H_2O$ .—The sample of asparagine was obtained from Messrs. Hopkin and Williams, and was in beautiful crystals. It was dissolved in water.

	Milligram.
Substance taken	= 3·65
NH <sub>3</sub> obtained	= 0·80
NH <sub>3</sub> per cent.	= 21·92.

II. *Piperine*,  $C_{17}H_{19}NO_3$ .—From Messrs. Hopkin and Williams, was well crystallised. It was dissolved in glacial acetic acid.

	Milligram.
Substance taken	= 4·25
NH <sub>3</sub> obtained	= 0·23
NH <sub>3</sub> per cent.	= 5·41.

III. *Chloride of Diamylamine*,  $(C_5H_{11})_2H_2NCl$ .—Prepared in



the laboratory of the London Institution, analysed, and found to be pure.

	Milligrams.
Substance taken	= 3.91
NH <sub>3</sub> obtained	= 0.31
NH <sub>3</sub> per cent.	= 7.93.

The volatility of the substance rendered it difficult to get complete action, which accounts for the NH<sub>3</sub> being too low.

Diamylamine gives a white precipitate with the Nessler-test.

IV. *Amylamine*, C<sub>5</sub>H<sub>13</sub>N.—Prepared in the laboratory of the London Institution, by the action of iodide of amyl on ammonia. Had a perfectly constant boiling point. Its chloroplatinate and chloride were analysed and found to be pure. It was very carefully freed from ammonia, and gave with Nessler-test a pure white (not a brownish) precipitate.

	I. Milligrams.	II. Milligrams.
Substance taken.....	2.70	1.10
NH <sub>3</sub> obtained.....	0.59	0.24
NH <sub>3</sub> per cent. = 21.8.	NH <sub>3</sub> per cent. = 21.8.	

V. *Diphenyl-tartramide*, C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>.—Presented to us by Mr. Perkin.

	Milligrams.	Milligrams.
Substance taken	= 7.2	19.4
NH <sub>3</sub> obtained	= 0.70	1.98
NH <sub>3</sub> per cent. = 9.72	10.21.	

The foregoing examples are instances of total conversion of the nitrogen of the substance into ammonia, as the following comparison shows:—

	Theory.	Found.
I. Asparagine.....	22.66	21.92
II. Piperine.....	5.96	5.41
III. Diamylamine Chloride	8.79	7.93
IV. Amylamine.....	19.54	21.8
V. Diphenyl-tartramide..	11.33	10.21

The first column of figures contains the calculated quantity of ammonia which 100 parts of the substance could give, if all its nitrogen passed into ammonia. The second column gives the ammonia obtained from 100 parts of substance.

Piperidine, hippuric acid, and narcotine, also give up the total nitrogen in the form of ammonia, on being boiled with strongly alkaline permanganate.

VI. *Morphine*,  $C_{17}H_{19}NO_3$ .—Obtained from Greville Williams, dried at  $100^\circ C$ .

	Milligrams.
Substance taken	= 20
$NH_3$ obtained	= 0.56
$NH_3$ per cent.	= 2.8.

VII. *Codeine*,  $C_{18}H_{21}NO_3H_2O$ .—Splendid crystals from Macfarlane, of Edinburgh.

	Milligrams.
Substance taken	= 6.5
$NH_3$ obtained	= 0.195
$NH_3$ per cent.	= 3.00.

VIII. *Papaverine*,  $C_{20}H_{21}NO_4$ .—From Macfarlane, of Edinburgh. In good crystals.

	Milligrams.
Substance taken	= 10
$NH_3$ obtained	= 0.22
$NH_3$ per cent.	= 2.2

This substance yields up the ammonia with extreme difficulty.

IX. *Strychnine*,  $C_{21}H_{22}N_2O_2$ .—From Messrs. Hopkin and Williams. In very good crystals, carefully dried.

	Milligrams.
Substance taken	= 5.5
$NH_3$ obtained	= 0.30
$NH_3$ per cent.	= 5.45.

X. *Iodide of Methyl-strychnine*,  $C_{21}H_{22}(CH_3)N_2O_2I$ .—From Dr. Crum Brown. Good crystals.

	Milligram.
Substance taken	= 7.2
NH <sub>3</sub> obtained	= 0.24
NH <sub>3</sub> per cent.	= 3.33.

XI. *Brucine*, C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>.—From Messrs. Hopkin and Williams.

	Milligrams.
Substance taken	= 10.
NH <sub>3</sub> obtained	= 0.46
NH <sub>3</sub> per cent.	= 4.6.

XII. *Sulphate of Quinine*, (C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>H<sub>2</sub>SO<sub>4</sub>.—From Messrs. Hopkin and Williams. It was carefully dried.

	Milligrams.
Substance taken	= 10.00
NH <sub>3</sub> obtained	= 0.45
NH <sub>3</sub> per cent.	= 4.5.

XIII. *Sulphate of Cinchonine*, (C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O)<sub>2</sub>H<sub>2</sub>SO<sub>4</sub>.—From Messrs. Bullock. It was recrystallised in the laboratory of the London Institution, and dried at 100° C.

	Milligrams.	Milligrams.
Substance taken	= 10.00	5.00
NH <sub>3</sub> obtained	= 0.57	0.27
NH <sub>3</sub> per cent.	= 5.7.	NH <sub>3</sub> per cent. = 5.4.

These numbers (as will be apparent from the tabular statement a little further on) are somewhat in excess of the theoretical quantity for sulphate of cinchonine.

As is abundantly evident, however, from the researches which have been published on cinchonine, that the formula of this substance is by no means well established. The formula just given yields 4.76 for half of the ammonia. Other formulæ which have been proposed give close on 5.00 for half of the ammonia.

XIV. *Nicotine*, C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>.—From Messrs. Hopkin and Williams.

	Milligrams.
Substance taken	= 1.99
NH <sub>3</sub> obtained	= 0.215
NH <sub>3</sub> per cent.	= 10.80.

Nicotine has no action on the Nessler-test.

XV. *Naphthylamine*,  $C_{10}H_9N$ .—Prepared by ourselves from nitronaphthaline. The hydrochlorate was analysed and found to be pure.

	Milligrams.	Milligrams.
Substance taken =	12·175	4·26
NH <sub>3</sub> obtained =	0·81	0·29
NH <sub>3</sub> per cent. = 6·65.		NH <sub>3</sub> per cent. = 6·81.

Naphthylamine has no action on the Nessler-test.

XVI. *Toluidine*,  $C_7H_9N$ .—A well-crystallised specimen, obtained from the Continent.

	Milligrams.	Milligrams.
Substance taken =	4·08	2·65
NH <sub>3</sub> obtained =	0·36	0·22
NH <sub>3</sub> per cent. = 8·83.		NH <sub>3</sub> per cent. = 8·30.

Toluidine has no action on the Nessler-test.

XVII. *Acetate of Rosaniline*,  $C_{20}H_{19}N_3C_2H_4O_2$ .—Dried at 115° C.

	Milligrams.	Milligrams.
Substance taken =	3·925	4·626
NH <sub>3</sub> obtained =	0·25	0·30
NH <sub>3</sub> per cent. = 6·37.		NH <sub>3</sub> per cent. = 6·49.

In the following table, under theory, there are numbers calculated on the principle that 100 parts of the substance should give up half its nitrogen in the form of ammonia :—

	Theory NH <sub>3</sub> .	Found NH <sub>3</sub> .
VI. Morphine .....	2·98	2·80
VII. Codeine .....	2·67	3·00
VIII. Papaverine .....	2·50	2·20
IX. Strychnine .....	5·09	5·45
X. Iodide of methyl-strychnine ....	3·57	3·33
XI. Brucine .....	4·32	4·60
XII. Sulphate of quinine .....	4·56	4·50
XIII. Sulphate of cinchonine .....	4·76	{ 5·7 5·4
XIV. Nicotine .....	10·49	10·80
XV. Naphthylamine .....	5·95	{ 6·65 6·81

	Theory NH <sub>3</sub> .	Found NH <sub>3</sub> .
XVI. Toluidine ... ..	7.95	{ 8.83 8.30
XVII. Acetate of Rosaniline.....	7.06	{ 6.37 6.49

An instance of the evolution of one-third of the nitrogen in the form of ammonia, is afforded by creatine  $C_4H_9N_3O_2$ . The specimen of creatine taken for the experiments, was kindly given to us by Mr. Greville Williams. It was dried and analysed, giving a correct result.

The mean of three accordant determinations of the ammonia evolved on boiling 100 parts with alkaline permanganate, is 12.6. The theoretical quantity, on the principle of evolution of one-third of the nitrogen as ammonia, is 12.98.

This result becomes intelligible when it is remembered that two-thirds of the nitrogen in creatine are present in the form of *urea*, and that the nitrogen of urea is evolved by alkaline permanganate, either as nitrogen gas or as nitric acid. Sarcosine, the form in which the residual third of the nitrogen is contained, will, we believe, be found to give up all its nitrogen as ammonia.

In theine we have found a substance which gives up one-fourth of the nitrogen as ammonia.

Found, NH<sub>3</sub> from 100 parts

= 8.54

Theory = 8.76 ( $\frac{1}{4}$  of the nitrogen).

The molecule of theine contains four atoms of nitrogen.

Theine,  $C_8H_{10}N_4O_2$ .

Uric acid also gives up a comparatively small fraction of its nitrogen in the form of ammonia.

Apparently, 100 parts of uric acid yield about 7 parts of NH<sub>3</sub>; we shall, however, experiment further on this substance. We subjoin determinations made on substances of which the molecular weight is unknown.

100 parts of gelatin have given 12.7 parts of NH<sub>3</sub>.

\*100 parts of casein gave 7.6 parts of NH<sub>3</sub>.

100 parts of dry albumin give about 10 parts of NH<sub>3</sub>.

\* Of very doubtful purity.

We mention, lastly, an experiment on a substance containing the whole of its nitrogen in the nitro-form, viz., picric acid  $C_6H_2(NO_2)_3HO$ . It gave no ammonia on distillation with alkaline permanganate, but yielded nitric acid, as was proved by subsequently getting abundance of ammonia on reducing the alkaline liquid by means of aluminium.

Before considering the general conclusions to be drawn from the experimental data contained in this paper, we think it useful to give a special description of the method of research which has been followed, and a discussion of some points connected with it.

The extreme minuteness of the quantities of substance subjected to quantitative determination is one of the most striking features of this investigation, and of those investigations more or less connected with it which have been published within the last year. On looking back, it will be seen that the quantity of substance taken for analysis varies from one to twenty milligrams, being generally much nearer the former than the latter limit. In short, it may be said, without greatly exaggerating, that we have substituted milligrams for the grams which are ordinarily experimented on. As will have been observed, we have, accordingly, all throughout the paper, given the weights in milligrams instead of grams.

The first point to be considered is the mode of effecting the requisite division of the substance. In one instance wherein the larger quantities were taken, as, for example, in the instance of diphenyltartramide, the substance was weighed on a bit of platinum foil, and employed in the solid state. In every other case, the substance was employed in solution. As was described at the beginning of the paper, the usual way of proceeding was to weigh out 100 milligrams of substance and dissolve it in 100 cub. cent. of water, or very dilute acid or alkali, according to circumstances. The dilute solution might then, if necessary, be weighed out accurately to a milligram, and so the substance experimented on would be capable of being divided accurately to  $\frac{1}{1000}$  of a milligram.

If ordinary care be taken, no fear need be entertained that the water used for making these dilute solutions will contain sufficient ammonia or other nitrogenous substance to vitiate the experiments. There is no great difficulty in preparing

distilled water of such purity as not to give so much as  $\frac{1}{100}$  milligram of ammonia per litre. But, for making these solutions, it is not requisite to use anything better than ordinarily well distilled water, which, made from the London water, seldom contains more than  $\frac{1}{1000}$  or  $\frac{1}{10000}$  milligram of ammonia per litre.

Thus, taking water of this quality, we will suppose 10 cub. cent. to be employed. There would be then 10 milligrams of substance employed, and an error of  $\frac{1}{10000}$  of a milligram of ammonia introduced by reason of impurity of the water. In short, a little consideration will easily show that there is no reason for apprehending the vitiation of results in consequence of error affecting the division of the substance taken for experiment.

By a proper system of washing the apparatus, carefully cleaning out the Liebig's condenser by distilling water through it immediately before using it for an experiment on the estimation of these minute quantities of ammonia, and by carefully testing all reagents employed, it is quite easy to avoid the introduction of extraneous ammonia, and to obtain perfectly regular results.

It may be well to refer specially to the precautions to be taken in making a delicate testing of the purity of distilled water. The utmost freedom from all traces of ammonia is essential, for instance, in the case of the half-litre of water which is destined to receive the small quantity of substance the ammonia evolved by the oxidation of which is to be estimated. In cases like this, it is not enough that 100 cub. cent. of the water should give no coloration with the Nessler-reagent, but 100 cub. cent. of the first distillate given by one litre of the water should give no reaction with the Nessler-reagent. Precise and detailed directions for the preparation and use of the Nessler-test will be found in the "Laboratory," vol. i., p. 267. To these directions we may add that we find it convenient to have our standard solution of ammonia of such a strength that one cub. cent. contains  $\frac{1}{100}$  milligram of ammonia, and that if, as sometimes happens, the Nessler-reagent should prove wanting in sensitiveness, the addition of a little solution of bichloride of mercury will render it sensitive.

Connected with the indications of the Nessler-test we have observed a point of some interest, which deserves to have

attention directed to it. We have not met with any base except ammonia which gives the peculiar brownish coloration with the Nessler-reagent. Amylamine, diamylamine, and piperidine in very dilute solutions give white opalescence or precipitate when treated with the Nessler-test; naphthylamine, toluidine, and nicotine under these circumstances occasion no reaction of any kind. (Although, however, these volatile bases cause no coloration, yet their presence more or less affects the tint which ammonia gives with the Nessler-test, and they thus to some extent interfere with the sharpness of the estimation of ammonia.)

There is, therefore, every reason for believing that the production of the brownish tint with the Nessler-test is quite characteristic of ammonia. The degree of precision attainable in reading the indications of the Nessler-test is much greater than would be imagined at first sight. The  $\frac{1}{1000}$  of a milligram of  $\text{NH}_3$ , in 100 c.c. of liquid is a quantity very easily seen. The difference between  $\frac{1}{1000}$  and  $\frac{2}{1000}$  of a milligram of  $\text{NH}_3$  will, we think, be visible to most people. With practice a higher degree of precision is attainable. When, instead of using 100 c.c. of water for the Nessler-test, a smaller bulk is taken, the indications become more delicate. So small a quantity as  $\frac{1}{1000}$  of a milligram of ammonia may be seen in a small bulk of liquid.

In short, the Nessler-determination of ammonia is susceptible of the most wonderful delicacy.

On referring to the results given by different substances, as described in this paper, it will be seen that, putting nitro-compounds on one side, organic nitrogenous substances in general evolve ammonia on being heated to  $100^\circ \text{C}$ ., with strongly alkaline solution of permanganates. This reaction is very general, as an inspection of the very varied list of substances contained in this paper is sufficient to show. The compound ammonias of all kinds, the amides of the acids, such substances as piperine, hippuric acid, creatine, the natural alkaloids, albumin, gelatin, and uric acid, evolve ammonia when treated in this way. Even so tough a substance as picoline, which, as is well known, is one of the most stubborn of organic compounds, yields ammonia when subjected to this treatment. Except in the instance of nitro-compounds, urea, and ferrocyanide of potassium, we have not met with any unequivocal instance of failure of an organic nitrogenous substance to evolve ammonia on being heated to  $100^\circ \text{C}$ ., with a strongly alkaline solution of permanganate.



In the matter of the nitro-compounds, there is, be it observed, some degree of resemblance between our process and the Will and Varrentrapp process.

This difference, however, is to be noted. The Will and Varrentrapp process gives irregular results when applied to nitro-compounds, part of the nitrogen of such compounds forming ammonia, and part not forming ammonia. Our process, on the other hand, does not convert *any* nitro-nitrogen into ammonia, but into nitric acid instead, being perfectly regular in its indications with nitro-compounds. It will be understood that, having converted the nitro-nitrogen into nitric acid, we may subsequently reduce that acid to ammonia by means of aluminium, as exemplified in the instance of picric acid above described.

On inquiring into the other peculiarities of structure which prevent alkaline permanganate evolving nitrogen of a given organic compound in the form of ammonia, our attention is arrested by the example of urea, which evolves none of its nitrogen as ammonia when so treated. The reason of this peculiarity is not far to seek, being at once visible in the formula. Urea is in a sense a perfectly oxidized substance, requiring the elements of water to transform it into carbonic acid and ammonia, and if simply oxidized, would exhibit a deficiency of hydrogen—there would be  $\text{CO}_2$ , and only  $4\text{H}$  along with the  $\text{N}_2$ .

As we have seen, compounds formed by the juxta-position of urea with another substance, with elimination of water (as for instance creatine, which, as is well known, is so formed from urea and sarcosine) share this property with urea, and do not give up their ureic nitrogen in the form of ammonia. Possibly uric acid furnishes so small a proportion of its nitrogen as ammonia, owing to the existence of nitrogen in the ureic state. And possibly the non-evolution of part of the nitrogen of albumin is due to the same cause.

On turning to the early part of the paper, it will be seen that whilst amylamine, diamylamine, and piperidine, substances all derived from homologues of marsh gas, undergo total conversion into ammonia, the bases toluidine, naphthylamine, and nicotine, substances which are derived from hydrocarbons lower than the homologues of marsh gas, undergo only a half-conversion into ammonia. This circumstance points to the

conclusion that derivation from a so-called saturated hydrocarbon implies easy conversion of the nitrogen into ammonia, whilst derivation from an unsaturated hydrocarbon interposes difficulties in the way of conversion into ammonia.

The conversion into ammonia of only half the nitrogen of so many of the natural alkaloids is an interesting fact. Some light is thrown upon it by the example of narcotine, which although it gives up all its nitrogen as ammonia, gives it up only slowly, and by dint of putting back the distillate; it doubtless also yields part of its nitrogen as methylamine in the first instance. A careful examination of strychnine has disclosed a somewhat similar state of matters in the case of that alkaloid. Apparently the missing half of the nitrogen in strychnine passes provisionally into the state of some volatile alkaloid. As we said at the commencement, we reserve the treatment of the residual nitrogen for a future occasion.

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XX.—*Note on the Estimation of Nitric Acid in Potable Waters.*

By ERNEST THEOPHRON CHAPMAN.

A METHOD for the estimation of nitrogen existing as nitrates and nitrites in potable waters, should be at once delicate and simple. I have been using for some time past a method which, in common with Fr. Schulze's method, depends on the reduction of the nitric acid to ammonia by means of aluminium in alkaline solution. Instead, however, of using a quantity of aluminium known to liberate a known volume of hydrogen, when treated with an alkali, and observing the diminution caused by the nitric acid, I measure the ammonia formed, either by the Nessler-test or by titration.

The first thing to be done is to obtain some idea of the quantity of nitrate contained in the water. For this purpose boil a little of it in a flask with caustic soda, free from nitrate, until a sample of it does not colour the Nessler-test, cool, and then introduce a strip of aluminium foil. As soon as this is dissolved, decant the liquid into a test-tube, add Nessler-test,

and note the colour produced ; should it be very dark, or should a precipitate be formed, either very little of the water (10 c.c. —25 c.c.) must be employed, or a tolerably large quantity, and the ammonia produced determined by titration. If, on the other hand, the colour is very pale, 200 c.c. will be a convenient quantity to employ ; for common waters, such as those supplied to London, 100 c.c. is ample. For waters of the Loch Katrine class, 300 c.c. would be a convenient quantity.

Having learned what sort of water is in hand, measure off the volume indicated by the preliminary experiments—introduce it into a non-tubulated retort, and add 50 to 70 c.c. of a solution of caustic soda containing 100 grms. of soda in the litre. This soda must be free from nitrates. If very little water has been taken, add some distilled water. The contents of the retort are now to be distilled until they do not much exceed 100 c.c., and until no more ammonia can be detected in the distillate by the Nessler-test. The retort is now cooled and a piece of aluminium introduced into it (foil will answer very well with dilute solutions, but I much prefer thin sheet aluminium in all cases). The neck of the retort is now inclined a little upwards, and its mouth closed by a cork, through which passes the narrow end of a small tube filled with broken-up tobacco pipe, wet either with water, or better with very dilute hydrochloric acid free from ammonia. This tube need not be more than an inch and a half long, nor larger than a goose-quill. It is connected with a second tube containing pumice-stone moistened with strong sulphuric acid. This last tube serves to prevent any ammonia from the air entering the apparatus, which is allowed to stand in this way for a few hours or over night. The contents of the pipe-clay tube are now washed into the retort with a little distilled water, and the retort as adapted to a condenser, the other end of which dips beneath the surface of a little distilled water free from ammonia (about 70 to 80 c.c.).\* The contents of the retort are now distilled to about half their original volume ; the distillate is made up to 150 c.c. ; 50 c.c. of this are taken out, and the Nessler-test added to them. If the colour so produced is not too strong the

\* Condensers are very apt to contain a trace of ammonia if they have been standing all night, and must, therefore, be washed out with the utmost care. I prefer to distil a little water through them until I can no longer detect ammonia in the distillate.

estimation may be made at once; if it is, the remainder of the distillate must be diluted with the requisite quantity of water.

Should it be desired to determine the ammonia by titration, a much larger quantity of the water must be employed. Half a litre or a litre must be evaporated down to a small bulk, and this small bulk treated in exactly the same manner, except that the distillate is received in dilute standard acid instead of water.

With regard to the precision attainable by this method, all that I can say is, it is limited by the precision of the determination of ammonia by Hadow's quantitative method founded on the Nessler-test. If, therefore, the quantity of nitric acid be above  $\cdot 0005$  grm. we may be sure of our result to 5 per cent., if the quantity be under this, the estimation will be somewhat less sharp. Even  $\cdot 00004$  grm. nitric acid may be detected and an estimation made by this method.

I need hardly remark that the purity of the reagents employed must be ascertained by making blank experiments. I have found common caustic soda, sold in lump, to be free from nitrates. Should the caustic soda contain nitrate, it may be purified by dissolving a small quantity of aluminium in its cold aqueous solution, and then boiling to expel ammonia.

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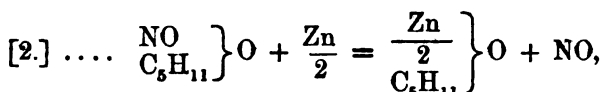
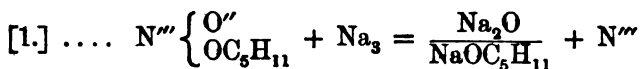
### XXI.—*Action of Zinc-ethyl on Nitrous and Nitric Ethers.*

By E. THEOPHRON CHAPMAN and MILES H. SMITH.

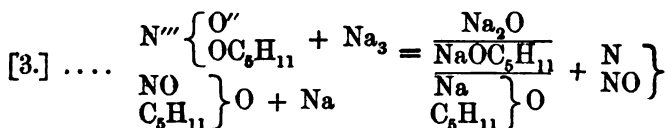
THE action of zinc-ethyl on nitrite of amyl resembles the action of metals on nitrite of amyl, and both actions are calculated to throw light on the mechanism of the solution of metals in nitric acid.

In a former paper\* we showed that when sodium or zinc acts on nitrite of amyl, there results nitrogen gas, or nitric oxide, or protoxide of nitrogen, according to the metals taken and the conditions of the operations, whilst amylate, or amylate and oxide of the metal, forms the complementary solid product. These reactions may be expressed as follows:—

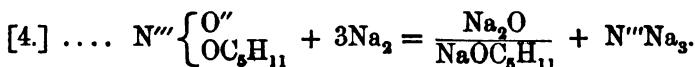
\* Chapman and Smith, *Journal Chem. Soc.*, December, 1867.



and combining [1] and [2], the formation of protoxide of nitrogen may be explained.



Another kind of reaction, which is a very interesting one, and not mentioned in our former paper, may also be observed if the progress of the action of sodium on nitrite of amyl be watched. As the sodium dissolves in this ether, it becomes more or less coated with a black substance, which, however, has only a transitory existence, disappearing as the operation progresses. This substance is probably nitride of sodium, and owes its formation to the reaction expressed thus:—



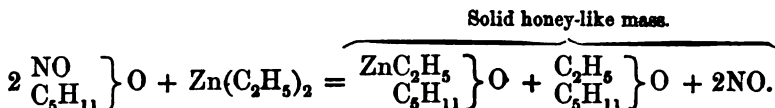
This equation carries us, so to speak, half way towards the generation of nitrogen gas. As will be easily understood, the subsequent action of  $N'''Na_3$ , on the Nitrite of Amyl, completes the operation for the production of free nitrogen.

The general modes of action which have thus been sketched are sufficient to render account, both of the reactions between metals and nitrite of amyl, and of the reactions between zinc-ethyl and nitrite of amyl.

Equations [2] and [4] have their parallels in the instance of zinc-ethyl. Equations [1] and [3] have not yet been shown to be illustrated by zinc-ethyl; but no particularly exhaustive search has been made for illustrations of these forms of reaction.

Undiluted zinc-ethyl attacks nitrite of amyl with great violence, bursting out into flame when placed in contact with it. If the zinc-ethyl be diluted with ether, its action on the nitrite becomes manageable, and may be studied.

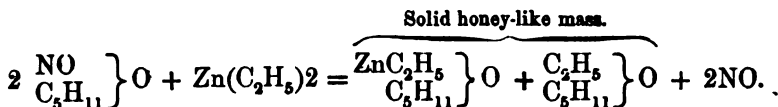
Zinc-ethyl first considerably diluted with ether, and then added to an excess of nitrite of amyl. Under these conditions the products are a gas, which proved to be nitric oxide, and a honey-like solid, which, on treatment with water, gave amylic alcohol, common alcohol, hydride of ethyl, and probably ethyl-amylic-ether. In this reaction we have an illustration of the kind of change expressed by equation [2], viz.:



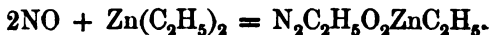
As will be at once understood, the substance  $\text{ZnC}_2\text{H}_5\text{C}_5\text{H}_{11}\text{O}$  (which may be written  $\text{Zn} \left\{ \begin{array}{l} \text{C}_2\text{H}_5 \\ \text{OC}_5\text{H}_{11} \end{array} \right\}$ ) will yield, according to recognized modes of reaction, when put into water,  $\text{Zn} \left\{ \begin{array}{l} \text{OH} \\ \text{OH} \end{array} \right\} + \text{C}_2\text{H}_6 + \text{C}_5\text{H}_{12}\text{O}$ , and thus we have the production of hydride of ethyl and amylic alcohol accounted for. The common alcohol, we believe, owes its origin to the action of water on the ethyl-amylic-ether, a substance which we believe existed in combination in the honey-like mass.

*Excess of zinc-ethyl, diluted with five or six times its volume of dry ether, and made to act on nitrite of amyl, the latter being dropt into the zinc-ethyl. Under these circumstances no nitric oxide is given off, and hardly any gas is produced.*

In spite of this obvious difference in the phenomena, the essential reaction is the same as in the other case where excess of nitrite was employed, viz.:



Instead of there being evolution of free nitric oxide, there is absorption of the nitric oxide by the excess of zinc-ethyl, and formation of Frankland's double compound of dinitro-ethylate of zinc and zinc-ethyl, which, as is well known, results from the action of free nitric oxide on zinc-ethyl, thus:—

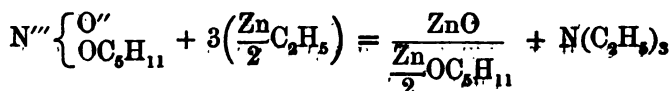


The following experimental data support the view here set forth.

Zinc-ethyl diluted with five or six times its volume of dry ether was placed in a retort, the neck of which pointed upwards and had an inverted Liebig's condenser adapted to it; nitrite of amyl was added through the tubulure of the retort from a stop-cock dropping funnel. Great heat was evolved on the mixture of the two liquids, and as the nitrite dropped from the funnel into the liquid, each drop left behind it a trail of white smoke. After a while an incrustation was formed at the end of the funnel, and on several occasions stopped it up completely. On one occasion however, the funnel was not completely stopped up, but a minute aperture only was left; this caused the nitrite of amyl to be projected in a very fine stream against the side of the retort above the level of the liquid. The heat developed by the passage of this fine stream of nitrite through the atmosphere in the retort was so great that the hand could not be borne on that portion of the retort where it impinged. When no more action was observed, the excess of ether was distilled off. There then remained in the retort, a clear substance which had the colour and consistence of honey; it set quite solid on cooling. On heating a portion of this substance in a test-tube, it first melted and then rapidly decomposed with a very slight explosion. On treating the substance with water, torrents of gas were evolved, and the substance swelled up very much. On adding more water and distilling, the distillate was found to contain amylic alcohol and common alcohol along with water. On filtering the residue in the retort, and evaporating a little of the filtrate to dryness, it was found that the residue so obtained still gave a small puff on heating. Carbonic acid was passed into the liquid, which was then boiled and filtered; and by this means a considerable quantity of zinc oxide was removed from it. The liquid was much coloured, and on evaporating it to dryness, though it showed signs of an inclination to crystallise, the presence of the colouring matter appeared to prevent its doing so. This substance, which was evidently the salt of an acid, was decomposed by adding baryta-water, and then passing carbonic acid through it, in the hope that the oxide of zinc together with the carbonate of baryta would carry down the colouring matter, and so render the substance crystallisable. On evaporating the solution of this salt to dryness, a white or slightly coloured uncrystallisable residue was obtained. It was very deliquescent, and, as will be seen from

the following numbers, contained a percentage of barium corresponding with that required by the dinitro-ethylate of that base, 3645 grm. of baryta salt giving 2703 grm. of sulphate of baryta. Ba per cent. = 43.6. The theory requires 43.49. As the copper salt of dinitro-ethylic acid appears to be one of its most characteristic compounds, we prepared it from the barium salt by adding sulphate of copper, &c. In this way a salt was obtained, having precisely the properties described by Dr. Frankland, as belonging to the dinitro-ethylate of copper. The percentage of copper was determined, and, as will be seen by the following numbers, this determination proves that the substance in hand is dinitro-ethylate of copper. 3625 grm. of the copper salt gave 0914 grm. of copper, or 25.21 per cent. of copper. The theoretical quantity for  $(C_4H_{10}Cu_2N_4O_4)_2H_2O$ , is 25.35 per cent.

When little ether is mixed with the zinc-ethyl prior to its action on nitrite of amyl there is produced triethylamine as follows:—



which illustrates equation [4].

The triethylamine was recognised as follows: It neutralised acids, and on being submitted to the operation of "Limited Oxidation," gave acetic acid and no other fatty acid. It consumed the theoretical quantity of oxygen corresponding to triethylamine.

*Zinc-ethyl and Nitrate of Amyl.*—When undiluted zinc-ethyl and nitrate of amyl are mixed together in an atmosphere of carbonic acid, there is no action at first, the substances mixing perfectly without apparent change. If this mixture be exposed for an instant to the action of the air, it explodes with a remarkably vivid flash of light, and a very sharp report. If it be gently heated (about 40° C is sufficient) it suddenly explodes with a degree of violence which is unsurpassed by any explosive mixture we have ever met with.

As in the instance of the nitrous ether, dilution with common ether renders the reaction manageable, and then it is even necessary to raise the temperature to about 100° C. to begin the reaction. The products are those of utter splitting up.

J. London Institution.



XXII.—*On the Occurrence of Prismatic Arsenious Acid.*

By F. CLAUDET.

WÖHLER,\* in the year 1832, discovered the dimorphism of arsenious acid, and described small crystals produced by sublimation, in a reverberatory furnace in which cobalt ores had been roasted.

These crystals, most of which were only  $\frac{1}{12}$  of an inch in length, were thin, colourless, transparent, hexagonal plates having a pearly lustre, and resembling crystals of stilbite. They were flexible like crystallised gypsum, with an easy cleavage parallel to the principal face. They were too small for measurement, but their form was incompatible with the monometric system, and, from the more recent researches of Pasteur, it seems probable that they were derived from the monoclinic.

This peculiar form of arsenious acid has not hitherto, as far as I am aware, been met with in nature. A considerable quantity of thin plates presenting all the characters described by Wöhler, was sent to me for examination by my friend Mr. James Mason, proprietor of the famous San Domingos Mines in Portugal, and they were found to consist of pure arsenious acid.

Some of these plates are over an inch in length; they are colourless, semi-transparent, of a pearly lustre, tough, flexible, and easily cleavable into thin laminæ; there are no perfect crystals, but a few of the plates present a hemitropy similar to that so well known in gypsum, and from this fact it may be fairly inferred that their form belongs to the same system of crystallisation. Their specific gravity at 60° Fah. 3.85; hardness 2.5. Under the microscope they depolarise polarised light.

In the state of crystals, this substance is with difficulty soluble in cold water, but on digesting an excess during four months with the aid of frequent agitation, the water took up 1 per cent. of its weight. When reduced to powder, it dissolved more rapidly, and in a few days the water had taken up 1.75 per cent. It is much more soluble in hot water, and a saturated

\* *Annales de Chimie et de Physique*, vol. II., p. 391.

solution, after cooling, retains 2·74 per cent.; a comparative experiment made with ordinary commercial arsenious acid gave 2·76 per cent.

At a low red heat it volatilizes without leaving any appreciable residue. This agrees with the result obtained by Wöhler, who concluded that the crystals did not contain arsenic in a higher degree of oxidation than arsenious acid. I also found, as he did, that it was impossible to reproduce the prismatic form, either by sublimation or by solution; the crystals obtained in these experiments being invariably regular octahedrons tetrahedrons.

The composition was ascertained by oxidising a given quantity, with nitric acid, and subsequently determining the weight of the arsenic acid produced by means of oxide of lead.

10 grains gave (mean of three experiments) 11·59 grains of arsenic acid, the calculated amount being 11·61 (As = 75 : O = 8).

As previously stated this substance was found in the mines of San Domingos, and the circumstances under which it seems to have been formed present peculiar interest.

The mine consists of a huge mass, of several millions of tons, of compact iron pyrites with a certain percentage of copper. It likewise contains small quantities of other minerals, and arsenic is invariably present. The following analysis represents the average composition of the ore:—

Sulphur	..	..	..	48·90
Arsenic	..	..	..	·47
Iron ..	..	..	..	43·55
Copper	..	..	..	3·10
Zinc ..	..	..	..	·35
Lead ..	..	..	..	·93
Lime ..	..	..	..	·20
Insoluble rock	..	..	..	·73
Moisture	..	..	..	·70
Oxygen and loss	..	..	..	1·07
				100·00*

\* In addition to the above, this pyrites yields traces of thallium, cobalt, nickel, manganese, silver, and gold, and also occasionally bismuth and antimony.

In the eastern part of the mine a considerable increase of temperature gives rise to the inference that spontaneous combustion has been going on for some years. This is attributed to the oxidation of the broken ore left in the old Roman Workings, which had remained full of water, from the time of their abandonment, until drained by the recent operations of Mr. Mason.

On the water being thus drawn off, the action produced by the exposure of the damp pyrites which had accumulated in the old mine, resulted in the chemical changes above referred to.

It is in crevices in the still hot ore that these crystals were found, lining the cavities. They seem therefore to have been produced in the same manner as those examined by Wöhler, but by a far slower process of sublimation, and on a much larger scale, which may account for the large size of the crystals.

With regard to the crystalline form, it may perhaps be ascribed to the influence of an atmosphere charged with sulphurous acid, which pervades that part of the mine. I propose making a series of experiments with a view of determining whether there is any truth in this conjecture, and of ascertaining to what extent the presence of sulphurous acid may modify the crystallisation of arsenious acid.

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XXIII.—*On the Hydride of Aceto-Salicyl.*

By W. H. PERKIN, F.R.S.

IN some considerations on the formation of coumarin by means of the hydride of sodium-salicyl and acetic anhydride, which I had the honour of laying before the Society only a short time since,\* I mentioned that the formation of this body appeared to be the result of two distinct reactions—the first consisting in the replacement of an equivalent of hydrogen in the hydride of salicyl by acetyl—the second in the removal of a molecule of water from this acetylic derivative. I also stated that I had succeeded in obtaining the body resulting from the first reaction, and which I termed the hydride of aceto-salicyl. The present

\* Page 60 of this volume.

communication is intended to give an account of the preparation and properties of this substance, and to show under what circumstances it may be converted into coumarin.

*Hydride of Acetosalicyl.*

To prepare this body, acetic anhydride is added to powdered anhydrous hydride of sodium-salicyl suspended in pure dry ether—the reagents being employed in equivalent quantities;—chemical action then gradually sets in, the sodium compound at the same time losing its yellow colour. After standing for twenty-four hours, the ethereal liquid is filtered off from the acetate of sodium which has formed, and evaporated upon the water-bath. In this manner an oily body is obtained, which gradually solidifies to a crystalline cake upon cooling. This is purified by pressure between bibulous paper, and subsequent crystallisation from alcohol. Three combustions of this body gave the following numbers:—

- I. ·2977 of substance gave  
·7161 of  $\text{CO}_2$ , and  
·1441 of  $\text{H}_2\text{O}$ .
- II. ·2286 of substance gave  
·5499 of  $\text{CO}_2$ , and  
·1051 of  $\text{H}_2\text{O}$ .
- III. ·2588 of substance gave  
·6240 of  $\text{CO}_2$ , and  
·1171 of  $\text{H}_2\text{O}$ .

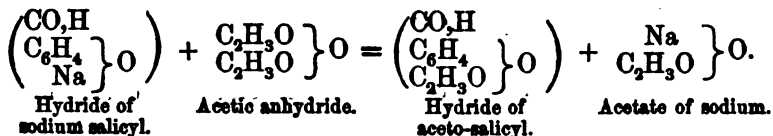
These numbers give percentages agreeing with the formula:



as the following comparisons will show:—

	Theory.		Experiment.		
			I.	II.	III.
$\text{C}_9$ .....	108	65·85	65·60	65·60	65·75
$\text{H}_8$ .....	8	4·88	5·37	5·10	5·02
$\text{O}_3$ .....	48	29·27	—	—	—
	<hr/>	<hr/>			
	164	100·00			

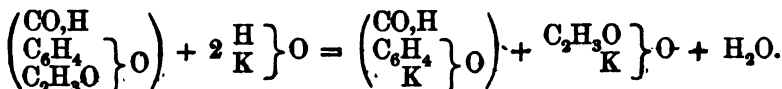
This substance represents the hydride of salicyl with an equivalent of hydrogen replaced by acetyl. The formation may be expressed thus:—



The hydride of aceto-salicyl melts at 37° C., and solidifies upon cooling into a satiny crystalline mass. At about 253° C. it boils, and distils with but little decomposition. It is extremely soluble in alcohol, from which it crystallises in fine silky needles. It is also very soluble in ether. The solutions do not give a purple reaction with ferric salts.

The hydride of aceto-salicyl is an aldehyde and combines with the bisulphites. It dissolves easily in the bisulphites of sodium and ammonium, and with the former forms a white pasty product; this, however, dissolves on standing, apparently owing to the decomposition of the hydride of aceto-salicyl.

This substance is also an acetate, and with alcoholic hydrate of potassium rapidly decomposes, with formation of acetate of potassium and hydride of potassium-salicyl (salicylite of potassium).



It is also decomposed into acetic acid and hydride of salicyl by boiling with water.

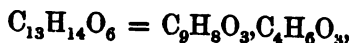
*Hydride of Aceto-salicyl and Acetic Anhydride.*

The hydride of aceto-salicyl and acetic anhydride, when heated together for three or four hours to 150° C., in a sealed tube, yield a clear, slightly brown solution. On agitating this with a solution of carbonate of sodium to remove any excess of acetic anhydride, a crystalline body is obtained, which may be rendered pure by one or two crystallisations from

alcohol. A combustion of this product gave the following numbers:—

·2513 of substance gave  
 ·5379 of  $\text{CO}_2$ , and  
 ·1226 of  $\text{H}_2\text{O}$ .

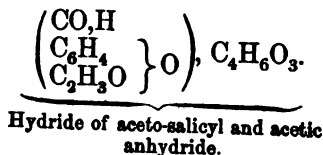
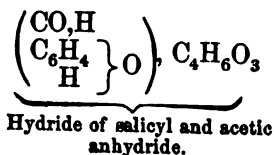
These numbers give percentages agreeing with the formula—



as the following comparisons will show:—

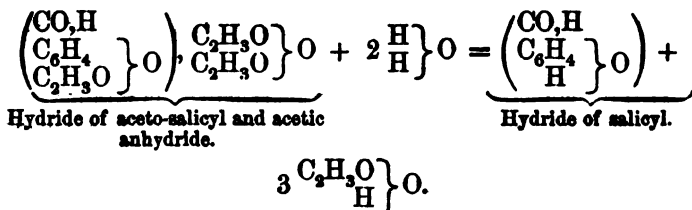
	Theory.		Experiment.
$\text{C}_{13}$ .....	156	58·64	58·37
$\text{H}_{14}$ .....	14	5·26	5·42
$\text{O}_6$ .....	96	36·10	—
	266	100·00	

This substance is therefore a compound of the hydride of aceto-salicyl and acetic anhydride, corresponding to that obtained from the hydride of salicyl under the same circumstances—



This compound melts at  $100^\circ$ — $101^\circ$  C. When distilled it decomposes, the products consisting chiefly of acetic anhydride and hydride of aceto-salicyl. When dissolved in acetic anhydride and the resulting solution exposed to the air, it is deposited in splendid brilliant oblique four-sided tables. It is easily soluble in hot, but only sparingly so in cold alcohol. It is also soluble in ether, tetrachloride of carbon, and benzole.

When it is heated in a sealed tube with water to  $100^\circ$  C., for several hours, the water becomes acid, and if the temperature be maintained at  $150^\circ$  C. for some time, it is entirely decomposed into acetic acid and hydride of salicyl.



*Formation of Coumarin from the Hydride of Aceto-Salicyl.*

From the formation of the last-described substance it is evident that acetic anhydride does not decompose the hydride of aceto-salicyl, even at a temperature of 150° C. I find also that no reaction takes place if these substances are distilled together, the acetic anhydride first coming over, and then the unchanged hydride of aceto-salicyl. Moreover, by the distillation of the combination of these two bodies, only traces of coumarin are produced. By what means then did I obtain coumarin by heating the hydride of sodium-salicyl and acetic anhydride, if the hydride of aceto-salicyl, being the first product of the reaction, is not dehydrated by acetic anhydride? Simply by what at first sight appeared to be of slight importance, viz., the presence of acetate of sodium as well as acetic anhydride.

On boiling a mixture of acetic anhydride, hydride of aceto-salicyl, and acetate of sodium for a few minutes, and then agitating the product with water to remove acetate of sodium and the excess of acetic anhydride, the remaining product on being distilled, at first yields a little acetic acid and anhydride; the temperature then rises rather rapidly to 290.5° C., when nearly pure coumarin distils over in considerable quantity.

The remarkable influence exercised by the presence of acetate of sodium in the foregoing experiments appears to be due to the presence of a sodium-compound analogous to the so-called anhydrous bracetate of potassium which Gerhardt obtained by heating acetate of potassium with acetic anhydride. That such a sodium-compound is produced I have proved by experiment;\* but why it should be so much more

\* Boiling acetic anhydride dissolves acetate of sodium, and the resulting solution on cooling deposits a new compound, crystallising in needles. This, when purified from adhering anhydride by pressure between bibulous paper, and

powerful a reagent than the anhydride itself is difficult to understand.

It will be seen that the foregoing results corroborate the views regarding the formation of coumarin brought forward in my previous paper.

I have not as yet produced the hydrides of butyryl- and valeryl-salicyl, from which the new homologues of coumarin were doubtless produced, but hope to do so shortly.

#### XXIV.—*On the Absorption of Vapours by Charcoal.*

By JOHN HUNTER, M.A., F.C.S., Chemical Assistant, Queen's College, Belfast.

THE present communication contains a number of experiments on the absorption of some vapours by cocoa-nut charcoal examined since the publication of my former papers on the same subject, and also the results of the effect produced by mixing together various liquids, of which the vapour-absorption was previously known. Ethylamine vapour is largely absorbed, one volume of cocoa-nut charcoal absorbing 124.5 volumes at 100° C. The experiments made with iodide of ethyl agreed very closely at 100° C., but at higher temperatures decomposition appeared to ensue when the charcoal was introduced, and the results were of a most contradictory nature, so that no number could be fixed upon as representing the absorption. By means of the apparatus described in my last paper the absorption of vapour of camphor was found to be 25.3 at 226.1° C., that of naphthaline 80.2 at 230.2° C., and that of nitrobenzol 45.6 at 225.3° C. Iodide of amyl is very slightly absorbed, one volume of charcoal absorbing 12.2 volumes at 161.4° C.

Having determined the absorption of absolute alcohol at 100° C., I next examined the effect produced by mixing the subsequent drying over hydrate of potassium, gave the following result upon analysis:—

54.53 of substance gave 26.36 of sulphate of sodium = 12.09 per cent. of sodium, the formula  $C_7H_5NaO_2 \cdot C_6H_5O_2$ , requiring 13.50 per cent. This substance is very deliquescent, and undergoes decomposition when exposed to the air.



alcohol in various proportions with water, and found that the absorption gradually increased with the amount of water added to the alcohol. Thus, at  $100^{\circ}\text{C}$ ., one volume of cocoa-nut charcoal absorbs 141.1 volumes of vapour of absolute alcohol; a mixture was then made of 10 c.c. absolute alcohol with 4 c.c. of water, and the absorption increased to 182.2; 10 c.c. of alcohol with 10 c.c. of water, gave a vapour-absorption of 187.2; 10 c.c. of alcohol with 20 c.c. of water, 246.1; and 10 c.c. of alcohol with 30 c.c. of water gave 255.4. Similar results were obtained when methylic alcohol and water were employed. When we repeat the same experiments at a temperature of  $155^{\circ}$  to  $160^{\circ}\text{C}$ ., there is no increased absorption on every addition of water; on the contrary, the absorption regularly diminishes, as might be expected, when we consider the difference between the absorption of water and alcohol at these temperatures, the former being absorbed 23.7 times, and the latter 87.0. The absorption of the other mixed vapours examined presents no peculiarity, the result being about the mean of the separate absorptions.

Several experiments were made, in order to determine whether any quantity of gas was contained in the pores of cocoa-nut charcoal, after being heated to redness out of contact with air, then plunged rapidly under mercury, and introduced into the vacuum of a barometer. The results of these experiments indicate that the charcoal always contains a certain amount of gas within its pores, the average volume given off being, when reduced to  $0^{\circ}\text{C}$ . and 760 mm., .015 times the volume of the charcoal. When the charcoal had previously absorbed ammonia, a portion of the condensed gas escaped on the introduction of the charcoal into the vacuum. In four experiments the average absorption of ammonia was 170.1 volumes, reduced to  $0^{\circ}\text{C}$ . and 760 mm., and the mean quantity given off, 13.1 volumes.

I employed meteoric iron as an absorbent, heating it in the same manner as the charcoal, and then introducing it into ammoniacal gas; in no case was any absorption observed.

In the following tables  $V$  represents the number of volumes of the vapour absorbed by one volume of cocoa-nut charcoal at the temperature and pressure at which the experiment is performed.  $T$  and  $\bar{T}$  are the initial and final temperatures in centigrade degrees;  $P$  and  $\bar{P}$  the pressures deduced by sub-

tracting the difference in level from the height of the barometer:—

## ETHYLAMINE.

	V	T	T'	P	P'
	58.9	187.8°	183.0°	576.5	553.7
	56.1	182.8	180.8	660.1	639.3
	55.3	188.5	189.5	599.0	579.4
Mean....	56.7	186.3	184.4	611.8	590.3
	92.5	143.8	140.0	662.1	649.6
	89.5	151.1	151.5	682.5	666.5
	93.0	148.3	148.3	678.0	666.5
Mean....	91.7	147.9	146.8	674.2	660.9
	129.6	100.0	100.0	700.1	677.6
	123.4	100.0	100.0	706.8	695.8
	124.1	100.0	100.0	704.9	688.4
	121.0	100.0	100.0	702.1	685.6
Mean....	124.5	100.0	100.0	704.6	688.3

## TRIETHYLAMINE.

	33.3	192.3	192.0	625.4	614.3
	35.3	177.0	174.0	510.0	509.5
	34.3	178.0	182.0	608.3	600.4
Mean....	34.5	182.4	182.7	581.2	574.9

## IODIDE OF ETHYL.

	38.7	100.0	100.0	680.9	675.4
	35.2	100.0	100.0	637.0	630.5
	34.3	100.0	100.0	705.5	700.0
	38.7	100.0	100.0	704.5	702.5
	34.1	100.0	100.0	703.5	700.5
Mean....	36.2	100.0	100.0	697.7	691.8

## ACETATE OF METHYL.

	99.5	100.0	100.0	678.3	656.8
	97.3	100.0	100.0	677.8	643.8
	94.3	100.0	100.0	668.5	644.5
	98.6	100.0	100.0	700.7	689.2
	94.2	100.0	100.0	700.9	670.7
Mean....	95.9	100.0	100.0	685.2	661.0

## OXALIC ETHER.

	58.3	196.6	196.2	580.5	578.6
	52.7	194.0	195.0	585.6	579.3
	57.7	198.0	195.3	576.3	571.4
Mean....	56.2	194.5	195.5	580.8	576.4

## HYDRIDE OF SALICYL.

	42.3	198.0	197.0	611.1	606.6
	35.7	196.0	196.5	569.5	567.3
	36.3	197.0	198.0	585.6	581.3
Mean....	38.3	197.0	197.5	588.7	585.4

SALICYLIC ACID.

	V	T	T	P	P
	41.3	230.1°	230.2°	636.4	614.7
	42.1	230.0	229.8	577.9	547.2
	45.4	230.2	230.2	557.8	549.7
Mean ....	42.9	230.1	229.9	590.7	570.5

IODIDE OF AMYL.

	10.6	160.5	162.5	681.5	675.0
	12.2	161.2	161.6	679.5	634.6
	12.9	162.4	163.0	675.8	672.5
	18.2	161.5	162.0	675.9	673.9
Mean ....	12.2	161.4	162.3	678.2	676.5

NAPHTHALINE.

	79.9	230.0	230.0	618.6	583.9
	80.8	230.2	232.5	589.8	571.5
	80.0	230.3	229.5	579.8	561.6
Mean ....	80.2	230.2	230.7	595.6	572.3

CAMPHOR.

	22.2	225.2	225.3	615.2	604.8
	27.2	226.8	227.0	642.3	633.2
	26.6	226.3	227.0	617.4	606.6
Mean ....	25.3	226.1	226.4	621.6	614.9

NITROBENZOL.

	47.8	225.2	226.0	589.2	569.3
	42.5	224.7	224.8	581.7	564.4
	46.6	226.0	227.0	594.9	555.3
Mean ....	45.6	225.3	225.6	585.3	563.0

BISULPHIDE OF CARBON.

	84.8	192.0	191.2	601.3	574.2
	82.9	192.0	192.0	582.0	551.2
	77.5	191.2	190.7	588.2	569.0
Mean ....	81.7	191.7	191.3	590.3	564.4

ALCOHOL.

	73.3	191.0	190.6	586.0	555.5
	72.9	192.0	192.0	572.7	518.5
	72.7	191.7	190.8	580.6	560.2
Mean ....	72.9	191.5	191.1	579.1	544.9

ACETONE.

	50.0	189.2	189.2	555.4	542.5
	54.5	190.0	192.5	574.8	561.8
	52.8	190.8	191.2	565.9	546.9
Mean ....	52.4	190.0	190.9	562.0	550.2

## HUNTER ON THE ABSORPTION OF

## METHYLIC ALCOHOL.

	V	T	T	P	P
	48.9 ....	191.0°	191.0° ....	805.0	581.4
	48.0 ....	191.5	192.7 ....	814.7	589.0
	48.0 ....	192.0	192.2 ....	827.6	592.6
Mean....	47.8 ....	191.5	192.3 ....	815.3	587.7

## ALCOHOL.

	88.5 ....	149.5	151.5 ....	710.0	699.0
	86.8 ....	157.8	159.0 ....	713.6	706.1
	89.7 ....	158.0	159.0 ....	711.8	699.6
	87.5 ....	158.0	159.3 ....	711.5	697.2
	87.6 ....	158.0	159.0 ....	709.3	696.8
Mean....	87.0 ....	156.2	157.5 ....	711.2	699.7

## 10 c.c. ALCOHOL + 4 c.c. WATER.

	182.9 ....	100.0	100.0 ....	696.5	662.5
	184.7 ....	100.0	100.0 ....	687.5	652.0
	181.1 ....	100.0	100.0 ....	690.5	649.5
	181.2 ....	100.0	100.0 ....	698.5	661.5
	181.0 ....	100.0	100.0 ....	694.5	654.0
Mean....	182.2 ....	100.0	100.0 ....	695.3	655.9

## 10 c.c. ALCOHOL + 10 c.c. WATER.

	185.7 ....	100.0	100.0 ....	710.5	669.0
	185.8 ....	100.0	100.0 ....	718.1	672.5
	190.3 ....	100.0	100.0 ....	788.7	692.7
	186.9 ....	100.0	100.0 ....	732.7	706.7
Mean....	187.2 ....	100.0	100.0 ....	723.2	685.2
	57.7 ....	158.8	159.0 ....	690.7	681.2
	58.2 ....	158.0	158.7 ....	700.1	689.1
	59.8 ....	158.0	159.0 ....	708.8	697.3
	56.9 ....	158.0	159.2 ....	709.0	700.0
Mean....	58.1 ....	158.2	158.9 ....	702.1	691.9

## 10 c.c. ALCOHOL + 20 c.c. WATER.

	248.8 ....	100.0	100.0 ....	716.2	670.7
	244.7 ....	100.0	100.0 ....	711.7	665.7
	246.1 ....	100.0	100.0 ....	714.7	677.7
	248.3 ....	100.0	100.0 ....	720.9	685.4
	242.3 ....	100.0	100.0 ....	718.4	677.4
	247.2 ....	100.0	100.0 ....	718.4	683.4
	248.5 ....	100.0	100.0 ....	711.1	686.6
	249.3 ....	100.0	100.0 ....	702.6	674.1
	245.7 ....	100.0	100.0 ....	694.6	658.6
	247.6 ....	100.0	100.0 ....	708.1	671.1
	242.9 ....	100.0	100.0 ....	709.7	679.7
Mean....	246.1 ....	100.0	100.0 ....	720.6	675.5
	46.8 ....	158.0	159.0 ....	703.0	696.0
	50.0 ....	158.7	159.0 ....	700.7	694.2
	48.0 ....	158.2	159.0 ....	701.6	685.6
	48.4 ....	158.8	158.2 ....	708.7	700.7
	47.4 ....	158.7	159.7 ....	707.5	700.0
	46.8 ....	158.7	159.8 ....	707.4	702.9
Mean....	47.8 ....	158.5	159.1 ....	704.8	694.9

10 c.c. ALCOHOL + 30 c.c. WATER.

	V	T	T	P	P
	256.7	100.0°	100.0°	698.1	660.1
	250.7	100.0	100.0	694.4	654.9
	259.4	100.0	100.0	698.9	669.4
	253.5	100.0	100.0	701.9	675.4
	255.5	100.0	100.0	708.6	687.1
	257.3	100.0	100.0	693.6	666.1
	251.9	100.0	100.0	694.6	668.1
	253.2	100.0	100.0	712.3	683.8
	258.3	100.0	100.0	700.3	671.8
	264.2	100.0	100.0	701.3	682.3
	253.6	100.0	100.0	710.2	682.7
Mean ....	255.4	100.0	100.0	700.4	672.4
	36.4	159.7	160.0	708.2	702.2
	37.2	159.3	160.2	706.3	700.8
	37.2	159.3	160.3	706.3	699.3
	37.6	159.4	160.2	707.0	701.5
Mean ....	37.6	159.4	160.2	706.9	700.9

METHYLIC ALCOHOL.

	150.7	100.0	100.0	709.8	695.3
	144.5	100.0	100.0	709.8	690.3
	168.2	100.0	100.0	713.3	696.3
	141.7	100.0	100.0	708.3	694.3
	147.5	100.0	100.0	708.3	690.8
Mean ....	149.5	100.0	100.0	709.9	697.4

10 c.c. METHYLIC ALCOHOL + 10 c.c. WATER.

	223.7	100.0	100.0	700.3	677.8
	229.4	100.0	100.0	645.3	654.3
	223.8	100.0	100.0	700.3	679.8
	224.6	100.0	100.0	711.3	695.8
	226.6	100.0	100.0	695.3	676.3
	223.8	100.0	100.0	717.3	696.3
Mean ....	226.1	100.0	100.0	695.0	680.3
	53.8	159.0	159.7	712.7	704.7
	53.9	160.2	160.7	712.7	704.7
	53.2	160.2	161.0	731.1	717.6
Mean ....	53.6	159.3	160.4	718.8	709.0

10 c.c. METHYLIC ALCOHOL + 20 c.c. WATER.

	263.3	100.0	100.0	712.2	702.0
	260.4	100.0	100.0	702.3	673.3
	260.4	100.0	100.0	711.7	688.7
Mean ....	261.3	100.0	100.0	708.9	688.2
	47.0	160.0	162.0	702.6	698.1
	49.4	160.3	162.2	719.1	711.1
	48.9	160.3	161.3	737.1	732.1
Mean ....	48.4	160.2	162.0	719.6	708.7

## 10 c.c. ALCOHOL + 10 c.c. ACETONE.

	V	T	†	P	ρ
	75.2	160.3°	162.0°	699.7	682.2
	72.6	159.0	160.7	713.2	697.2
	72.3	159.3	160.2	703.8	681.3
	75.7	159.3	160.3	696.8	672.3
Mean....	73.9	159.5	160.8	703.4	683.3

## 10 c.c. ALCOHOL + 30 c.c. ACETONE.

	74.8	160.0	161.2	721.0	704.5
	69.2	160.5	162.3	689.7	675.4
	74.6	160.4	162.2	702.7	687.2
	71.1	161.0	163.3	705.7	688.7
Mean....	72.4	160.5	162.2	704.8	689.0

## 10 c.c. PERCHLORIDE OF CARBON + 10 c.c. ALCOHOL.

	75.5	160.8	162.8	714.2	705.7
	70.6	159.3	160.7	695.8	686.3
	74.5	160.2	160.8	697.8	688.8
Mean....	73.5	160.1	161.4	699.2	687.1

## 30 c.c. PERCHLORIDE OF CARBON + 10 c.c. ALCOHOL.

	45.8	160.3	160.7	711.7	704.2
	45.8	159.0	160.3	716.7	709.2
	40.8	160.2	161.2	714.7	710.7
Mean....	43.4	159.8	160.7	714.0	708.0

## 10 c.c. BISULPHIDE OF CARBON + 20 c.c. ALCOHOL.

	89.2	160.0	164.0	707.7	686.7
	92.1	160.7	163.1	706.7	690.2
	84.4	160.2	161.3	679.2	660.2
Mean....	88.5	160.3	162.8	697.9	679.0

## XXV.—CHEMICAL CONTRIBUTIONS.

By Dr. H. KOLBE.

1.—*On Carbanilic Ether.*

By Dr. WILM and Dr. WISCHIN.

WITH the expectation that aniline might act on chlorocarbonic ether in the same manner as ammonia, and consequently give rise to anthranilic ether, the authors added chlorocarbonic ether (1 eq.) by drops to aniline (2 eq.) contained in a flask

connected with an inverted condenser. Under these circumstances the two bodies combine, with considerable evolution of heat, and the whole finally solidifies to a crystalline mass. If this mass, when cold, be freed from adhering aniline by dilute hydrochloric acid, then washed several times with cold water, dried, and submitted to distillation, a colourless oily distillate is obtained, which quickly solidifies to a crystalline pulp consisting of slender needles.

This product has the composition of anthranilic ether, but its chemical behaviour shows that it contains neither anthranilic, amidobenzoic, paramidobenzoic, nor any known acid isomeric with these. It is rather indeed to be regarded as the ether of the true carbanilic acid, quite distinct from the acid formerly designated by Chancel as carbanilic acid, which was really amidobenzoic acid.

It is well known that carbamic acid cannot be separated from its ether (urethane) without decomposition; neither can it be transferred to other bases. In like manner it has not been found possible to prepare carbanilic acid in the free state, or to form any other salts of this acid from the ether.

Carbanilic ether melts at  $52^{\circ}$ , sublimes in long beautiful needles, volatilises without decomposition, and boils at  $238^{\circ}$ . Its vapours strongly excite tears. It is insoluble in cold, slightly soluble in boiling water, from which it crystallises in needles on cooling; easily soluble in alcohol and in ether.

Dilute acids do not act upon it; but strong aqueous bases decompose it into alcohol, aniline, and carbonic acid. Aqueous ammonia at  $160^{\circ}$  converts it into aniline, urea, and alcohol.

Strong potash-ley partly decomposes carbanilic ether into carbonic acid, alcohol, and aniline, and the aniline reacts with the undecomposed carbanilic ether in such a manner as to form diphenyl-carbamide or diphenylurea.

## 2.—On Ethylic Sulphocyanate.

By Mr. IRELAN.

Ethylic sulphocyanate decomposes when mixed with alcoholic potash solution, even in the cold, with separation of potassium cyanide. Mr. Irelan has examined this process more closely,

and has found that potassium cyanate and pure ethylic bisulphide are likewise produced.

The cyanogen of the ethylic sulphocyanate is therefore removed without replacement, and then acts upon the potash in the same manner as free cyanogen.

Ethylic sulphocyanate exhibits an exactly similar reaction with an alcoholic solution of potassium sulphide, the products being ethylic bisulphide, cyanide, and sulphocyanate of potassium.

Ethylic sulphocyanate suffers a remarkable and, apparently, more complex decomposition when heated to 160° for several hours with water. A large quantity of gas is evolved, chiefly carbonic acid; an oily product is formed, apparently consisting of ethylic bisulphide; and the aqueous solution contains sulphocyanate of methylammonium.

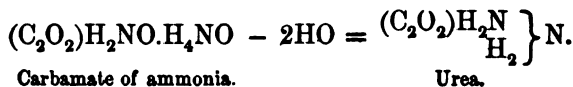
### 3.—*Direct Conversion of Ammonia-Carbamate into Urea.*

By ALEXANDER BASAROFF.

From the conviction that urea is not carbamide, but the amide of carbamic acid, as represented by the following formulæ:—



I have, for several years, made numerous experiments, and induced my pupils to make others, with the view of converting carbamate of ammonia into urea by direct abstraction of water:



After many fruitless attempts this problem has at length been solved by Mr. Basaroff.

Carbamate of ammonia is easily obtained, pure and in large quantity, by passing carbonic acid and ammonia gases, both perfectly dry, into cold absolute alcohol, separating the copious crystalline precipitate by filtration from the greater part of the liquid, and heating it with absolute alcohol in a hermetically



sealed tube to 100°, or above. The liquid on cooling deposits carbamate of ammonia in large crystalline laminae.

Basaroff has analysed these crystals, and found them to agree exactly in composition with the formula  $(C_2O_2)H_2NO.H_4NO$ .

The transformation of this salt into urea is effected quite simply, as Basaroff has found, by heating it, after perfect drying over sulphuric acid, in a strong hermetically closed glass tube, to 130°—140° C., for a few hours. If the contents of the tube be afterwards heated in the water-bath, the excess of ammonia carbamate, volatilises, together with the ammonia carbonate produced, and pure urea remains, with all its characteristic properties.

Basaroff has since found that ordinary commercial ammonia carbonate, when treated in the manner just described, likewise yields urea. It remains to be determined whether this carbonate of ammonia contains carbamate, and whether this salt is the real source of the urea obtained from the commercial carbonate.

#### 4.—*On the Electrolysis of Acetic Acid.*

By H. KOLBE.

Having twenty years ago resolved acetic acid into carbonic acid and methyl, by the electrolysis of the aqueous solution of its potassium salt, I further examined the behaviour of free acetic acid towards oxygen evolved by electrolysis, in the hope of thereby oxidising it to glycollic or dioxyacetic acid.

I have lately resumed these experiments, using as the electrolyte, glacial acetic acid, mixed with just enough water and sulphuric acid to render it capable of conducting the galvanic current. For electrodes, I used two platinum plates, which were immersed in the liquid without any separating diaphragm, and the liquid was kept cool during the electrolysis.

If, after the action of the current has been continued for twelve hours, the liquid be freed from sulphuric acid by baryta-water, and then evaporated, there remains a small quantity of a viscid non-volatile substance, which exhibits strong acid properties, and crystallises slowly over oil of vitriol.

My expectation that this acid might be glycollic acid has not

been realised. Its behaviour, and more especially the properties of its salts, are quite distinct from those of glycollic acid, and yet its calcium salt has exactly the composition of glycollate of calcium.

The quantity of this acid obtained being always very small, I have not hitherto been able to analyse any of its other salts.

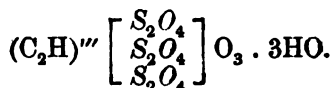
If the further investigation of this interesting acid should establish its isomerism with glycollic acid, the result might, perhaps, tend to support the assumption that the four hydrogen atoms of marsh gas, or the three hydrogen atoms of methyl, are not of equal value.

### 5.—On *Methintrisulphonic Acid*.

By Dr. THEILKUHLE.

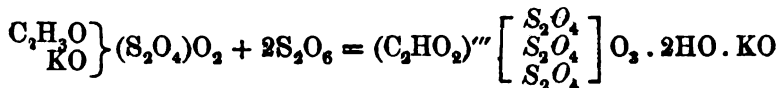
As ethylsulphuric acid is converted by the action of fuming sulphuric acid upon its potassium salt, into the isomeric compound isethionic acid, it appeared probable that methylsulphuric acid would, under similar circumstances, be converted into a homologue of isethionic acid.

The experiments undertaken with this view by Dr. Theilkuhle have not hitherto yielded the desired result, because the action of the sulphuric acid goes too far; but they have led to the discovery of another compound, forming the first member of a hitherto unknown series of acids. Dr. Theilkuhle has, in fact, discovered that the action of fuming sulphuric acid on methylsulphate of potassium, gives rise to a tribasic trisulphonic acid, corresponding to the tricarbonic and carbosulphonic acids, and having the composition,



This acid he designates as methin-trisulphonic acid.

The reaction above mentioned might be expected to give rise to oxymethintrisulphonic acid, according to the equation:



Methylsulphate of potassium.

Oxymethintrisulphonate of potassium.

This acid could not, however, be detected; it is probably reduced, as soon as formed, to methintrisulphonic acid, by the sulphurous acid produced at the same time.

Methintrisulphonic acid is a very strong and permanent acid, easily soluble in water, crystallisable, and forming beautifully crystalline salts with various bases. The barium salt is very slightly soluble in water, and is precipitated in the crystalline form on mixing the solution of the acid with chloride of barium, even when the solution contains a large quantity of free sulphuric acid.

Dr. Theilkuhl is now endeavouring, by suitable modification of his experiments, to obtain the compound  $(C_2H_3O_2)[S_2O_4]O.HO$ , homologous with isethionic acid, and hopes, by means of it, to produce also the compound  $C_2 \left\{ \begin{array}{c} H_2 \\ H_2N \end{array} \right\} [S_2O_4]O.HO$ , homologous with taurine.

## XXVI.—*On the Constitution of Glyoxylic Acid.*

By W. H. PERKIN, F.R.S., and B. F. DUPPA, F.R.S.

WE have been prevented, by a variety of circumstances, from pursuing an investigation published some years ago in the Journal of this Society,\* in which we, cursorily and without giving numbers, stated that we had obtained from dibromacetic acid, or more correctly bromoglycollate of silver, "a new acid, having the formula  $C_2H_4O_4$ ." This acid has since been regarded as glyoxylic acid.

We now beg to lay before the Society, the analysis on which our assertion was founded, together with other matter since obtained, which may prove of use in helping to clear up the question as to what is the probable constitution of this acid.

Before directly describing the production of the acid above referred to, it is necessary to enter a little into some of the details pursued by us in the production of the substance with which we started, viz., of pure dibromacetate of silver.

\* Chem. Soc. Qu. J., vol. xii, p. 5.

Dibromacetic acid, as is well known, is difficult to obtain in a state of absolute purity, the impurities consisting of traces of monobromacetic and hydrobromic acids. As distillation was found incapable of separating the last traces of monobromacetic acid, the following method, founded on the great difference between the solubilities of the two amides, mono- and dibromacetamide, was adopted.

Crude dibromacetic acid was raised to a temperature of  $140^{\circ}$ — $150^{\circ}$  C., in a retort, and alcohol slowly added; this immediately etherified the acid, every trace of which was converted into dibromacetate of ethyl, containing a trace of monobromacetate of ethyl, both of which distilled over as soon as formed, together with water and a little alcohol. To this crude product an aqueous solution of ammonia was added in small portions, the mixture being well shaken at each addition, and care being taken to avoid any great excess of ammonia. The mixture was now allowed to stand for some hours, when an abundant crop of crystals of dibromacetamide made its appearance; this was filtered off from the mother-liquor, well washed with cold water, and purified by being re-crystallised from alcohol and water, and again washed. The mother-liquors and washings yielded further crops of crystals of dibromacetamide, on being evaporated on the water-bath. This amide was the source from which we obtained the pure dibromacetates used in the course of this investigation.

For the conversion of the amide into dibromacetate of silver, the following method was pursued: Crystals of dibromacetamide were placed in a stoppered bottle, with a large quantity of water, and aqueous solution of hydrate of potassium, added in small portions, and the whole well shaken at each addition, the amide being kept in excess; the temperature during the operation was kept as low as possible by means of ice and water, otherwise bromide of potassium was formed, and an impure salt the result. The excess of amide was then filtered off from the solution of potassium salt formed, and the liquid, which was very alkaline from the ammonia generated in the re-action, was neutralised with dilute nitric acid, and then a few drops more of the same acid were added to render the solution decidedly acid.\* Into this acid solution nitrate of

\* This was done for the purpose of ascertaining when all the nitrate of silver had been washed out, for the salt was washed until the washings were neutral to test paper.

silver was poured until no further precipitation took place, and the whole was allowed to stand for three or four hours. If the operation, as above indicated, be properly performed, the resulting precipitate will consist entirely, after thorough washing with cold water, of pure dibromacetate of silver.

Bromoglycollic acid is prepared by taking some freshly prepared dibromacetate of silver, placing it in a flask, adding water in sufficient quantity to form a deep layer over it, and heating the whole to  $100^{\circ}\text{C}$ ., and lastly allowing it to boil until no further formation of bromide of silver takes place; this is readily known by the aqueous layer losing all turbidity, and the metallic bromide appearing as a brilliant yellow curdy mass. The liquid filtered off from the bromide of silver contains the bromoglycollic acid in solution.

When bromoglycollic acid is treated in the cold with carbonate or hydrate of silver, a white crystalline salt is produced, consisting of bromoglycollate of silver; but as it is difficult, when operating in this manner, to avoid an excess of silver, we found it best to convert the acid into the potassium salt, and then add nitrate of silver, by which means no excess of silver could be present, after the precipitated salt had been well washed.

By boiling this bromoglycollate of silver with water, the whole becomes yellow from the formation of bromide of silver, the acid to which we assigned the formula  $\text{C}_2\text{H}_4\text{O}_4$  being found in solution.

This acid has been called glyoxylic acid, owing to its possessing the same composition as that originally assigned by Dr. Debus to the acid obtained by the oxidation of alcohol.

Wishing to compare the salts of our acid with those obtained from Dr. Debus's acid, we oxidized some alcohol with nitric acid, and prepared the glyoxylates of calcium and silver. On comparing these salts with those obtained from our own acid, we found them to agree in form and general appearance, with the exception that the silver salt of Dr. Debus's acid blackened when exposed to light, whilst the corresponding salt obtained from dibromacetic acid remained unchanged even after many months' exposure to daylight. This, however, can scarcely be regarded as evidencing a difference between these two compounds, as the presence of a very minute quantity of

a foreign body, will often cause a silver salt to blacken very rapidly.

Dr. Debus has shown that our calcium salt possesses the same solubility as his own, and also that when boiled with hydrate of calcium, it undergoes the same decomposition.\* Our experience perfectly confirms this latter statement.

We have discovered a very characteristic reaction for glyoxylic acid, dependent upon the rapid manner in which its aniline salt undergoes decomposition. When a solution of glyoxylate of calcium is mixed with a solution of oxalate of aniline and the resulting oxalate of calcium filtered off, a colourless liquid is obtained; but if this solution be boiled, or even left to stand for a few hours, an insoluble bright orange-coloured precipitate is formed. We find that both acids give the reaction, affording further evidence of their identity.

We here append analyses of silver and calcium salts, made from the acids obtained from the two separate sources.

- I. ·1090 of silver salt gave  
·0478 of CO<sub>2</sub> and  
·0170 of H<sub>2</sub>O and  
·0592 of metallic silver.
- II. ·2456 of substance gave  
·1072 of CO<sub>2</sub> and  
·0388 of H<sub>2</sub>O.
- III. ·3748 of substance gave  
·1694 of CO<sub>2</sub> and  
·0736 of H<sub>2</sub>O.
- IV. ·3905 of substance gave  
·1681 of CO<sub>2</sub> and  
·0606 of H<sub>2</sub>O.
- V. ·3113 of substance gave  
·1693 of silver.
- VI. ·2404 of substance gave  
·1302 of silver.

These numbers when calculated out, are found to agree with the formula—



\* Journ. Chem. Soc., Ser. II, vol. iv, p. 19.

	Calculated.		I.	II.	III.	IV.	V.	VI.	Mean.
C <sub>2</sub> ..	24	12·06	11·96	11·90	12·32	11·73	..	..	11·97
H <sub>3</sub> ..	3	1·51	1·73	1·75	2·18	1·78	..	..	1·86
Ag. 108	54·27	54·31	..	..	..	54·88	54·15	54·28	54·28
O <sub>4</sub> ..	64	32·16	..	..	..	..	..	..	31·89
	199	100·00							100·00

In the above table of analyses, Nos. I, II, and III were made with acid prepared from dibromacetic acid as just described; the analyses IV and V were made by us in 1858, and on these numbers we made the statement that we had obtained an acid having the composition C<sub>2</sub>H<sub>3</sub>O<sub>4</sub>. No. VI is a silver determination, made from a silver-salt obtained with Dr. Debus's acid.

The calcium salts of the two different acids furnished us with the following numbers:—

- I. ·0924 of glyoxylate of calcium prepared from dibromacetic acid gave  
·0562 of sulphate of calcium.
- II. ·2758 of glyoxylate of calcium made from oxidized alcohol gave  
·1234 of carbonate of calcium.

These analyses give numbers agreeing with the formula—



as seen below:—

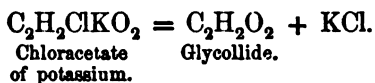
	Calculated.		Found.	
			I.	II.
C <sub>2</sub> =	24	21·62	—	—
H <sub>3</sub> =	3	2·70	—	—
Ca =	20	18·02	17·91	17·89
O <sub>4</sub> =	64	57·66	—	—
	111	100·00		

From these results we may conclude, with Dr. Debus,\* that the acids derived from alcohol and dibromacetic acid are not only identical in their reactions, but also in their composition.

\* Journ. Chem. Soc., Ser. II, vol. iv, p. 19.

Having thus far established the identity of these two acids, we proceeded to make experiments with the view of ascertaining what is the true formula and constitution of glyoxylic acid.

From the labours of Kekulé, we know that monochloracetate of potassium, on being heated, splits up into chloride of potassium and glycollide, a little glycollic acid being formed at the same time, owing to the difficulty of getting this salt perfectly dry. We have also found that dry monobromacetate of potassium yields glycollide in very large quantities. Dr. Debus has further pointed out that perfectly dry chloracetate of potassium, when heated, should yield nothing but chloride of potassium and glycollide,\* thus—



If we treat dibromacetate of silver in a similar manner, we obtain an analogous result, viz., bromide of silver and a substance which is evidently bromoglycollide.

We find that if dry dibromacetate of silver be heated with pure dry ether in a sealed tube, it is converted into a yellow powder. The ether with which it has been heated, on being tested with litmus, is found to be neutral, and on being evaporated is found to contain nothing.

If water be added to the yellow powder, it will be found to dissolve nothing, but if, on the other hand, it be treated with hydrate of barium or potassium, a bromoglycollate of barium or potassium will result, and if the said salts be boiled with an excess of either of the above hydrates, then a metallic bromide, oxalate, and glycollate† will be produced.

\* Chemical Gazette, xvii, p. 297.

† We here append the analyses of the glycollates of silver and barium, prepared from the product of the above reaction.

I. 2296 of glycollate of barium gave—

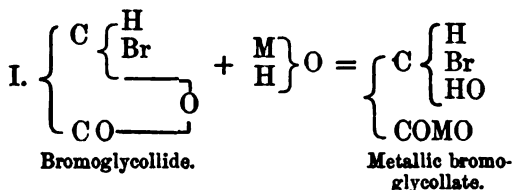
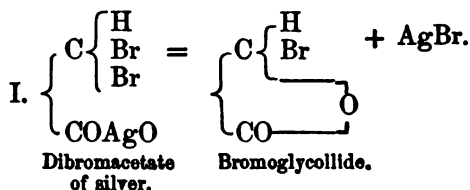
1864 of sulphate of barium, corresponding to 47.73 per cent. of barium. The formula  $\text{C}_2\text{H}_3\text{BaO}_3$ , requiring 47.73 per cent. of barium.

II. 2246 glycollate of silver gave—

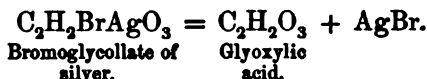
18500  $\text{CO}_2$   
 0874  $\text{H}_2\text{O}$  and  
 1380 of Ag.



By this reaction we obtain in the yellow powder bromide of silver and insoluble bromoglycollide, and this latter, when treated with a hydrate yields a bromoglycollate. The last change is caused by the formation of a glyoxylate which, with the excess of hydrate employed, decomposes into a glycollate and oxalate. The first two changes may be represented thus:—



Reasoning from these results we concluded that, if dibromacetate of silver, when heated alone or with dry ether, yields bromide of silver and an anhydride, then bromoglycollate of silver ought, in like manner, to yield bromide of silver and an anhydride, and not an acid as proposed by Dr. Debus, who writes the decomposition thus:—



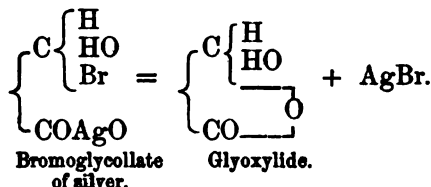
To test this point by experiment, dry bromoglycollate of

These numbers correspond with those required by the formula  $\text{C}_2\text{H}_2\text{AgO}_3$ .

	Calculated.		Found.
$\text{C}_2$ .....	24	18.11	12.89
$\text{H}_2$ .....	3	1.64	1.85
$\text{Ag}$ .....	108	59.01	59.21
$\text{O}_3$ .....	48	26.24	26.05
	188	100.00	100.00

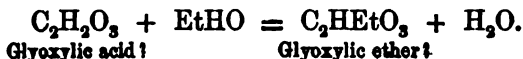
silver was heated with pure dry ether in a sealed tube; this furnished a yellow powder insoluble in ether, and yielding no sort of acid to that substance, as it remained perfectly neutral, whereas had glyoxylic acid been produced, it would have been found in solution. Water also did not dissolve anything from this yellow powder; but on boiling it with hydrate of barium, it quickly yielded the products of the decomposition of glyoxylic acid, viz., an oxalate and glycollate, showing that glyoxylic acid is found only by the hydration of the organic portion of the yellow powder.

So far this reaction appears conclusive as to the fact of an anhydride and not an acid being formed by the action of heat upon dry bromoglycollate of silver. The reaction may be thus expressed :—



Wishing further to test the correctness of this equation, we decomposed bromoglycollate of silver in the presence of a water-molecule of such a nature that we might be able to trace the position taken up by the atoms of hydrogen; for this purpose we employed absolute alcohol.

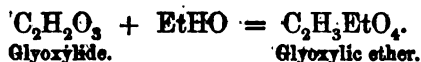
Now should the product  $\text{C}_2\text{H}_2\text{O}_3$  produced from bromoglycollate of silver be an acid, as Dr. Debus considers it to be, we should obtain the following result :—



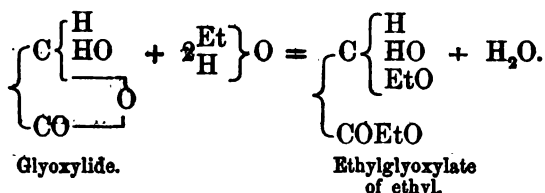
In this case we should obtain an acid liquid and not a neutral one, on account of the presence of water generated in the reaction, as this, according to the researches of Berthelot,\* would prevent perfect etherification.

\* Recherches sur les Affinités. De la formation et la décomposition des Ethers; par MM. Berthelot et Péan de Saint Gilles. Paris, 1862.

If on the other hand it be an anhydride, we should get the following reaction :



There is still another reaction just possible, and that is the formation of an ethylglyoxylate of ethyl :



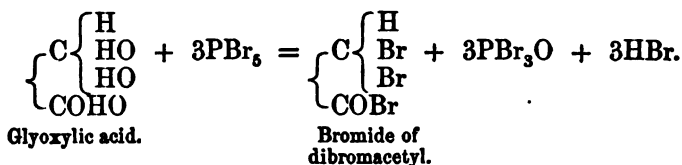
But in this case we should again obtain an acid solution, on account of the water formed in the reaction.

With the view of ascertaining which of these three reactions took place, dry bromoglycollate of silver was heated with a large excess of anhydrous alcohol for several hours in a sealed tube in the water-bath. On examining the tube, it was found to contain a clear liquid and a bright yellow powder. Test-paper was applied to the liquid, which proved to be totally neutral; the test-paper moistened with the liquid was now brought into contact with a drop of water, when it immediately began to turn red, the red colour in the course of a few minutes reaching its maximum, proving very plainly that an ether was undergoing decomposition. After the liquid had been decanted, the excess of alcohol was evaporated off in vacuo, and a rather thick neutral liquid remained behind, which was perfectly soluble in water, to which it quickly communicated an acid reaction. This no doubt was glyoxylic ether, produced according to the second reaction described above. As a further proof of its being a glyoxylate, a little was added to a solution of hydrate of calcium, when it produced a perfectly clear solution which, as soon as boiled, gave the reaction so characteristic of glyoxylate of calcium.

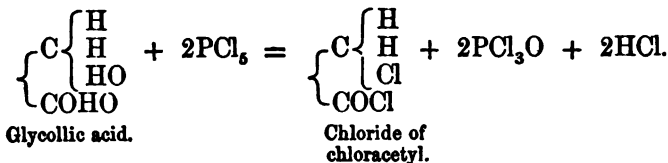
Not feeling satisfied of the ether being so perfectly free from alcohol as to fit it for analysis, we attempted to distil it, when unfortunately it suddenly underwent decomposition. From

want of material we were unable to prepare a further quantity of this ether.

Being foiled in our attempt at the production of glyoxylic ether sufficiently pure for analysis, we thought it desirable to attack the subject from another side, viz.: the readiness with which hydroxyl, HO, is replaced in acids and other bodies by chlorine or bromine when submitted to the action of the chlorides or bromides of phosphorus. This suggested to us the idea that, should the constitution of glyoxylic acid be such as we supposed it to be, and the acid derived from alcohol be identical with that derived from dibromacetic acid, then, by treating Dr. Debus's acid or its salts with pentachloride or bromide of phosphorus, we ought to obtain the chloride or bromide of dichlor- or dibrom-acetyl, according to the following equation :



The reaction is analogous to that which takes place when glycollic acid is distilled with pentachloride of phosphorus :



Acting upon this suggestion, we submitted perfectly dry glyoxylate of calcium with a sufficient amount of the pentabromide of phosphorus, to distillation; hydrobromic acid was evolved, and a mixed liquid consisting of oxybromide of phosphorus and another substance came over. The mixed liquid was added in small portions to an excess of alcohol, and when all action had ceased, a large quantity of water was added, causing the immediate separation of a heavy oil. This oil was separated from the supernatant liquid, washed with water, and was found to possess all the irritating properties of dibromacetic

ether. On adding ammonia to this substance, in the same manner as described in the preparation of dibromacetamide, an abundant crystalline precipitate was produced. This, on being recrystallised, was found to possess both the form and characteristics of dibromacetamide.

To prove the identity of this substance the following analyses were made:—

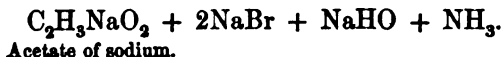
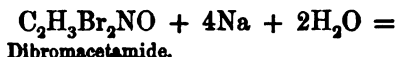
- I. ·2505 of substance gave  
·1010 of CO<sub>2</sub> and  
·0374 of H<sub>2</sub>O.
- II. ·1430 of substance gave  
·2464 of AgBr.
- III. ·4168 of substance gave  
·7258 of AgBr.

These numbers give percentages agreeing with those calculated from the formula—



	Calculated.		Found.			Mean.
			I.	II.	III.	
C <sub>2</sub> .....	24	11·06	10·99	—	—	10·99
H <sub>3</sub> .....	3	1·38	1·65	—	—	1·65
Br <sub>2</sub> ....	160	73·73	—	73·32	74·10	73·71
N.....	14	6·45	—	—	—	—
O.....	16	7·38	—	—	—	—
	<hr/>	<hr/>				
	217	100·00				

To show that this substance was really ordinary dibromacetamide, we treated it with sodium amalgam and water, when the following decomposition took place:—

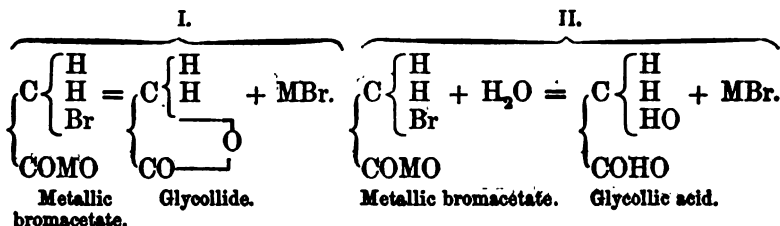


These results show clearly that the liquid accompanying the oxybromide of phosphorus was the bromide of dibromacetyl, which, by the action of alcohol, was converted into the corresponding ether, and this in its turn when treated with

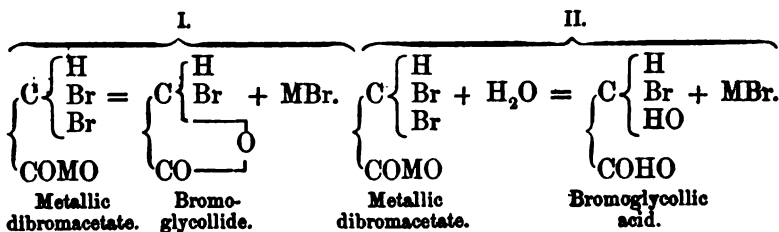
ammonia decomposed, yielding dibromacetamide, thus further confirming our view of the constitution of glyoxylic acid.

If we now take a general view of the results of the various experiments described in this paper, we shall see how each step forward in this enquiry is supported by those which preceded it.

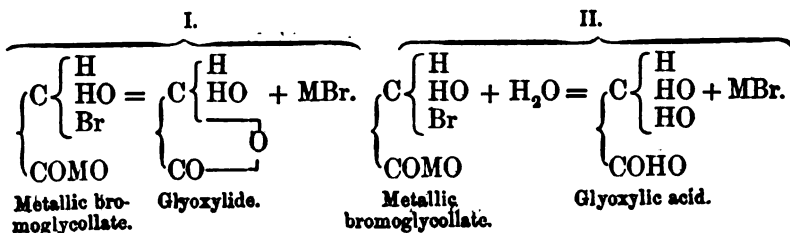
We first find, as is agreed on all hands, that a metallic chloracetate, or bromacetate, when heated alone, yields nothing but a chloride or bromide and glycollide, but when heated with water yields a chloride or bromide and glycollic acid.



We then find that when a dibromacetate is heated alone, and also in the presence of water, analogous reactions take place.

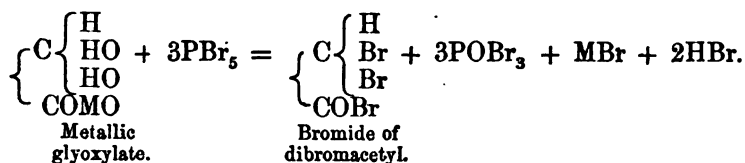


And, lastly, that by heating a bromoglycollate alone, we obtain, as in the two preceding examples, a neutral body and a bromide, and, if water be present, an acid and a bromide. From this we conclude that perfectly analogous equations to those used above will express these two reactions:



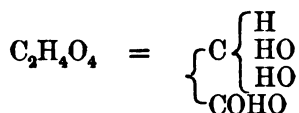
This last equation we further corroborated by the decomposition of bromoglycollate of silver in the presence of alcohol, whereby a neutral ether only was produced.

To further support our views of the existence of HO in the places previously occupied by bromine, we reversed our mode of proceeding and again placed the bromine in its original position, this change being effected by means of pentabromide of phosphorus:—



The resulting bromide of dibromacetyl was converted into dibromacetic ether, then into dibromacetic, and, lastly, into acetic acid, thus completing the circle of transformation back to our original starting-point, viz., acetic acid.

We are therefore forced to conclude, that glyoxylic acid, whether obtained from acetic acid or alcohol, possesses the formula—



which, as shown in our previous paper, bears a relationship to a triatomic alcohol similar to that borne by glycollic acid to a diatomic alcohol.

Dr. Debus gave the formula,  $\text{C}_2\text{H}_4\text{O}_3$ , to glyoxylic acid, from the analysis of the ammonia salt, all other salts giving numbers corresponding to  $\text{C}_2\text{H}_4\text{O}_4$ . Seeing the rapidity with which glyoxylate of aniline changes, may not the ammonia salt likewise change, and, when dry, correspond to an amide, which, on being dissolved in water, is again converted into the ammonia salt?

#### APPENDIX.

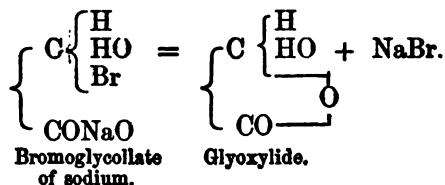
Since writing the foregoing paper, we have made a few further experiments on the formation of glyoxylic acid. We have already shown that when bromoglycollate of silver is decom-

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posed by heat alone, or in the presence of dry ether, glyoxylic acid is *not* produced, but a yellow powder, consisting of bromide of silver and an insoluble organic body, is the result. This organic body we regard as the anhydride of glyoxylic acid, analogous to glycollide. It appeared to us that, could we obtain a similar decomposition with some other metallic derivative of bromoglycollic acid, containing a metal capable of forming a bromide easily soluble in water, we might obtain this anhydride in a separate state. Acting upon this suggestion, we prepared a small quantity of the bromoglycollate of sodium, carefully dried it, and then heated it in the air-bath to a temperature of 120° to 130° C.; at this temperature it gradually decomposed, and on the addition of water was found to be principally converted into bromide of sodium and an insoluble amorphous white powder.

The white powder dissolves perfectly in boiling water, forming a strongly acid solution; and this, if heated with hydrate of barium, immediately yields a precipitate of oxalate. When it is neutralized with an alkali and then treated with an aniline salt, a yellow precipitate is produced. Both of which reactions prove the presence of glyoxylic acid.

We therefore regard this substance as pure glyoxylide, having the formula  $C_2H_2O_3$ , as shown by the following equation representing its formation:—



This substance dissolves very easily in aqueous ammonia, producing a solution which is evidently a glyoxylate, as it gives the yellow aniline reaction freely.

Glycollide, with aqueous ammonia, yields glycollamide; this substance ought, therefore, under the same circumstances, to yield glyoxylamide; but it would appear that this amide, as soon as formed, assimilates water and becomes an ammonia salt, a result which bears strongly upon the concluding remarks of our paper.

We hope to make further experiments with the anhydride, and to establish its formula by quantitative experiments.



XXVII.—*On the Solubility of Xanthine (Uric Oxide) in dilute Hydrochloric Acid.*

By H. BENOE JONES, M.D., F.R.S.

IN the Journal of the Chemical Society, vol. xv., 1862, p. 78, I have published a note on a deposit of crystallised xanthine in human urine.

The deposit dissolved in dilute hydrochloric acid, and when evaporated to dryness gave microscopical six-sided laminar crystals, which were so remarkable, that a sketch of some of them was given.

The solubility of the crystalline deposit in hydrochloric acid led to a doubt whether the substance really was xanthine, for in many chemical books xanthine was said to be insoluble in hydrochloric acid. Liebig and Gmelin\* say, "in hydrochloric or oxalic acid, xanthine is not soluble, or only very slightly, and by this it may be distinguished from cystine." Berzelius in his Chemistry repeats this statement on the above authority. Dr. Golding Bird, in his book on Urinary Deposits, 1844, p. 103, says, "uric oxide is insoluble in hydrochloric acid," and Professor Fownes, in the first edition of his Chemistry, p. 525, says, "xanthic oxide is not soluble in hydrochloric acid." Lehmann (Physiological Chemistry, vol. i. p. 145), says it is distinguished from cystine by its insolubility in hydrochloric acid.

On the other side, Dr. Marcet, the discoverer of this substance, in his book on calculous disorders, p. 106, says, "the mineral acids also dissolve it, though not near so readily as the alkalis. The residues of its solution in the muriatic and sulphuric acids are white." Schlossberger, in his Chemistry (fifth edition, p. 580), says, "contrary to what has been stated, it dissolves in mineral acids, freely in hot hydrochloric acid, and on cooling the combination with hydrochloric acid is deposited in a crystalline form."

A section of a calculus of this substance weighing 19 grains, removed from a boy four years old in the Punjaub, having been discovered by Mr. T. Taylor, in the collection of the College of Surgeons, a very small portion was given to me to determine whether it was soluble in hydrochloric acid, and whether it would give the six-sided crystals which I have described in the Journal of the Chemical Society (vol. xv, p. 78).

\* Ann. Ch. Pharm. xxvi, 340.

The stone consisted entirely of dark brick-coloured xanthine. It gave the characteristic yellow reaction with nitric acid becoming reddish with ammonia or potash. It was distinctly soluble in dilute hydrochloric acid, even in the cold; it dissolved much more rapidly when heated; and on evaporating the solution to dryness, it gave the most characteristic, microscopic, six-sided crystals, soluble in water.

The calculus dissolved in dilute sulphuric acid, and on evaporating the liquid, and examining the residue by the microscope, very distinctive tufts of acicular crystals were obtained.

The solution in nitric acid also gave microscopic crystals; but these were much less distinctive than the crystals from the hydrochloric or sulphuric acid solutions. They had more resemblance to the crystals of xanthine that were met with in the urine, of which a drawing is given in my former note.

Having thus found that, as regards the solubility in hydrochloric acid, and the form of the crystals deposited on evaporating the solution, xanthine agreed perfectly with the deposit which I have described, I endeavoured to obtain the same crystals that I found in the urine, by dissolving the powdered xanthine in healthy urine.

The xanthine dissolved slightly in healthy acid urine by the aid of heat, but on allowing the solution to evaporate, no crystalline deposit was obtained.

When the xanthine was dissolved in urine rendered slightly alkaline by ammonia or soda, no crystalline deposit formed on standing or on evaporating.

These experiments were frequently repeated, but I failed to reproduce artificially the crystals of xanthine which occurred naturally in the urine. Still the solubility in hydrochloric acid, and the form of the crystals obtained on evaporating the solution, leaves no doubt whatever that the crystalline deposit which I observed in the urine was xanthine.

It is by no means impossible that such crystals have often been considered, from microscopic examination alone, to be uric acid. At least, long since, the solubility of similar crystals on the application of heat has been passed over by me as remarkable.

From the occurrence of the xanthine in Langenbeck's boy, in the Punjaub boy, and in my boy, it is probable that these crystals are most likely to be found in the urine of children.

XXVIII.—*On Chemical Geology.*

[A Lecture delivered before the Fellows of the Chemical Society, Feb. 20, 1868.]

By DAVID FORBES, F.R.S., &c.

IN considering a subject so extended and important as Chemical Geology, it is evidently impossible, within the limits of one lecture, to put forth anything like a complete exposition of its principles, or to enter into details; this evening, therefore, I propose, after a few introductory remarks explanatory of the principles which have guided me in my investigations, to venture upon a short sketch of the chemical geology of what may be termed the cosmogenetic era in the history of our globe, and then to attempt an explanation of some of the phenomena connected with the great changes which have taken place in the earth, from that early period down to the present time, in which chemical action has played an important part.

The history of the natural sciences fully shows how often their votaries have allowed themselves to be influenced by some often preconceived hypothesis, which has led them to ascribe to some one favourite cause effects which in reality have proved to be the result of a combination of several causes.

To this tendency may be attributed the formation of the opposing schools of geology, the Plutonic and Neptunic, or igneous and aqueous. Yet it must at the same time be remarked that this occurred at a time when experimental science was hardly out of its cradle.

The rapid strides in advance made by all the natural sciences in every direction, have now, both by the accumulation of facts, and the elucidation of the laws which govern them, shown how difficult, if not impossible it is, in the study of nature, to draw any sharp line of demarcation as to where any one cause ceases, and another begins to operate.

Increasing and more exact knowledge shows that mere fire and water are not the only great agents that work the changes which have taken place, and still do take place in our globe, and that the geologist, in order to arrive at sound conclusions, must take the various effects produced by chemical action, heat, light, electricity, and mechanical force into full consideration.

The study of the correlation of these forces is also one which, although as yet but in its infancy, promises great results in the explanation of geological phenomena. It has now been satisfactorily proved, that mechanical force may, if not directly, at least indirectly, be converted into chemical action, or in other words, cause forces, formerly regarded as purely chemical, to be brought into play, so that the assumption that mechanical forces can only give rise to what have been termed mere mechanical results, must be guarded against in consideration of nature's phenomena.

Every geologist admits the great part which mechanical energy has taken in bringing about the changes in the physical configuration of this globe ; as for example, amongst others, the compression, crumpling up, and consolidation of strata, and in the elevation, depression, and dislocation of enormous rock masses, effects which have characterised and still do characterise the history of the earth ; and as it is known that the expenditure of mechanical power is attended by a corresponding development of heat, which in its turn may give rise to a proportionate amount of chemical action, it evidently becomes a subject of great interest to inquire into how far such conversion of mechanical into chemical force may have assisted in the metamorphic alteration of rock-masses.

The familiar experiment of striking a light with flint and steel is an excellent illustration of the conversion of mechanical force into heat, along with the development of chemical action ; for the effect of the mechanical energy exerted is to heat the minute particles of metal detached from the steel to such a degree as to enable them to combine chemically with the oxygen of the air ; the heat generated being then so intense, as to fuse the product into minute spherules of magnetic oxide of iron, as can be seen when the sparks are collected on paper, and examined under the microscope.

Whilst directing attention to the importance of the study of this subject, the geologist not versed in chemistry must, however, be warned against attributing too much to such agency, especially when examining what appears to the eye to him to be the transition (or transmutation) of one rock into another ; for before accepting such evidence, the chemist will insist upon previous proof by chemical analysis that there are present in the one rock the chemical elements requisite for the formation

of the other; or if not, that there is a rational mode of explaining how any deficiency in component parts has been supplied, or any surplus removed.

The study of electricity (with magnetism) in its relations to geology is not unlikely to throw light upon some now obscure points, but has not as yet been much attended to, and I must confess that an examination of what has been written upon the application of electricity to explaining the formation of mineral lodes, makes one suspect that the effect has at least in some cases been mistaken for the cause; and that the electricity which was supposed to have brought about certain chemical changes, may have in reality been the result of these very changes, and not their cause.

After thus insisting that the investigator in the study of chemical geology must of necessity call in to his assistance a knowledge of the collateral branches of the natural sciences, I may here state, that in appearing before the society to-night, I do so not as a partisan of any school of geology, whether Plutonic, Neptunic, quiescent, or cataclysmic, but as an independent observer, who believes that the principles upon which all these schools have been founded have each had a share in nature's operations, and that they therefore must be taken into equal consideration, and who further assumes that most, if not all the phenomena of nature have been effected by a combination of more forces, and that the same identical phenomena may at times be the result of agencies, totally different from those which at other times may have given rise to them.

The study of mineralogy, which is the alphabet of petrology, shows that very many mineral species, and amongst them some of the most common rock-constituents, may have at different times been formed by very different processes.

Thus, amongst the specimens here on the table before us we have crystallised silica or quartz occurring in nature—

As an igneous product in recent volcanic lavas.

As an aqueous product from crystallisation and deposition from solution.

And as a gasolytic product in tubes from the decomposition of its compounds with fluorine.

Sulphur is also seen—

As an igneous product from volcanoes.

As an aqueous product, both from hot springs and as a product of decomposition of sulphides.

And as a gasolytic product from fumeroles.

And several others.

Experimental researches on the artificial formation of minerals also prove satisfactorily that the same mineral or product may be obtained artificially by very different, often the most opposite processes and reactions.

Thus we find silica in the hearths of iron furnaces, formed by igneous action, apparently by the oxidation of silicon.

In the wet (or aqueous) method, silica is obtained in the decomposition of silicates by acids.

And lastly, it can be produced as a gasolytic product from the decomposition of these compounds of silicon with chlorine and fluorine.

Again, we can produce, by analogous processes, sulphur and carbon, either as igneous, aqueous, or gasolytic products, and amongst other specimens on the table will be found fine specimens of crystallised metallic copper, produced artificially, both by igneous and aqueous process, as well as from condensing the vapours which are evolved from the copper refineries.

Felspar has been produced artificially as a furnace product, as well as by the action of water; and even some of the zeolites or hydrated silicates have been produced experimentally, both by igneous agency as well as by aqueous actions.

Numerous other examples might be brought forward in addition to those here mentioned; and the conclusion I would deduce from their consideration, is that it is impossible to be over-cautious in attributing the formation of minerals, or of the rock masses in which they occur to any one cause, to the exclusion of other agencies.

Before proceeding further, it appears advisable, in order to prevent misunderstanding, that the precise meaning attached to certain terms employed in geological inquiry, should be clearly defined, as they are likely to occur repeatedly, in the course of this evening; amongst these the terms igneous, aqueous, and gasolytic are of most importance.

*Igneous action* in geology is equivalent to volcanic action, being the action of heat as is seen in the active volcanoes of the present day, the study of which led to the foundation of the plutonic or igneous school of geologists.

This action, is not as occasionally has been misrepresented, a mere dry fusion, such as would take place when the chemist fuses anhydrous substances in his crucible, and of which, as observation shows, no example can now be seen in nature's operations, but is one in which, whilst heat undoubtedly plays the grand part, is in nature invariably accompanied by the action of vapour and gases; and any one who ever has seen a volcano in eruption can bear testimony to the enormous volumes of vapour and gases which are emitted, and which, could means be discovered of measuring or weighing them, would be found to bear a very considerable ratio, to the total amount of solid matter actually sent forth by the eruption.

*Aqueous Action.*—The action of water (fresh or saline), such as we are accustomed to observe on the present surface of the earth; this is not however the mere solvent action of the pure water employed by the chemist in his researches in the laboratory; but is one in which the air, gases, salts, and other bodies contained in natural waters, along with the action of heat (by raising or lowering the temperature) materially alter the solvent powers of the water itself.

*Gasolytic Action.*—The action of gases and vapours more or less assisted by heat.

All these agencies are subject to be modified by the effects of chemical action and mechanical force, but whilst in all these cases, we have the action of heat, of water, and of gases, each playing a more or less prominent part; there can still be no grounds for misunderstanding or confusing the meaning of the three terms.

In igneous or volcanic action, we find that, whilst the effect of heat predominates, still the presence of heated vapours and gases exercises a most important influence in modifying the results; in this case, the water present is in the form of steam, although it is possible that a minute amount of water may be imagined to exist as water entangled in the melted rock under enormous pressure.

In aqueous action on the other hand, the water which acts as a liquid, not as a vapour, is the main agency; yet the effects of the air, gases, and solid constituents, as well as of its temperature, must be taken into full consideration, since they often may very materially affect the result.

In now attempting to apply the principles of chemistry, to

the explanation of the changes which our globe has undergone, it appears most systematic and convenient, to commence at a point as far back in its history as the evidence furnished by the sciences of astronomy and physics can carry us, and from this point to work out step by step the subsequent phases which it has passed through. As however the first stages in such a chemico-geological chronicle must necessarily be but hypothetical, it is important, in the first instance, to assume as little as possible for granted; and therefore the sole axiom, on which this sketch is based, is the conclusion which astronomers and natural philosophers appear to have very generally arrived at, viz., that our globe was at one period in so highly heated a condition, that its entire solid contents were in a state of complete liquidity.

I am fully aware, that some observers have gone still further back, and imagined the whole of the constituents of the globe as having been previously in the gasiform condition as a nebula in space; and that they find evidence in the recent discoveries made by the spectroscope in support of this view; also that others have conjectured that the chemical elements in such a nebula would be in a "disassociated" state of chemical indifference to one another, until a lowering of temperature brought about combination and condensation.

Without disputing either the possibility or probability of these views, I consider that in the present state of our knowledge of the subject, it would be imprudent to adopt them; for too little is known either of the effect of such intense degrees of heat, or of the state of "disassociation" or indifference of heated gases, to warrant confidence being placed in conclusions based upon such imperfect data.

Chemists will no doubt admit that it is but fair to assume, that the chemical elements which then made up the world were the same, and possessed the same properties as those now recognised, as of course it puts an end to all reasoning upon this subject, if this be not granted; for the very supposition that the interior of the earth (with the exact nature of which we are and ever must remain ignorant) was composed of elements unknown to the chemist, would at once annihilate all calculations or deductions.

Having now an intensely heated world given us for consideration, it is in the first place inferred, that this would be composed



of bodies of two different characters—solid and gasiform; which, by their situation and rotation, would bring about the formation of a molten sphere of the more refractory bodies, surrounded by an intensely heated gasiform atmosphere of the more volatile.

In considering the distribution of the chemical elements in this sphere and atmosphere, we must be guided by the knowledge we possess of the effect of intense heat upon the elementary bodies and their compounds; and it naturally follows that the more volatile bodies would remain longer in the atmosphere than the more refractory ones, which would be condensed previously into the sphere. It must also be remembered, that at so intense a temperature we should not only find in the atmosphere those bodies which are gaseous at ordinary temperatures, but in addition, many others, such as the vapours of various metals, &c., &c., which do not assume that form, except when exposed to extremely high heats.

The affinity of bodies for one another would no doubt also be considerably different at this temperature, and their mutual chemical reactions might also be expected to vary considerably from those which are known to take place at ordinary temperatures; and it is to be regretted that the effects of heat in modifying the affinity of bodies for one another, are as yet but very imperfectly understood, although it is proved that they possess a very strong influence in so doing: we know for example, that sodium will, at comparatively low temperatures, decompose carbonic acid, yet at much higher temperatures, carbon decomposes soda. Again iron at a red heat decomposes water, whilst hydrogen at a similar heat decomposes the oxide of iron.

Under these circumstances, it is evident that great latitude is given to chemists when explaining the reactions which may be conjectured to have characterised this epoch in the earth's history, as at present it would be impossible to produce sufficient experimental evidence, to prove or disprove various different and apparently contradictory opinions which might be advanced to account for such phenomena.

I shall therefore here give a summary of the main conclusions, which the examination of this subject has caused me to arrive at, and then go into an examination of the arguments for and against their adoption.

Supposing the grand battle of chemical combination at an

end, and the compounds so formed, resting as it were during an armistice of neutralization, whilst at the same time the whole world still continued in a state of intense incandescence, I have ventured to imagine the state of things at this moment, as follows :—

Both in the molten sphere, and in the atmosphere surrounding it, the first impulse of these newly formed compounds would be to obey the laws of gravity, and so arrange themselves in strata or zones according to their respective densities; here I would remark that these separations are only to be regarded as approximative, for there would always be some greater or less admixture of the substance of one zone with another, either from mechanical entanglement or diffusion.

The solid sphere would resolve itself into some three grand zones (probably with subzones), it is imagined, somewhat as follows :—

An external layer or crust of highly acid silicates, with most probably much free quartz, the bases of these silicates being chiefly alumina and potash with minor quantities of soda, lime, magnesia, &c. Below this a second zone of silicates of more basic character and greater density, the bases being lime, magnesia, alumina, oxide of iron, soda, with but minor quantities of potash, &c.; and still deeper, a far denser sphere or nucleus, containing most of the denser metallic elements, in part, at least, in combination with sulphur, arsenic, &c.

Whilst, on the one hand, the zones formed in the earth are considered to have possessed a somewhat stable or permanent character, those formed in the atmosphere would, on the contrary, be the reverse; for no sooner had the gasiform products forming them, by, in the first instance, obeying the impulse of gravity, and so overcoming the counteracting tendency of the laws of the diffusion of gases, than these latter would assert themselves, and in process of time entirely obliterate this arrangement.

In the first instance, however, we should have the atmosphere next the earth composed of a dense vapour of those compounds volatile only at a high temperature, amongst which the vapour of chloride of sodium or salt would be probably one of the most prominent. Above this we should find the carbonic acid, then oxygen and nitrogen, whilst the vapour of water would be elevated still higher. As before stated, such an arrangement

would be gradually obliterated by diffusion, but as the element of time is one of vital importance for considering the effects of diffusion, it is imagined that before being obliterated this arrangement may possibly have had considerable influence in modifying the chemical reactions which took place at this period in the earth's history.

The effect of the cooling of such an atmosphere would be, in the first place, to condense the vapour of salt and other chlorides, &c., upon the already solidified crust of the earth, covering it with a layer of these substances in a solid state, the chloride of sodium in which has been calculated to have alone been sufficient to clothe the entire sphere with a coating of salt some ten feet in thickness.

A still further reduction in temperature would now condense the steam in the atmosphere, which falling as rain on this saline crust, would, in greater part, dissolve it, forming the ocean, which would thus be salt from the first moment of its appearance on the face of the globe. The atmosphere now surrounding the earth would contain much less oxygen, and all the carbon in the form of carbonic acid (excepting only the amount of that acid carried down with the rain), but otherwise would probably not differ much in composition from what it is at the present moment.

Regarding the above as merely a sketch, in the main correct, I would, however, remark that it would be absurd to attempt to define, with any sharpness, the exact action and extent of the reactions, or to insist upon that the entire amount of any one element entered only into one particular state of combination, to the exclusion of all other reactions, which might have been influenced by circumstances, amongst others, of position and time. My meaning may be best explained by an experimental illustration. If we suddenly throw a little sulphuric acid into a solution containing both lime and baryta, the precipitate which is at once thrown down is not pure sulphate of baryta, but an indefinite mixture of the sulphates of baryta and lime; for the sulphuric acid immediately seizes upon the earths nearest it at the moment, and before it has time to obey its superior affinity for baryta, it is carried out of the field of action as a precipitate of mixed sulphates.

I will now enter into a consideration of the arguments which are brought forward in opposition to this view.

It is advanced, in the first place, that the chlorine, instead of uniting with the sodium, as supposed by me, would have combined with the hydrogen and gone into the atmosphere as hydrochloric acid. Believing that the hydrogen would have united with the oxygen to form water, I also contend that the affinity of sodium for chlorine is greater than for hydrogen, since sodium, both in the cold as well as hot, decomposes hydrochloric acid, whilst, on the contrary, hydrogen, whether cold or hot, does not affect chloride of sodium.

It is further advanced that the sodium really united with oxygen to form soda, which would be converted into silicate of soda by the mutual reactions between soda, steam, and silica. In this explanation secondary reactions are dealt with, instead of primary, which are supposed to be specially characteristic of this stage in the world's history. It must also be remembered that carbon, at a high temperature, reduces soda, and that the volatility of sodium would bring it in contact with chlorine in the atmosphere, whilst the silica remained below in the earth's mass in the solid form at this temperature. A portion of the sodium is, however, admitted by me to have combined with oxygen, and to have subsequently become silicate.

Against my supposition that the sulphur mainly united with the denser metals to form sulphides which at once sunk through the still fluid external zone of silicates, and so became protected from oxidation, it is contended that the sulphur would have united with oxygen and gone into the atmosphere as sulphurous acid. Here it must be remembered, however, that this reaction took place in the presence of a vast amount of hydrogen, carbon, silicon, phosphorus, &c., along with alkaline and earthy metals, all ready to seize the oxygen, and capable of decomposing sulphurous acid if formed.

Sulphurous acid is decomposed by the other metals at an elevated temperature, with the production of oxides and sulphides of these metals, as also by carbon, with the greatest ease, with the separation of sulphur (the subject of a patent taken out by Gurlt some years back for the recovery of sulphur from the fumes of metallurgical works). In addition to all this it must not be forgotten that the atmosphere then contained an overwhelming amount of carbonic acid and nitrogen, which would both act as a shield against oxidation, as well as dilute,

if not entirely prevent, the effect of any strong oxidizing action, this being proved by the comparatively small amount of oxygen present in atmosphere of this epoch.

In considering that the central nucleus of the earth must contain a vast accumulation of the denser metals and their compounds, I have done so for the following reasons :—

The mean specific gravity of the earth is proved to be about 5·4, and, leaving the water out of consideration, the mean density of the solid exterior with which we are acquainted cannot be assumed to be higher than 2·75; it follows, therefore, that the internal portion of the earth must possess an immensely greater density than the exterior.

This has been explained by supposing that the increase in density towards the centre arose entirely from the increased pressure, but experimental inquiry does not appear to warrant a conclusion which would require that even the most solid and compact rock we know at the surface should be (if found at the centre of the earth) condensed into a mere fractional part of its volume; for, so far as experimental inquiry has gone, it has tended to show that after a certain point bodies either attain a maximum density or that the condensation bears a less and less ratio to the increase in pressure employed, thereby indicating the necessity of seeking for other explanation than the mere mechanical effects of pressure, in order to account satisfactorily for the great density of the earth's interior.

A simple calculation will show that if we regard the mean specific gravity of the earth as 5·44, and that of the external zone or crust as 2·75, and imagine that the earth is composed of three concentric layers of equal thickness, and of densities increasing respectively in arithmetical progression, there would be respectively an outer crust of specific gravity 2·75, an intermediate one of 10·82, and a central kernel, or nucleus, of 18·89; and if, instead of three zones, more than this number are imagined, then a similar calculation will show that the specific gravity of the central nucleus will be still higher.

. Knowing, therefore, that but few, even of the metallic elements, possess (at the earth's surface) a density equal to that of either the nucleus or intermediate zone, as shown by such calculations, I infer, therefore, that it requires not only the assumption that bodies do become greatly augmented in density by the application of pressure, but also that there must

be a great accumulation of the densest bodies we know (the heavy metals and their compounds) in the interior of the earth, in order to account for the high mean specific gravity of our globe.

The mineral and chemical composition of the original exterior, or crust, of the earth immediately after its solidification must ever be an open question in chemical geology, for neither do we, nor can we, even, expect to meet with any portion of the same in any part of the world, when we reflect upon the great changes it must have experienced during countless ages, and the vast amount of the *débris*, directly or indirectly the result of its wear and tear, which since has been spread over the surface of the globe by mechanical agency.

The conjectures I have ventured to form as to its probable nature are based upon a study of the mineral and chemical composition of rocks, which, in the present state of geological science, are recognized as being the most ancient on the face of our globe; and as quartz enters into the composition of these as a most prominent constituent, I, therefore, infer that it had been derived from the *débris* of the original crust.

It is necessary for me now to take into consideration any arguments which have been brought forward in opposition to the conclusion which I have thus arrived at.

In the first place, we have the assertion that the composition of the primitive crust would have excluded free silica. It might as well be advanced that the composition of cast-iron would preclude the existence in it of free carbon. A very analogous example, and, therefore, I leave it to the Society to decide whether it is not as correct reasoning to infer by analogy that quartz may have crystallised out of a solution of silica in highly acid silicates upon a lowering of temperature, as that the graphite in the specimen on the table before us has crystallised out of a solution of carbon in cast-iron, upon its temperature being lowered, which we know to be the fact.

But we have further proof of the contrary than merely reasoning from analogy, for, as is well known, the true volcanic lavas of both hemispheres contain abundance of free silica crystallised as quartz, and the study of the physical structure and crystallisation of this quartz furnishes complete proof that it could not have been mere entangled fragments of quartz, but

that it must necessarily have crystallised out of the melted mass of the rock.

Of late years another argument has been brought forward in order to prove that rocks containing quartz could not have been of igneous origin; and this argument is based upon a study of the specific gravity of silica.

The specific gravity of hexagonally crystallised silica, *i.e.*, the mineral species, quartz, in many cases of undoubted aqueous origin, is found to be 2.6, and the quartz out of many granites is also found to be 2.6.

On the other hand, silica artificially fused before the oxyhydrogen blowpipe to an amorphous glass, is found to possess a specific gravity of only 2.2.

On these few data the conclusion has been based, that quartz could not have been formed by igneous agency, but must invariably have been an aqueous product.

Now let us examine the value of this evidence impartially, for it is a question of vital importance in the study of chemical geology.

In the first place, we find that the transparent, vitrified, amorphous product, or glass, produced by the fusion of crystallised or uncrystallised silica, before the oxyhydrogen blowpipe, is not considered by the mineralogist as quartz at all; for it does not possess either the crystalline characters, physical properties, or chemical behaviour of the mineral species quartz.

The chemist further proves that its chemical reactions are totally different in very important points from those of crystallised silica; and would infer therefrom the probability of silica being dimorphous.

Further research informs us that the low specific gravity, chemical reactions, and physical properties of this vitrified product are not alone peculiar to the silica which has been fused before the oxyhydrogen blowpipe, but are common to other varieties of silica, both natural and artificial, whose origin could not have been from igneous fusion, as, for example the silica formed by the decomposition of gaseous compounds of silica or silicon; many varieties of silica from aqueous deposition; the silica of the carapaces of infusoria, &c.: facts which, if not considered as conclusive in totally invalidating, must at least create much doubt as to the soundness of a conclusion thus hastily arrived at.

It seemed strange, however, that before so much importance has been attached to an argument so evidently inconclusive, the simple test of its correctness should not have been resorted to, by taking the specific gravity of some of the quartz crystals found in true volcanic lavas, where there could be no doubt as to their origin; as I could not discover that this had been done by other observers, I have done so myself, with the most conclusive results for the specific gravity of quartz crystals broken out of some of the volcanic trachytes of Europe and America, was found to be exactly 2.6, or the same as that of the quartz from granite, or from undoubted sedimentary rocks.

This result would have been anticipated by the mineralogist, who regards hexagonally crystallised silica as quartz, whether it be of aqueous, igneous, or gasolytic origin.

Having thus treated at some length of the chemical reactions, which I have supposed had characterised what might be termed the cosmogenetic era in the history of our globe, a few words will now be devoted to the consideration of the physical structure and configuration of the earth at this epoch.

I assume that the cooling of the molten sphere ultimately resulted in the production of a globe in major part solid, yet containing in its interior a vast reservoir or reservoirs of still fluid igneous matter, which are still supposed to exist, although it is believed that the amount and character of their molten contents has varied considerably from period to period in the earth's history.

This being the case, it is quite immaterial to my views whether it is imagined that the earth commenced solidifying first at the centre, or at the surface; I am inclined to the opinion, however, that even if the earth, as is considered probable, owing to the influence of pressure, actually did commence solidifying at the centre, that on the other hand, long before this solidification had reached the exterior, a crust had also commenced forming at the exterior towards the centre, owing to the effects of cooling, and that there thus might be at the same moment a solid nucleus and crust, separated from one another by still, liquid, igneous matter.

It has been advanced, however, that such a crust could not form, since it would be heavier than the molten matter from which it had congealed, and therefore would sink down into it.

It is admitted that silicates, when solid and cold, are slightly denser than when molten; but as this crust would be formed in



all parts simultaneously, by a cooling action, taking place uniformly on all sides, it would be a hollow sphere, capable fully of sustaining itself, since its particles would mutually support one another.

The results of experiments upon some bodies which contract in cooling prove that the effect of heat in many, if not in all cases, was first to expand the previously cold substance more and more, up to about its point of fusion, when it again contracted in the act of becoming liquid, showing that although the cold substance really was heavier than when molten, that on the contrary the same body expanded by heat was actually lighter than when molten, and would float on the surface of the molten liquid just like ice upon water.

Applying this deduction, and remembering that the crust of the earth was not formed cold, but, on the contrary, solidified at a very intense temperature, it becomes easy to explain both the probability of its formation and the possibility of its not sinking into the fluid matters below it.

Upon the complete solidification of this crust over the entire exterior of the earth, it may be supposed that the surface of the sphere would in the first instance present a tolerably even appearance or contour; this uniformity would, however, soon become disturbed by cracks and fissures produced by the contraction of the mass in cooling still further, and the subsidence of portions of the crust thus broken up may be conjectured to have caused some of the still melted matter below to be protruded upwards into these cracks and fissures, forming dykes in the original crust.

The sides of these cracks or fissures would also be frequently more or less dislocated, and so form lines of faults interrupting the previously regular contour of the surface, and forming the first elevations or mountains on the globe, which, by giving direction to the action of the water in the ocean and rivers, would in a great measure determine the main features of the physical geography of this epoch. Nor would these features be readily obliterated, since by in turn giving direction also to the deposition and demarcation of sedimentary matter, their primeval influence, when not counteracted by subsequent cataclysmic action, might be handed down through long ages and formations, even in some cases to the present period.

We have now concluded what might be termed the chapter

of Genesis, or the cosmogenetical era of the history of the earth, since from this period up to the present day I regard all the changes which have taken place in our globe as having been effected by agencies similar, if not identical, with those now in operation. Sedimentary rocks were formed from the wearing down and disintegrating action of water and the atmosphere, or as it is termed, the weathering of the primitive crust, and the subsequent stratification of the *débris* so formed by the action of rivers and of the sea, just as at the present moment they are in the course of formation from the *débris* of pre-existing rocks. Eruptions of igneous matter from sources in its interior from time to time disturbed and broke through the primitive crust, and the rock strata above it, in course of formation from its *débris*, just as at the present day (though possibly on a somewhat smaller scale) similar outbursts are produced by volcanic action.

The primitive crust of the earth, split up as before stated by the effects of contraction, would be further broken up and pulverised by the mechanical force of water, powerfully assisted by the disintegrating and decomposing action of the carbonic acid present in such great excess in the primeval atmosphere, and thus would in process of time be so comminuted as to enable its particles to be sorted by the action of rivers and the sea, which would arrange them in sedimentary beds of varying density and character.

A large portion of the quartz, more or less free from other silicates, would at once be formed into beds of sandstone and grits; the silicates, however, would first undergo a partial decomposition from the action of carbonic acid and water, causing the removal of a large portion of their alkalis, which would be carried into the sea in the state of carbonates, and there react upon the earthy and metallic chlorides contained in the ocean. Particles of metallic sulphides entangled in the silicates (for as before stated no mechanical separation according to densities can be in nature regarded as perfect) would become oxidized into sulphates and also carried into the sea, which would receive a further amount from the gaseous compounds of sulphur which are supposed to have accompanied the outbursts of igneous matter from the interior of the globe.

The partially decomposed silicates, along with more or less quartz, would, by the action of the sea and rivers, also be

sorted, and deposited as sedimentary beds, forming the argillaceous and arenaceous strata of that period, which were subsequently altered in character by metamorphic action.

The development of organic life, at first of the lowest type, would now introduce another character of deposits into the sedimentary series, as by abstracting the lime contained in the ocean (in the form of carbonate, sulphate, and phosphate, the two latter compounds being the probable source of the sulphur and phosphorus which play so important a part in the vital economy of both animals and plants), this would gradually afford the materials for the building up of limestones and calcareous strata, whilst at the same time vegetation, by assimilating the carbonic acid in the atmosphere, would, from the remains of its organic structure, also introduce beds of carbonaceous character into the series; and further, by clearing the atmosphere of the overwhelming excess of carbonic acid originally contained in it, and returning a corresponding amount of oxygen to the air, it gradually paved the way for the increased development of animal life, and eventually effected the purification of the atmosphere to such a degree as to permit of the existence of air-breathing animals upon the face of the earth.

By these means, therefore, we are enabled to explain the formation of the more important classes of rock masses which characterize all sedimentary formations from the most ancient up to the most recent, namely:—the arenaceous, argillaceous, calcareous, and carbonaceous strata, with the numerous deposits of intermediate character formed from a greater or less admixture of the materials of two or more of the above.

These causes would operate through all time; for although in the first instance or commencement, they could act only upon the primary crust and its *débris*, they would in later ages have a far larger field for work in the destruction of all the stratified and unstratified rocks preceding them, and the reconstruction of new formations from their ruins.

The formation of these sedimentary strata, did not proceed uninterruptedly however, for any long period; for from time to time outbursts and intrusions of the igneous matters contained in the earth below, disturbed and broke through the strata.\*

\* These eruptive rocks, in cooling, become solidified first at the exterior, and  
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forming dykes, ramifications, and bosses, as well as sheets sometimes overflowing, and at other times intercalated between the beds themselves. Showers of volcanic ashes may, probably, in some instances, have accompanied these outbursts, and by falling upon the land, or into the sea, have formed beds in the series of a totally different character to those before alluded to, which were merely derived from the breaking up and disintegration of previous rocks, or from the action of organic life. When currents of lava from these eruptions poured into the sea, or forced their way from below up through the bed of the ocean, the igneous matter would be converted into tuffs; that is to say broken up, disintegrated, and so brought into a state of division more or less fine, in proportion to the greater or less cooling action of the water mass in immediate contact with it. The action of the waves would then assist in spreading out these igneous products, and arranging them in beds similar to those of ordinary detrital origin, whilst the texture of such beds would vary from that of the coarsest breccia down to the finest mud, and, as is commonly the case, such deposits present themselves as alternating beds of coarse and fine character. Upon the consolidation of such masses, rocks are formed, closely identical in chemical and mineralogical composition to the original eruptive rock from which they were derived, and in external appearance, particularly when close-grained, often undistinguishable from it by the naked eye; in most cases, however, the microscope can distinguish between them with certainty; but it has long proved an enigma to both the chemist and the geologist, when he finds a rock taken out of an apparently normal stratified or sedimentary deposit, to have the same chemical composition as one of undoubtedly eruptive or igneous nature.

To the difficulty in discriminating between such rocks, I

by contraction are frequently, more especially when in larger masses, split up by joints and fissures, which occasionally might be immediately filled up by the still liquid part forced into them from below by the general contraction of the mass of rock; this accounts for what may be called contemporaneous veins in these rocks, which in general present a different external appearance to that of the rest of the rock, owing to different conditions of cooling and crystallisation from that of the rest of the mass. As acid silicated rocks, like granite, contract more in cooling than basic ones, like dolerites, these veins are found to occur more commonly in the former than in the latter. They must not, however, be confounded with those veins or dykes produced by subsequent eruptions of igneous outbursts, cutting through the previously erupted rocks in later geological periods.

attribute in great measure the conflicting opinions which have divided geologists as to the origin of granites and various other of the older plutonic rocks, and my experience in the field, assisted by the microscope and laboratory, has satisfied me that very many of the so-called granites and gneisses are really sedimentary products of the breaking up of true igneous eruptive rocks, stratified by aqueous agency, and subsequently, as it were, reconstructed or consolidated. At the same time, however, I have also come to the conclusion that there also are true eruptive granites of igneous origin, *i.e.*, the products of action similar to volcanoes, the only apparent physical distinction being that probably the conditions of pressure may have been somewhat different in the older periods.

This is a point of great interest and importance in the study of the older rocks, and therefore I will attempt to answer the arguments which I find advanced against the igneous origin of granite, not by a reference to authorities on the subject, but by what may be called volcanic facts, that is, data obtained in the examination of the mineralogy and petrology of volcanic districts. The main arguments brought against the probability of the aqueous origin of granite and several other plutonic rocks are—

1. That granite contains free quartz. As before stated, this is also the case in many volcanic lavas, and the remarks made on this subject, when considering the possibility of the presence of free silica in silicates, are all applicable here.

2. The quartz in granite is of specific gravity 2.6, or the same as that of quartz of aqueous origin; as previously stated, this is also the case with the quartz from volcanic lavas.

3. The quartz from granite contains water.

This is also the case with the quartz out of the rocks of the volcanic island of Ponza in the Bay of Naples, and in the volcanic lavas from Peru.

4. That in granites, some of the more fusible minerals have often solidified and crystallised before the less fusible ones.

In the lavas from Vesuvius it is common to find crystals of refractory leucite sitting upon the easily fusible augite, which had crystallised first.

5. That granite frequently contains hydrated minerals.

The quartz, felspar, nepheline, and idocrase from Vesuvius all contain water. A specimen on the table, broken out of the

lava current of March, 1865, whilst still flowing from Etna, contains crystals of stilbite.\*

It appears to me, therefore, that when the facts and arguments on both sides of this question have been impartially considered, the conclusion will be drawn that there are true eruptive igneous granites, and that the arguments advanced against the igneous origin of granite are inconsistent, as well as inconclusive.

Many of the outbursts of plutonic rocks which, as described, had thus disturbed the sedimentary strata, are accompanied, at the same time, by mineral veins or lodes, which most frequently are found traversing the strata in the vicinity of such disturbances, and would, therefore, appear to be intimately connected with these outbursts or intrusions. The minerals contained in such lodes are also observed to vary according to the nature of the eruptive rock which appears to have caused their formation.

The solid matters injected into the strata and brought up by these eruptions, whether poured out over the land or into the water, would ultimately, by their disintegration and decomposition, yield up some of their constituents in a more or less soluble form, as part of the alkalis, lime, magnesia, &c. This process will explain how some portion, for example, of the lime requisite for keeping up the supply of that earth in the ocean for the assimilation of organisms, which continually abstract it from the same, can be accounted for.

In like manner, since these eruptions are considered to have had most features in common with volcanoes, it is inferred that they also would have been accompanied by great volumes of vapours and gases, amongst which, as in the case of the active volcanoes of the present day, the products of the oxidation of sulphur would have been prominent, and by their subsequent reactions assist in accounting for the large quantity of sulphates known to exist in the ocean.

Many deposits of sulphates, chlorides, and other compounds,

\* Bunsen has proved experimentally that hydrated silicates, analogous to those in eruptive rocks, can be formed at high temperatures, and retain their water at such temperatures, as long as enclosed in their matrix; if extracted from this, however, the water contained in them can be expelled at a very gentle heat. Laurent has also shown that borate of potash fused at temperatures above the melting-point of silver retains water which, singularly enough, can be expelled in bubbles by reheating the vitrified mass over a spirit-lamp so as hardly to soften it.

such as gypsum, rock-salt, carnallite, &c., have no doubt resulted from the evaporation of lagoons or arms of the sea, cut off from the ocean by movements such as the elevation of the line of coast, &c.

The rocks formed on the solidification of the molten matter brought up by these outbursts or intrusions, which, as before mentioned, have disturbed the sedimentary beds from the oldest period up to the present day, possess a common general physical structure and arrangement, but otherwise are not all of one character, since they differ very considerably in *chemical* and mineral constitution, according to the geological epoch of their appearance in the crust of the earth.

Unfortunately, however, the attention of geologists has been but extremely little directed to this subject, and consequently trustworthy data as to the geological occurrence and mineral contents of such rocks are at present far from being sufficiently numerous or exact to allow of a decided conclusion being arrived at by their study. The result of a prolonged inquiry led me some time ago to announce the probability that—

1. Eruptive or intrusive rocks of identical mineral constitution have made their appearance or intrusion into the earth's crust at similar geological epochs.

2. That the minerals, or classes of minerals, accompanying or associated with such rocks may serve as a means of distinguishing the several eruptions in geological chronology.

3. When the geological epochs of the appearance of two or more intrusive or eruptive rocks are known to differ, these rocks will then also be found to differ essentially in mineral constitution.

As far as I have yet been able to obtain trustworthy data, these views have been confirmed, but the evidence is as yet far too imperfect to put these forward as proved, although I indulge in the belief that further researches will show them to be correct.

The chemical analyses of eruptive rocks show, in the first place, that they may be divided into two general classes of acid and basic rocks; but when the geological age of the appearance of these rocks is inquired into, it is found that we encounter both acid and basic rocks which have made their appearance at all periods.

Just as in the oldest periods we find acid granites which cor-

respond to the acid trachytes of the modern volcanoes, so in the oldest times also we find more basic norites, dolerites, &c. the equivalents of the more basic lavas and dolerites of the volcanoes of the present day; and although the facts collected are at present not sufficiently numerous to decide this point conclusively, it would appear probable that the acid eruptive rock characteristic of each geological period was accompanied by, or connected in some way with, the contemporaneous eruption also of a more basic rock equally characteristic of this same period.

Believing as I do that the origin of all these eruptive rocks may be ascribed to causes similar to those producing the active volcanoes now seen on our globe, it naturally brings us now to the consideration of such volcanic action.

As I have before explained, when considering the solidification of the globe, I contended that there then existed, and still exists in the interior of the earth, some great reservoir or reservoirs of fluid igneous matter, from which source all the igneous rocks, from the oldest to the most recent, have been derived, and I regard this probable for two reasons: first, because when the torrents of molten lava covering vast extents of country are seen issuing from a volcano, it is naturally inferred that it must come from some receptacle in the earth below; and, secondly, that as we know that considerable areas of the solid crust of our sphere have at times been depressed or sunk down to great depths, it appears equally natural to conclude that this could not have happened if the globe was entirely solid, and that there consequently must be some great hollow or chamber below filled either with gas or liquid matter, which, by its mobility, would make room for the mass thus depressed.

Whether, however, there may be only one or more reservoirs, and whether there may be, as some have imagined, two distinct reservoirs, containing respectively acid and basic, or trachytic and pyroxenic silicates, or whether both acid and basic silicates may not have been derived from the same source, I do not venture to decide; but I am inclined to believe that the sources of volcanic matter must have some intimate connection with one another, since it is known that volcanic rocks taken from any part of the world, no matter how far distant from one another, from Iceland or Tierra del Fuego, from Etna or Java,



are identical in mineral and chemical constitution, and in their physical and optical properties.

That volcanic action is something more than the mere local outbursts which have been compared to insignificant pimples on the face of the globe, is proved by a mere glance at a map showing their geographical extent and distribution. The innumerable volcanic islands of the Pacific Ocean for example, extending from longitude  $80^{\circ}$  W, some  $50^{\circ}$  of equatorial longitude further westwards to the coast of Asia, present one continuous scene of recent and present volcanic activity, extending in length over more than one eighth of the equatorial or greatest circumference of the globe.

The hypothesis that volcanic, granitic, and other plutonic rocks, are all local products resulting from masses of ordinary sedimentary strata melted up by being depressed into the body of the earth, so as to come within the action of the earth's central heat, has to encounter the difficulty of explaining how these masses could be let down deep into the substance of a solid globe in which no vacuity is supposed to exist; then it is requisite to know why, if the earth's central heat at a certain depth is considered sufficient to melt up these strata when so depressed, the entire substance of the earth at that depth is not in a molten state. Both the chemist and geologist will also, I think, hesitate before believing that rocks which we know are of such definite and constant mineralogical and chemical constitution wherever they are encountered in nature, could be formed by the melting up of mere mechanical aggregates of rock *débris* whose composition is known to vary to the widest possible extremes.

Knowing, for example, that limestones, often in immense beds are found in all sedimentary formations, it appears difficult to imagine that a granite, felsite, or other plutonic rock, specially characterised by containing only traces of lime, but much alkali, could be formed by the depression and melting up of such strata. In like manner, it appears equally difficult to suppose a basic dolerite, containing but comparatively little silica, formed from the melting up of other formations specially characterised by an enormous thickness of sandstones and highly silicious beds. In practice it would be difficult to select any piece or portion of the sedimentary formation we are

acquainted with on the earth's surface likely to possess a mean chemical surface composition which would, when melted together, give the percentage composition of a granite, diorite, dolerite, or other such rock.

On the other hand, as it is admitted that the presence of water has had some share in igneous action in nature, and that many minerals found in plutonic rocks do contain small amounts of water, either entangled under pressure or in a state of chemical combination, it is advanced that this could not be the case if the igneous matter had really come from any receptacle or reservoir in the interior of the earth, since no water could reach such sources.

The very emission of vapour and the presence of water in some volcanic minerals proves that the water really had got down by some means, and I see no difficulty in accounting for the infiltration of water when the effects of capillary action and heat are taken into consideration. An excellent illustration of how this may be effected is afforded by a glance at the action of an ordinary Gifford's injector, so commonly used to force the water supply into high-pressure boilers, in which case the very pressure, which under ordinary circumstances would prevent the entrance of the water, becomes actually the means of forcing it in.

Before concluding, I would, however, add a few words on a subject, which may almost be called the "bête noire" of geologists, namely, "metamorphic action," the study of which, intricate enough in itself, appears to have been rendered still more difficult and perplexing by the constant attempts to bring all the phenomena under one head, or in other words to ascribe to the action of one cause, results which are doubtless due to many very different agencies.

The study of metamorphism offers a wide field for exploration, especially to the chemist and microscopist—for the microscope is an indispensable instrument in these researches. Much however remain to be done, for but little is as yet satisfactorily demonstrated, and very many points of importance are still extremely obscure.

The results of metamorphic action are so varied and numerous, that the first step required seemed to me to be an attempt to classify the facts under the heads of the causes which are imagined to have influenced them.

A rough attempt resulted in the formation of six different classes:—

1. By pressure alone.—Alterations by compression and induration, often inducing cleavage, as in clay-slates. This metamorphic change is truly mechanical, but occasionally a slight amount of chemical change (combination apparently) has taken place, which possibly might have arisen from the indirect conversion of mechanical into chemical action.

2. By heat alone.—Many soft beds, like shales and clays become strongly indurated and converted into porcellanite and similar products, in near contact with basaltic dykes, &c. The microscopic and chemical examination shows that, beyond the mere expulsion of the water, the change is similar to the baking of stoneware; such rocks *in situ* are found to be generally more compact from being at the same time subjected to more or less pressure.

3. By heat in conjunction with chemical action and crystallisation.—When in the last-mentioned case, the rock may contain substances which might unite with one another to form new compounds, this is frequently found to have taken place.—Thus, if a calcareous and ferruginous shale or clay be subjected to a heat much below fusion, whether in nature or artificially, we have a complete change in its appearance and mineral composition, produced by the recombination of its constituents, and the formation of new minerals, such as, for example, epidote and garnet, both of which are silicates of alumina, iron, and lime. These reactions explain how extremely common it is to find such minerals developed in the rocks at the point of contact with igneous eruptions, as most of the sedimentary rocks contain the constituents silica, alumina, lime, and sesquioxide of iron which enter into their composition.

When in these cases, pressure constant, but not necessarily great, is also brought into play, we may produce artificially most striking results, as will be seen by examination of the specimens here exhibited, which show the conversion of ordinary clay slates, some of them slightly chloritic and micaceous, into a rock much resembling some natural schistose, or gneissic rocks.

These were produced by keeping the rocks exposed to a heat below their softening point for several months, whilst they were

protected from oxidation and subjected to a pressure varying from about 77 lbs. to 15 lbs. per square inch. If fusion or softening takes place, all structure is not only at once obliterated, but new reactions are called into play, resulting in the production of quite different chemical compounds in the fused product. The parallel structure was found to become developed at right angles to the pressure, or in other words, in the lines of least resistance in the rock.

Another specimen of rock shows the effect of similar treatment upon a block of compact soapstone, which, as will be seen, has been greatly changed in appearance, now possessing a finely developed foliated structure, with large crystalline plates or leaves. In this case it is probable that the effects are entirely due to recrystallisation; and to a similar cause may be attributed the formation of many of the metamorphic crystalline limestones and marbles, when the contact with igneous eruptions may have heated them sufficiently to bring about such molecular changes.

4. By aqueous action, either inducing crystallisation, by introducing or dissolving out certain mineral substances, by forming hydrated compounds with others, or by effecting chemical changes through the agency of the gases or solids, or both, held in solution by the water, all of which effects may be more or less assisted by heat and pressure.

The simplest example of this action is seen in the destruction and obliteration of the structure of organic limestone, which may thus be converted into crystalline rock, showing no trace of their original origin. Thus can be explained the veins of crystallised calcite which are found in modern coral reefs. Infiltration of water holding carbonate of lime in solution will account for the formation of calcareous sandstones, grits, and tuffs, and the filling up of the pores of many vesicular rocks and lavas with carbonate of lime, whilst the reverse effects would follow from such rocks being subject to the action of waters which could dissolve out such bodies previously existing in the pores of rocks. Certain zeolites or hydrated silicates in rocks may have been formed by the water entering into chemical combination with previously anhydrous silicates, and on the table is seen a specimen of the noted example of this action from the ancient Roman aqueduct at Plombières. Again by the chemical

reactions between the constituents of the rock and the compounds held in solution in waters which infiltrate into and permeate through rock-masses, great changes may be effected. Many of the magnesian limestones and dolomites appear to have been thus formed, from limestones of true organic origin, by the action of solutions containing magnesia. Other similar limestones have been converted into ironstones by the analogous reactions with solutions containing iron, as in the case of the Cleveland ironstones; and these effects would naturally vary with the chemical nature of the agent held in solution by the water.

5. By gasolytic action. The action of vapours and gases, at times strongly acid, as seen in solfataras and fumeroles, has also frequently played an important part in affecting metamorphic changes, both by the decomposition and reconstruction of rocks; by such means we often find limestone converted into gypsum, deposits of kaolin and clays formed from the decomposition of felspathic rocks, &c.; and many of the compounds of boracic acid appear also to have been derived from such sources.

6. By a combination of two or more of the above agencies. In the study of the physical and chemical geology of the older and more characteristic metamorphic deposits, all the above agencies appear to have combined (if not at once, at least at different times) to produce the extraordinary and varied appearances which are now visible in these rock-formations.

Many of the mica shists appear to have been originally mere micaceous sandstones, such as are now found in the later formations, subsequently recrystallised, probably by the long-continued action of a gentle heat, causing the particles to expand, and permitting a molecular movement, whilst the combined effect of pressure gave the direction to them, and caused the lines of foliation and re-arrangement of the particles to take place. The quartzites in part appear to have been mere sandstones, recrystallised and indurated by similar causes, whilst others appear to be sandstones or grits, the particles of which have been cemented together by a minute quantity of gelatinous silica, produced from the decomposition of felspars originally associated with them, and this mass consolidated by pressure, assisted or not by heat—a result very analogous to the formation of Ransome's patent stone.

Much of the gneiss appears to be the result of a stratified reconsolidation of the matter derived from sub-aqueous or sub-aerial granite outbursts, such as I have previously alluded to, whilst another species of gneiss, granite gneiss, or gneiss granite, appears (as I in 1854 described in the case of many Norwegian rocks) to have resulted from true granite eruptions, in which the foliated or parallel structure has been subsequently induced by a re-arrangement of the mineral molecules in the solid mass, very possibly effected by the long-continued action of moderate heat and pressure, as in the case of the artificial specimens on the table before us.†

Although I admit that what has been termed hydrothermal action has taken part in these metamorphic changes, and that this action may have been much assisted by the alkaline or other matter in the water, I am not inclined to consider either hydrothermal action, or the view that the metamorphic rocks have been formed from ordinary strata, softened and brought into a pasty state by the combined effects of enormous pressure, heat, and water (a sort of *Papin's digester* process), as the grand cause of the metamorphism of rocks.

The results of experimental research, on the contrary, show that in order to imitate such effects, the heat must be so low as to prevent any softening or fusion; that the pressure need be but very moderate, but must be constant; that oxidation must be guarded against;\* and that time is a most important element in all these changes.

The examination of natural metamorphic rocks by the microscope further leads to the deduction that the water present in these rocks has in all probability been derived from the water originally present in the unaltered stratum; and we know that all beds of aqueous deposition invariably contain more or less water; further, that the arrangement of the particles and crystallisation of the rock is compatible only with the view that the metamorphism had been effected whilst the rock itself was in a solid condition.

I have therefore come to the conclusion that the great metamorphic changes seen in the older strata have, in the main, been

\* In nature the supposition that the rocks when metamorphosed were below the ocean, or under superincumbent strata, would account both for their protection from oxidation, and for the required pressure.

effected whilst these rocks were in a perfectly solid condition, by what may be termed *moleculo-chemical action*, *i.e.*, a combination of chemical force and molecular movement, which may have been brought into activity by any one or more of the previously described agencies.

In concluding this necessarily very incomplete sketch, in which I have endeavoured to touch upon the most prominent points of chemical geology, I would add that I believe that many, if not all, of the views which I have adopted, so far from being new, have long ago been enunciated by other observers. My labours have consisted in examining into their soundness, and attempting to build up a whole by the agglomeration of what might be termed "disassociated" data; and throughout this lecture I have attempted, as far as possible, to support my views by reference to facts and experiments in preference to the opinions of authorities.

Although, from its very nature, some parts of such a sketch must be necessarily extremely theoretical, yet I believe the Society will support me in considering that the interests of science may be benefited by occasionally attempting to bring an accumulation of facts under some theoretical, but systematic, arrangement, even if this be but regarded as temporary, and found subsequently to require much modification by the advance of our knowledge of the subject; and in now bringing forward this summary of my investigations on the subject, I may state that I am fully prepared to reject such points as may be proved to be unsound, my object being the elimination of truth, and not the defence of any opinions which notwithstanding that I now hold to be correct, may possibly be hereafter shown to be untenable.

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XXIX.—*On the Manufacture of Glass.*

[A Lecture delivered before the Members of the Chemical Society, on March 19th, 1868.]

By HENRY CHANCE, M.A.

THE manufacture of glass may be divided into two parts, the chemical and the mechanical. The former comprises the preparation of the materials, their admixture in certain proportions, their decomposition by heat, and the union of the non-volatile elements into a uniform mass of melted glass. The latter consists of the conversion of this melted mass into the endless shapes which glass is capable of assuming.

In a paper read before the Society of Arts, in 1856, I gave a somewhat detailed account of the mechanical portion of the manufacture of crown and sheet glass. On the present occasion I propose to notice some points of interest in connexion with the chemical part of this manufacture, and also to call your attention to the question of devitrification, as illustrated by experiments upon basaltic stone.

To the manufacturer, conducting operations on a large scale, results often present themselves in a more marked and distinct manner than to the chemist experimenting upon the same substances in his laboratory. But the manufacturer is for the most part unable, from want of time, or it may be, from want of ability, to carry out the investigation of these results far enough to ascertain their true scientific bearing and importance. It is for the patient student of science, untrammelled by the perplexities of daily business, to undertake this task. I doubt not that there are among this audience some who answer to this description. It is with the hope that the facts which I am about to lay before you may lead these labourers in the field of science to fresh investigations, and not from any special importance which the facts themselves possess, that I venture to address you this evening.

The three principal elements of which crown and sheet glass are composed, are, as you are well aware, silica, soda, and lime. Of these by far the largest element is silica, which is now universally supplied in the form of sand. There are numerous



sources of sand adapted for glass-making. The American sand is perhaps the finest of all, but it is too expensive when imported into this country for ordinary use. Messrs. Copeland exhibited at Paris some very fine flint glass, manufactured at Stourbridge from this sand, and surpassing in purity of colour all other specimens of glass, whether British or foreign. French sand, from Fontainebleau, is also remarkably pure, and is generally used for the best kinds of glass. The sand used by the Belgian glass manufacturer is of good quality, but inferior to the French. Vitreous sand is found in various parts of England, but nowhere (in any available quantity) so pure as that of France or America. The sand used by our firm is obtained from Leighton Buzzard, and although of a yellowish tint, is more free from iron than many kinds of sand which are whiter in appearance. The whiteness of sand is a very uncertain test of its purity. Sand having a strong reddish hue may be made nearly white by calcining it with a small quantity of common salt, but the iron is still present, though in a different form. Again, two kinds of sand, which are shown by analysis to be precisely similar in their composition, may produce very different results, as regards both the colour and quality of the glass. As an instance of this I may mention that we had at one time occasion to use some Welsh sand, the analysis of which was almost identical with that of the sand from Leighton. When this sand was employed in the manufacture of rolled plate glass, which is formed by rolling a lump of glass upon an iron table, the glass, though good in other respects, had a wavy appearance upon its surface, of so marked a character, that it was necessary to discontinue the use of this sand in the process in question. In reference to this peculiarity, Dr. Richardson remarks, "I believe there is considerable difference in sand in neutralising the bases, according to the proportion of soluble and insoluble silica it contains. This variation may produce glass with different specific gravities, so as to affect the action of rays of light, as noticed by Faraday, in some flint glass which underwent decomposition, in some cases to the extent of separating particles of silica." This Welsh sand, of which I have spoken, when used in the manufacture of ordinary plate glass, produced a glass full of striæ.

Sand which does not contain more than one-half per cent.

of oxide of iron may be considered a good sand for ordinary glass. The Fontainebleau sand is almost entirely free from iron, and is well adapted in all respects for the manufacture of white glass.

The most important change that has been made in the chemical part of the manufacture of crown and sheet glass, is the substitution of carbonate of soda for kelp, and subsequently the use of sulphate of soda in place of carbonate. In reference to this point, I may perhaps be permitted to quote from my paper (to which I have already referred) the information which Mr. Bontemps was kind enough to give me,—“Thirty years ago crown and sheet glass were manufactured from crude alkali obtained from the ashes of a certain seaweed, and in this country known by the name of kelp. The preparation of kelp for this purpose employed a large population on the northern shores of Scotland and the West of Ireland, and the abandonment of this material plunged whole districts into idleness and misery. The kelp was used in combination simply with sand, the kelp containing soda and potash, and furnishing the lime necessary for the composition of the glass. But the glass thus produced was of a very variable character, arising from the uncertain quality of the kelp, and also of a very inferior colour, evidence of which is still to be found in the old windows of ancient houses, which have escaped the ravages of improvement.

“A similar crude alkali was employed in other countries, under the name of soda of Alicant, and at Venice and in the south of France this was mixed with a natural product, called the Natron of Egypt, and containing carbonate, muriate, and sulphate of soda.

“The discovery of Le Blanc, in 1792, which effected the conversion of common salt into carbonate of soda, was the commencement of a new epoch in the history of this glass. The manufacturers of soap at Marseilles ceased to import the soda of Alicant, and employed this new alkali in its place. Their example was followed by the manufacturers of plate glass, and before long the employment of the old crude alkali was discontinued also in the manufacture of blown window glass, and an improved colour and quality were the result.

“The alkali thus obtained was the carbonate of soda of commerce, containing, besides carbonate, a considerable portion of undecomposed sulphate. The further improvement which

followed, viz., the substitution of simple sulphate of soda for this carbonate of commerce, was due to the researches of the celebrated Gehlen; but some time elapsed before his ideas were carried out in Germany, and it was not until 1825 that the manufacturers of France, released, through the exertions of M. Clement Desormes, from the absurd veto which the Government had pronounced on the sale of sulphate of soda, were enabled to turn their attention to the employment of this cheaper material. They proceeded with caution in the introduction of this new ingredient, first mixing a small quantity of sulphate of soda with a large proportion of carbonate, then half of each, and finally they adopted the sole use of sulphate, to the injury, doubtless, of the colour of their glass, but they were gainers by the employment of a cheaper and more manageable material. Where colour, however, is an object, as in the manufacture of plate glass, the use of carbonate is still generally retained.

“The introduction of carbonate of soda prepared from salt into the glass manufacture of England dates from the year 1831. Proceeding cautiously in the steps of their foreign brethren, the English glass-makers, after they had established the use of carbonate, made trial of the effect of a small quantity of sulphate in a large quantity of carbonate. The latter was gradually diminished, until, at length, in the manufacture of blown window glass, sulphate stood alone. But here, as abroad, the manufacturers of plate glass adhere generally to carbonate.”

Glass made with sulphate of soda is less liable to devitrify, or, as it is termed, to become “ambitty” in the pot during the time of working, and will, therefore, bear a larger proportion of lime than carbonate glass. This is of great advantage, as, from the increased quantity of lime, the glass is harder, takes a better polish, and is less liable to the exudation on its surface which is technically termed “sweating.” The use of sulphate of soda involves the introduction of an ingredient, which is not required where pure carbonate only is employed, namely, carbon. This is generally introduced in the shape of a coal very rich in carbon, such as anthracite, or of charcoal.

The carbon used is in about the proportion of one equivalent to two equivalents of sulphate of soda. If there were no other substances present, we should look, not for a uniform action of the carbon upon the whole of the sulphate, but for various

degrees of deoxidation of a part of it, the rest remaining (in the presence of so small a proportion of carbon) as undecomposed sulphate. But as silica is present in large quantities, the moment that the sulphate of soda loses one equivalent of oxygen, the silica steps in and takes possession of the soda, and thus the whole is gradually converted into silicate. There is, however, sufficient evidence to show that the decomposition of the sulphate is not wholly dependent on the carbon employed. At least 25 per cent. of the quantity of carbon which is ordinarily introduced can be withdrawn for a time without interfering with the quality of the glass; and I have found by actual experiment that glass can be made with sulphate of soda in a covered pot without using any carbon whatever. There was indeed, in this case, considerable difficulty in reducing the materials to glass, and a large amount of undecomposed sulphate remained floating on the surface of the metal, but still a sufficient quantity of it had been decomposed to form a transparent glass. In making this experiment I found that, in proportion as the quantity of carbonate of lime was increased, so was the decomposition of the sulphate facilitated; but the increase of the lime was limited by its devitrifying tendency, so that it was impossible to carry the addition of lime sufficiently far to prove the possibility or otherwise of effecting a perfect decomposition of the sulphate.

This result would seem to show that carbonate of lime is of material assistance in decomposing the sulphate of soda. To suppose that carbonate of soda and sulphate of lime are formed in the glass pot would be of little service; for the question would still remain, how is the sulphate of lime to be decomposed, and sulphate of lime is notoriously difficult of decomposition. I would suggest that such an interchange being on the point of taking place, it is stopped on the threshold, as it were, by the silicic acid, which, the moment that the elements are loosened, seizes upon the soda and lime, and prevents its further progress. The above experiment was conducted in a covered pot, so as to avoid the possibility of any carbon being introduced into the materials from the fuel in the furnace. It is probable, however, that in an open pot, even without the aid of any extraneous carbon, a much larger decomposition of sulphate would have been obtained; for I found, by a long series of experiments, that even, with the full quantity of carbon added to

the mixture, it was impossible in a covered pot to arrive at a thorough decomposition of the sulphate. I attribute this partly to the difficulty (owing to the peculiar nature of the pot employed) of getting rid completely of the gases which are evolved, and partly to the fact that (for the same reason) there is no direct action of the flame upon the materials. Glass made from sulphate of soda is of a bluish, while that made from carbonate is of a yellowish tint. An excess of carbon in the mixture not only increases this blue tint, but also makes the glass very coarse. In one of the glass-works in the north of France which I visited some years ago, so small a proportion of coal was used that a certain quantity of the sulphate was always left undecomposed, and at the termination of the melting was found floating on the surface of the glass, and had to be ladled off. The object of thus using the smallest possible quantity of carbon was to produce a glass of a very pure colour. In this respect the result was very satisfactory; but the process of ladling off the undecomposed sulphate is a very troublesome one, and, though practicable with the small pots used abroad, would be impossible with the much larger pots employed in England. Any undecomposed sulphate remaining on the surface of the melted glass would produce what are called salt-blisters in the blown pieces.

Dr. Richardson says, "the question of the decomposition of sulphate of soda has long attracted my attention, and I have made numerous experiments. In the case of glass-making I am strongly inclined to think well of a plan for its decomposition, by sulphuret of sodium in this proportion:  $3(\text{SO}_3.\text{NaO}) + \text{SNa} = 4(\text{SO}_2.\text{NaO})$ , which latter would be instantly decomposed by the Silica. It is also a question (he remarks) whether sulphuret of sodium in solution could not be decomposed either wholly or partially by boiling with sand, and thus save the great cost of the operation in a glasshouse pot."

The third principal ingredient in crown and sheet glass is lime, which, in glass made with sulphate of soda, is almost invariably introduced in the form of carbonate, whereas in carbonate glass caustic lime is used. Chalk and limestone are found to answer equally well. It is a curious fact that the glass made from limestone is harder and more difficult to grind than that which is made from chalk. This may, perhaps, be due to the carbonate of magnesia which is found generally in

limestone, but in a much smaller degree in chalk. Limestone possesses, moreover, the property of causing the glass to cool and set more rapidly when worked into shape.

Although glass can be produced from sand and alkali without any other addition, lime is a very important element, as giving to it hardness and insolubility.

In flint glass this ingredient is replaced by lead, which gives far greater brilliancy to the glass than lime, but at the same time, owing to the difference between its specific gravity and that of the other materials, is the cause of innumerable striæ. A lump of the purest and most beautiful flint glass would, if blown out into a sheet, be so full of these striæ as to be utterly worthless, while, on the other hand, a vessel made of the very finest crown glass is dull in colour, and altogether wanting in the brilliancy which characterizes lead glass.

In some works it is the custom to supply alumina in the shape of pipeclay. I have frequently tried this in small quantities, but have not found it either to improve or to damage the quality of the glass. It is to be found in all kinds of glass, and its presence may be accounted for by the action of the alkali upon the clay of the pot. In glass made for optical purposes, which undergoes a careful examination, it is found that the outside portion of the glass, next the pot, always contains more striæ than the interior of the mass; and this difference may be fairly attributed to the presence of alumina, derived from the clay of the pot, which has combined, but not thoroughly blended itself, with the glass.

This action of the alkali upon the clay of the pot is sometimes carried to such an extent that the inside of the pot is completely eaten into holes, and myriads of small stones are scattered through the glass.

On comparing the proportions of the materials in the mixture with the composition of the glass produced, it is found that the two are so nearly identical as to lead to the conclusion that very little alkali is lost by volatilisation during the intense heat to which it is subjected. I do not find in any case a difference of more than one per cent. between the alkali in the mixture and that in the glass produced, and this includes the waste which must necessarily arise in mixing, in carrying the materials to the furnace, and in throwing them into the pots. I ought to mention, however, that, in estimating the quantity

of available alkali in the sulphate of soda, no account is taken of the chloride of sodium, which is present to a small extent even in the strongest salt-cake, it being presumed that the whole of this is volatilised.

English crown and sheet glass may be said to contain generally 73 per cent. of silica, 13 per cent. of soda, and 13 per cent. of lime. On the continent less sulphate is used than in England, and 74 per cent. of silica, 11 per cent. of *soda*, and 14 per cent. lime, may be taken to represent the component parts of foreign sheet glass. The remainder is in both cases made up of alumina and oxide of iron. Two specimens of ancient glass recently analysed gave the following results:—The first, of the twelfth century, contains silica 51 per cent., alumina 2·16 per cent.; protoxide of iron 1·58, lime 8·04, magnesia 2·22, alkali 34·40. The second, of the sixteenth or seventeenth century, silica 54·60, alumina 8·96; oxide of iron ·75, lime 19·31, magnesia 3·43, alkali 12·95.

Ancient glass contains generally a considerable proportion of alumina and magnesia. These bases render the glass less homogeneous and more refractive. The silicates of alumina and magnesia not blending thoroughly with the other silicates, and the numerous striæ thus caused being elongated by the process of blowing, the glass presents a much richer and more brilliant appearance than is afforded by a perfectly homogeneous medium.

To the three ingredients of which I have already spoken, silica, soda, and lime, it is generally the custom to add a small quantity of arsenic and of peroxide of manganese, of the former to assist in oxidising any carbonaceous impurities and to promote the decomposition of the other materials; of the latter to peroxidise and thus reduce the colouring property of the oxide of iron present. But there is, as Dr. Richardson has pointed out, a manifest inconsistency in employing in the same mixture, carbon as a reducing, and peroxide of manganese and arsenic as oxidising agents.

It is true that this difficulty may be in a great measure obviated by introducing the arsenic and manganese towards the end of the melting, when the carbon has almost entirely done its work, but, on the other hand, it is not likely that metallic oxides, introduced, at so late a period, will be thoroughly incorporated with the melted mass. A gentleman who has recently visited

the Belgian glass works informs me that the manufacturers have for the most part discontinued the use of these oxides.

The colour of the glass is derived chiefly from the impurities in the materials employed, but partly also from the operation of melting, and partly from the colouring matter contained in the fuel. When covered pots are used, the latter source of colour is entirely eliminated, and we are able to look to the two former as the sole causes. In this case it is found that potash gives a more brilliant colour than soda, and lead than lime. The purest colour is obtained from sand, potash, and lead. When (as is the case in one kind of optical glass) a portion of the lead is replaced by lime, and the mixture consists of sand, potash, lead, and lime, there is a falling off in colour as compared with the pure flint glass mixture, and when the whole of the red lead is withdrawn and lime takes its place, a further falling off is observable. In other words, the purest crown glass is inferior in colour to the purest flint, and between these two comes the glass which may be called half-crown and half-flint. When, however, the proportion of lead is largely increased, and we reach what is called heavy flint glass, a strong yellowish tint is observable.

In comparing the colour of pure crown and flint glass, it is of course important to bear in mind that the difference may be in part attributable to the difference of the heat required for melting the two kinds of glass; but I do not know of any means of determining what share in the result is to be assigned to this particular cause. It may indeed be remarked generally, that we are very much in the dark as to the effect of the action which takes place in the furnace upon the colour of the glass produced, and it is much to be desired that a series of careful experiments should be made which might tend to throw some light upon this question.

It has been well remarked, that it is better to obtain glass of a pure colour by using pure materials, than to endeavour to correct impurities by the use of manganese and other agents. Any slight improvement in the tint which the use of manganese may effect is far more than counterbalanced by its tendency (especially when used in any quantity) to cause the glass to change its colour under the action of sunlight. A greenhouse, roofed with glass in which manganese has been used, will display, after a lapse of time, almost every variety of tint.



Many of you are, no doubt, familiar with the pamphlet published by Mr. Thos. Gaffield, of Boston (United States), in which he has described at length a series of very interesting experiments upon the action of sunlight on glass. It is to be regretted, however, that he did not acquaint himself with the composition of each kind of glass which he tested.

His experiments, in 1864, and two following years, proved to him that nearly every kind of window-glass which he exposed could be changed in one year; that a rose or pink colour (or some tint approaching them) could be produced in various kinds after a few months, and that some kinds of greenish-white glass would, after exposure, assume a bluish tint, or bluish-white.

Mr. Gaffield quotes the statement of Pelouze:—"I do not believe that there exists in commerce a single species of glass that does not change its shade in the sunlight," and affirms, as the result of his own experiments, that a longer or shorter exposure to the sun's rays will probably alter in some degree the colour of all, or nearly all kinds of window-glass.

There is, however, undoubtedly (from whatever cause it may arise) a marked difference in the rapidity with which various kinds of glass are affected by exposure. A piece of optical glass, composed of sand, potash, lead, and lime, changed colour after a few years; while a piece containing no lead, remained unchanged. It is possible that a longer exposure of the latter glass might confirm the assertion of M. Pelouze and Mr. Gaffield. There is considerable difference of opinion as to the precise cause of the change in question. In a great number of cases the change may probably be correctly ascribed to manganese, but this does not explain the alteration of the colour of glass in which no manganese has been used. I can affirm from my own experience, that white glass, in which there is no trace of this ingredient, has, after considerable exposure, assumed a strong yellowish tint.

The theory of M. Pelouze, that sunlight acts upon the protoxide of iron and sulphate of soda existing in certain kinds of glass, and provokes a reaction, from which results peroxide of iron and sulphide of sodium, may, as Mr. Gaffield remarks, have some weight in determining the cause of the yellow or pink colour, but does not account for the alteration which he observed in a specimen of plate, of crown, and of sheet glass

from a greenish-white to a bluish tinge, not mingled with either yellow or purple.

I would conclude my brief remarks on this difficult question in the words of Mr. Gaffield: "How the change takes place is a matter on which writers differ. It is my opinion that the precise explanation can only be given after a multiplication of experiments, and a thorough examination of exposed and unexposed specimens of glass by quantitative and qualitative analysis, and perhaps by spectral analysis and observations of photogenic effects, or photogenic tests."

I shall now proceed to notice briefly some interesting experiments and processes, of comparatively recent date, in connection with the manufacture and treatment of glass.

By far the most important change that has been made of late years in the process of melting glass, has been the adoption of the well-known regenerative system of Mr. Siemens. The novelty of this system consists, as you are well aware, in taking up the waste heat from the furnace, in large chambers filled with open brickwork, and in making use of the heat thus saved in raising to a high temperature the elements of combustion. In order to carry out successfully the working of this process, the fuel is placed, not in the furnace itself, but in large receptacles, called "producers," at some little distance from it. The whole of the fuel, excepting the inorganic portions, is converted into gas, there being no reason for separating the illuminating from the non-illuminating products. Thus a very much larger amount of gas per ton of coal is produced, than when, as in making gas for illuminating purposes, a considerable residue is left behind in the form of coke. Mr. Siemens estimates, that by the utilization of the whole of the carbon, the quantity of gas is increased fivefold.

The gas and air passing through separate channels, and having each been heated to a high degree in the waste heat chambers, meet on entering the furnace, and there ignite. The intensity of the heat thus produced may be imagined when I mention that on one occasion one of the glass pots having given way, a piece from its side fell against the side of the furnace, and so soft was the clay of the furnace that the impression of the pot falling against it was as distinct as if it had fallen upon wax. An idea of the enormous heat may be also thus conveyed. A sheet glass furnace contains 1,800 cubical feet,

or thereabouts, equal to a room 20 feet long, 10 feet broad, and 9 feet high. This chamber contains 8 large pots of clay, and in them materials equivalent to about 16 tons of glass. In 25 hours (without any previous fritting) the materials are melted, and refined into a liquid transparent mass.

The amount of fuel saved by this process is dependent, in a great measure, on the change which can be effected by it in the quality of the coal employed. Where, as, for instance, in the manufacture of flint glass, large coal is ordinarily used, and small coal, or slack, can, under the system of Mr. Siemens, be substituted, the saving of fuel is very considerable; but in processes in which an inferior description of coal is already in use, the margin for economy is very much smaller. But whatever question may be raised as to the cheapness of the process, its cleanliness is undeniable, and for glass made in open pots this is a matter of no small moment. In Belgium the small size of the pots, the great depth of the grate-room, and the nature of the coal employed, admit of a very quiet method of working under the ordinary system, and the injury sustained by the glass from exposure to the smoke is comparatively trifling; but in England, especially where non-bituminous coal is used, the amount of coal-dust carried into the pots is considerable, and the system of Mr. Siemens is proportionately beneficial. To affirm, however, that no impurities or deoxidizing agents from the fuel find their way into the glass in Mr. Siemens's gas furnace would be contrary to the experience of many who have not been able to obtain in any of these furnaces in open pots glass as pure and bright as can be obtained in covered pots. For this reason the process has not yet been applied generally with success to the manufacture of flint glass in open pots. M. Bontemps informs me that the Company of St. Louis have at length succeeded in overcoming this difficulty, and are using open pots for flint glass, with coal as the fuel, with certain modifications of Mr. Siemens's system. Mr. Siemens, however, states, in a recent communication, that the furnaces which he erected at the St. Louis flint-glass works do not differ in construction from others erected by him since 1863. The gases enter the furnace in combustion through a single orifice in the *sidé* near one end, and pass away through a similar orifice near the other end, and *vice versa*. By this arrangement the construction of the furnace is much simplified,

and the result is much more satisfactory, both as regards heating power and economy of fuel.

Mr. Siemens adds that the consumption of fuel under this system is, in the manufacture of crystal glass, 15 cwt. of small coal per ton of glass worked out and cut, while in plate glass works it does not exceed 7 cwt. per ton of glass poured.

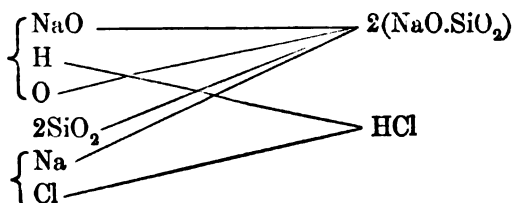
In metallurgical processes Mr. Siemens estimates the saving of fuel at 40 to 50 per cent. In steel melting, 14 cwt. of coal will fuse 1 ton of steel, in the place of 3 or 4 tons of hard coke, as used at Sheffield.

The production of silicate of soda from the decomposition of common salt by silicic acid has long engaged the attention of chemists. I need only briefly refer to the well-known process patented by Mr. Gossage. Chloride of sodium, in the state of vapour, and mixed with steam, is passed through a tower filled with white hot flints. Silicate of soda and hydrochloric acid gas are produced; the former flows downward in a melted state, the latter passes upwards. I believe I am correct in stating that Mr. Gossage has not as yet been successful in producing by this process, silicate of soda suitable for the manufacture of glass.

In the *Annales du Génie Civil*, March, 1867, mention is made of the process of M. Brisse for effecting the same object, the chemical reaction on which it depends being the same as in Mr. Gossage's process. M. Brisse commences by melting common salt in a suitable reverberatory furnace. When the fusion is complete, a jet of superheated steam is injected on the surface of the salt, and finely powdered silica is, from time to time, thrown into the furnace. Hydrochloric acid is given off, and silicate of soda remains.

Mr. George Gore, of Birmingham, has recently made some very interesting experiments with reference to the production of silicate of soda from common salt in the glass pot itself, which, with his permission, I will briefly notice. Mr. Gore has devised a mixture of glass materials in which steam shall be liberated throughout, at a high temperature only, and, therefore, under the conditions most effective for decomposing the common salt. In this mixture, sulphate of soda, and consequently coal or charcoal, are dispensed with altogether, and substituted for them is a chemically equivalent mixture of hydrate of soda ( $\text{Na.OHO}$ ) and common salt, these two ingredients being also

in quantities chemically equivalent to each other, and representing together, as nearly as possible, the amount of alkali contained in the ordinary sulphate mixture. The mixture thus modified consisted of sand, cullet, or waste glass, chalk, common salt, hydrate of soda, arsenic, and manganese. The chemical reaction of these new materials is represented by the following chemical equation and scheme of decomposition:—



In this reaction the water (HO) of the hydrate of soda decomposes the common salt (NaCl) at high temperatures, and forms hydrochloric acid (HCl) and anhydrous soda (NaO). The former escapes as gas, the latter unites with the silica. Mr. Gore succeeded in obtaining by this process a transparent glass; but the cost of the caustic soda is such as to render the mixture more expensive than with sulphate. It is, moreover, much to be feared that the vapourised salt would, by its action upon the clay of the pots, cause so rapid a wear and tear as seriously to interfere with the success of the process. Whenever in a carbonate mixture there is present more than an ordinary proportion of chloride of sodium, the effect upon the pots is very marked. But whatever may be the obstacles to the use of chloride of sodium in the glass pot itself, there is good reason to hope that before many years have elapsed the direct conversion of this material into silicate in the furnace will be successfully accomplished.

Monsieur Bitterlen has patented a process for the use of sulphate of baryta and felspar, in the place of carbonate or sulphate of soda in the manufacture of glass. His mixture consists of silica, sulphate of baryta, felspar, and carbonate of lime.

A cylinder of this glass was exhibited at Paris, and it was

stated that these substances were employed in their natural state, without having been subjected to any preparation beyond that of grinding.

In connexion with the exhibition, I may allude to another very interesting process, I mean that patented by M. Maréchal, for the employment of neutral fluorides of the alkalies in etching upon glass. This process has already been mentioned in one of the numbers of the *Chemical News*; but, as it may be new to some of you, I may be pardoned for saying a few words respecting it.

Hydrofluoric acid in a liquid state is used extensively, as you are well aware, in the engraving of glass. When applied to the surface of glass, it produces upon the parts exposed to its action an appearance resembling that of wheel-cut glass.

Hydrofluoric acid gas imparts, on the contrary, a dead dull surface, somewhat similar to that of white enamelled glass.

This latter method of engraving is exceedingly effective, but the use of hydrofluoric acid gas is objectionable, not only on account of its deleterious properties, but because the semi-opaque effect which it produces is to some extent destroyed by the liquid hydrofluoric acid which is formed while the action of the gas is going on.

To avoid these difficulties, M. Maréchal has had recourse to solutions of the neutral fluorides of the alkalies. The addition of hydrochloric acid to these solutions disengages hydrofluoric acid, which, coming in contact, in the nascent state, with the silicic acid of the glass placed in the liquid, produces rapidly a deadening upon the surface exposed.

In order to render the fluorides of lead and calcium insoluble, or nearly so, in the liquid in which they are formed, and thus to prevent any counter-action upon the surface of the glass, it is necessary to saturate the solution with sulphate of potash, or some other substance, which will effect the same purpose.

The French companies of St. Louis and Baccarat have adopted this process; and by varying the degree of action of the acid upon the glass, and combining the bright with the dull etching, have succeeded in carrying out very rich and artistic designs, avoiding on the one hand the costly process of cutting, and on the other the comparatively coarse and less permanent result obtained by the use of enamel.

I shall conclude my paper with some remarks upon a process

which, though not at present in use, may possibly be some day revived, and which, even if looked upon as finally extinct, possesses, nevertheless, considerable interest in its relation to the manufacture, and especially the devitrification of glass. I refer to the process of melting basalt, and of converting the melted glass thus obtained into a substance very closely resembling the original stone.

The successful accomplishment of this conversion depends upon the well known fact that glass, by slow cooling, becomes more or less devitrified, that is to say that its atomic condition is altered, the constituent parts remaining the same. The more bases a glass has, the more easily is it devitrified. Glass made with carbonate of soda, as I have already mentioned, displays this tendency more than sulphate glass. As far as our experience goes, devitrification follows more readily from the use of soda than of potash. Our optical glass, which contains potash only, and is cooled slowly down in the pot in which it is made, is not subject to this change; but I have here a sample of soda glass, containing more lime and less alkali than our potash glass, which after the same slow method of cooling, shows very decided symptoms of devitrification. I have also specimens of our ordinary crown and sheet glass, which have undergone this change in various degrees. The basalt of South Staffordshire, known in that district under the name of Rowley Rag, is well adapted for reconversion, when melted in its original form, both from the small quantity of alkali, and the variety of bases which it contains. The following may be taken as an average analysis:—Silica, 48; oxide of iron, 16; alumina, 16; lime, 9; moisture and volatile matter, 5; soda, 4; hydrochloric acid, 1.

The fusibility of basalt and the facility with which, by slow cooling, it can be reconverted to its original form, was demonstrated by Sir James Hall, at the commencement of the present century; but I am not aware that it was proposed to render this material available for manufacturing purposes, until in the year 1851, Mr. Adcock, a civil engineer, suggested to our firm its employment in the manufacture of pipes as a substitute for iron. No difficulty was found in melting the Rowley Rag in an ordinary reverberatory furnace. At first iron moulds were employed, but the heat to which they had to be subjected in order to effect thorough devitrification, was such as to warp and spoil them. It was then suggested that

sand moulds might be made available, and it was found that a mould of sand, cased round with iron, could be heated in a close oven to a bright red heat without injury, and that the liquid glass, when cooled slowly down in this mould, was completely converted into stone.

The melted material was tapped from the furnace into iron vessels, having at the bottom a moveable plug. The part next the inner side of the vessel and that on the top formed a crust which kept the mass within in a liquid state. Repeated experiments proved, that the longer the melted material was allowed to remain in the iron ladle, before casting, the stronger and sounder was the stone, and that when it was poured into the mould immediately after it had left the furnace, the stone was rotten, and not thoroughly devitrified. The tenacity of the stone seemed to be increased by allowing it to become as stiff as possible before casting. When the sand moulds were not sufficiently heated, or the cooling was not gradual enough, partial devitrification only ensued, nodules of stone being scattered through the glass; but there was invariably in this case a coating of stone, of greater or less thickness, against the sand. From this fact it would appear that the process of devitrification commenced not from the interior, but from the outside of the casting.

The glass or stone produced from any melting could, by remelting, be produced in the same form, or could be converted from glass into stone, or stone into glass, according to the rate of cooling, successive meltings having no effect whatever upon the power of conversion or reproduction.

After repeated trials, pipes were produced completely reconverted to stone; but the difficulty of uniformly obtaining thorough devitrification, when dealing with so small a mass, appeared to be insuperable, and we were reluctantly compelled to abandon this branch of the manufacture.

Attention was then given to the production of stone for building purposes, and in this, so far as the manufacture itself was concerned, we were entirely successful, the devitrification of the material being accomplished with the greatest certainty; but the cost of the process was too great to admit of its being carried out successfully as a commercial undertaking.

Notwithstanding these failures, there is still a wide field open to any one who might be tempted to carry out this interesting



process from the point at which it was left. Large blocks of stone, for pavements, for sea-walls, fortifications, or other places where great strength and durability are required, can be cast with the greatest facility, and, of course, at a much cheaper rate than when, as in the case of ornamental stonework, the cost of the moulds is a serious item. There is one fact bearing upon this question, of great importance, which we ascertained by repeated experiments—namely, that if a large number of pieces of the natural basalt be placed in and heated up with the sand mould, and the melted material be then poured in in the ordinary manner, not only is the devitrification of the fused portion perfect, but the cementation is so complete that a block thus formed is stronger than when composed of melted basalt only. It is scarcely necessary to point out that the quantity of fused stone required being thus greatly diminished, the cost of the process is greatly diminished also.

The effect of rapid cooling was taken advantage of to produce sheets of black glass. The melting of the basalt in the glass pot, and the process of rolling it out upon the table was accomplished without difficulty, but the annealing, owing to the hardness of the glass, required considerable care. It was proposed to use this glass for roofs in the place of slates, and a railway station in Scotland was covered with it; but the composition of the glass was such as to render it unable to resist sudden changes of temperature, and nearly every sheet was cracked during the alternations of a variable winter.

The addition of a certain quantity of alkali would, no doubt, overcome this difficulty, but the increased cost would quite counterbalance the advantage of using a cheap material as a basis.

I have spoken of the glass as being black. When gathered on a trying rod from the furnace it appears so; but when seen in a very thin film, it is nearly transparent, its opacity increasing with its thickness through shades of yellow and brown to the deepest black.

On comparing the basaltic stone produced by the process which I have described with the natural basalt, it was found that the latter was of a closer grain than the former. The difference of circumstances under which the fusion and devitrification took place may account for the difference in the result.

The amount of devitrification is dependent, not only on the

rate of cooling; but upon the temperature at which the process of cooling commences. If the moulds are not sufficiently heated, the conversion to stone will be imperfect, however gradual the subsequent loss of heat may be; and the same result will follow from a too rapid gradation in the downward temperature, however high it may have been at starting.

It would, no doubt, be possible to devitrify a solid mass of basaltic glass by continuous exposure to a very high degree of heat; but as all our experiments were made with this glass in a melted state, I am not able to affirm from actual observation that such would be the case.

I may add that incomplete devitrification was invariably shown, not by a conversion of the whole of the melted material into a semi-stony state, but by the formation of nodules of stone, varying in number according to the conditions of cooling, the residue retaining the form of a perfect glass.

Some experiments which were made with ordinary window glass, by melting and cooling it in a manner similar to that adopted for basalt, proved that, without the addition of lime, it was very difficult to obtain complete devitrification. When lime was added, a greenish white stone was the result of slow cooling. Small pieces of lime, however, remained in the casting, and as these absorbed moisture and expanded, the mass was blown in a few hours into a thousand pieces.

It was also found that ordinary window glass, by grinding it into powder, and moulding it (with the aid of moisture) into shape, with or without the addition of sand, could be cemented by a strong heat into a solid and thoroughly devitrified mass; but, the result was not sufficiently satisfactory, as regarded hardness and durability, to make the process of much practical use.

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XXX.—*On the Tetraphosphoric Amides.*

By J. H. GLADSTONE, Ph.D., F.R.S.

IN previous communications I have described a series of acid amides which may be viewed as pyrophosphoric acid, in which one, two, or three molecules of HO have been replaced by  $\text{NH}_2$ . The formulæ of these bodies, of course, contains  $\text{P}_2$ . I have now to describe another series of acid amides which require formulæ containing  $\text{P}_4$ , and may, therefore, be termed tetraphosphoric.

So far as is known at present, these compounds are produced only by the action of water on the amidated oxychlorides of phosphorus.

If the oxychloride  $\text{PCl}_3\text{O}$  be saturated with dry ammoniacal gas, either at a low or a moderate temperature, the resulting white mass will dissolve in water, with the exception, perhaps, of a little pyrophosphotriamic acid. The solution is sure to contain pyro-diamic acid, but, generally speaking, on the addition of alcohol a precipitate appears. It is not, however, uniform in character, sometimes being a viscid liquid, at other times a light solid, and more frequently a sticky flocculent precipitate, very suggestive of the idea that it is a mixture of the two. The ultimate analysis of different preparations confirmed this idea, or rather led to the belief that there were more than two compounds precipitable by alcohol from the aqueous solution. Notwithstanding the ingenuity and perseverance of my assistant, Mr. Tribe, it was found impossible to determine the conditions under which one or other of these acids was formed, or to separate them in a perfectly satisfactory manner; still I believe that I am in a position to assign formulæ to the liquid and the light solid compounds.

## AMIDES INSOLUBLE IN ALCOHOL.

*Liquid Compound.*—Two different preparations gave very limpid liquids. They were purified by washing with alcohol, or by solution in water and reprecipitation with spirit. They were dried over sulphuric acid in vacuo, but were found to be very hygroscopic, and very difficult to free from the last traces

of water. The analysis was effected by boiling with hydrochloric acid, which resolves all these compounds after a while into orthophosphoric acid and ammonia.

I. 0.197 grm. of the first preparation gave 0.556 grm. of the ammonio-chloride of platinum.

II. 0.271 grm. gave 0.307 of pyrophosphate of magnesium.

III. 0.0955 grm. of the second preparation gave 0.108 grm. of pyrophosphate of magnesium.

IV. 0.2115 grm. gave 0.595 grm. of ammonio-platinum salt.

V. 0.2565 grm. gave 0.291 grm. of pyrophosphate of magnesium.

These numbers, reduced to a percentage, give—

	First preparation.		Second preparation.		
	I.	II.	III.	IV.	V.
Phosphorus . . . .	—	31.63	31.58	—	31.68
Nitrogen . . . . .	17.70	—	—	17.65	—

These numbers show that the equivalents of P and N are in the ratio of 4 to 5, and they approach to what is required by the formula  $P_4N_5H_{17}O_{11}$ :—

Phosphorus . . . . .	32.04
Nitrogen . . . . .	18.09
Hydrogen . . . . .	4.39
Oxygen . . . . .	45.48
	100.00

This body combines with ammonia to form a liquid compound less soluble in water, and insoluble in alcohol, from which, however, unlike the acid, it does not readily separate in drops. On treating this ammonium compound with a weak acid, the original liquid is restored.

An aqueous solution of this body gives solid precipitates with many metallic salts, but its composition seems generally to be altered by union with the metal. Indeed, those salts which have been analysed always contained less than five atoms of nitrogen; and when any of them were decomposed by an acid, the liquid body was not reproduced, or, at any rate, was mixed with the solid tetraphosphoric amides, and with pyrocompounds. Nitrate of silver, for instance, gives, in a slightly acid solution, a white flocculent precipitate, which seems to be

somewhat soluble in water; in an ammoniacal solution, a very heavy yellow compound, which increases in weight and in depth of colour on standing for some days with the ammonio-silver salt. Neither of these gave uniform results on analysis, and neither of them contained nitrogen in a larger proportion than three atoms to four of phosphorus; indeed, the yellow compound contains the smaller amount, and seems to consist, in a great measure, of orthophosphate of silver.

It would appear, therefore, that the elements of ammonia are easily separable from this liquid. It will stand a heat of  $100^{\circ}\text{C}$ . without decomposition, but a cold solution of hydrate of potassium makes it give forth an ammoniacal odour. It may be regarded as an acid ammonium-salt, and for theoretical reasons, to be explained presently, I am disposed to call it *terammoniated tetraphospho-diamic acid*,  $\text{P}_4(\text{NH}_2)_2(\text{NH}_4)_3\text{HO}_{11}$ .

A portion of this liquid acid remained perhaps a year covered with alcohol. Crystals grew about it, and eventually it seemed almost wholly converted into crystals. A solution of the best of them in water gave indications of their being the ammonium-salt of some unknown acid, which yielded a white silver-salt, but no ferric compound, either at the ordinary temperature or on boiling. The mass was dissolved in water, and evaporated in vacuo; but the substance, after crystallisation, was found to have changed into ordinary phosphoric acid and ammonia.

*Solid Acid.*—It has already been stated that when the liquid compound is treated with a metallic salt, and the resulting precipitate is decomposed by an acid, more or less of the solid acid is obtained; but this is a very destructive process, and another method of preparing the substance seemed practically to give better results. It was found that the sticky flocculent precipitate often thrown down when alcohol was added to the solution of mixed acids, contained between 4 and 5 atoms of nitrogen to 4 of phosphorus; but it was also found that by the action of strong acids upon it a change took place in its physical properties, and the percentage of phosphorus was gradually raised. This was easily effected by dissolving the mixed acids in water, adding a very large quantity of some mineral acid, reprecipitating by alcohol, and repeating the process until the flocculent substance became rather sparingly soluble in water, and quite friable when dry. This also was a destructive process, but while imperfect preparations showed that this solid acid contained less

amidogen and less oxygen than the liquid acid already described, two specimens, the one prepared by hydrochloric, the other by sulphuric acid, gave numbers agreeing well with the formula,  $P_4N_4H_{10}O_9$ .

0.170 grm. of acid gave 0.225 grm. of pyrophosphate of magnesium.

0.085 grm. gave 0.227 grm. of ammonio-chloride of platinum.

		I.	II.
That is,—	Phosphorus..	36.96	—
	Nitrogen....	—	16.75

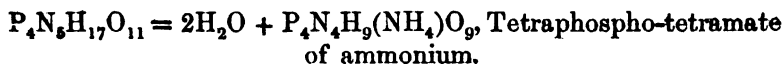
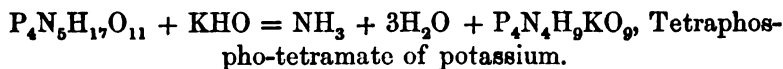
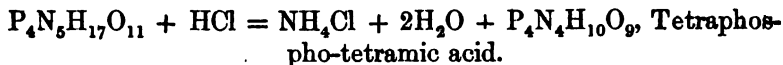
almost identical with tetraphospho-tetramic acid  $P_4(NH_2)_4H_2O_9$ .

Phosphorus .....	37.12
Nitrogen .....	16.76
Hydrogen.....	3.00
Oxygen....	43.12
	100.00

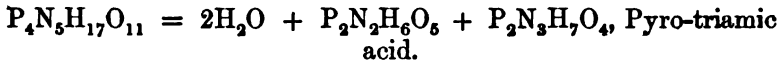
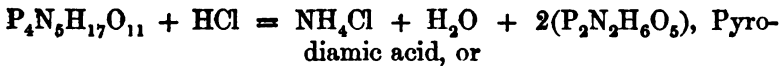
The symmetrical formula given above assumes that none of the nitrogen exists as ammonium, and this is justified by the fact that a solution of the compound gives no immediate precipitate with bichloride of platinum.

This solid acid can be produced equally well by the action of acids or alkalis on the liquid compound; for instance, of cold strong solutions of nitric acid, or of carbonate or hydrate of potassium, or by boiling it for an hour or two with pure water. Pyrophospho-diamic acid, and other compounds are generally produced at the same time, while in two or three instances there was a little white solid formed, which was practically insoluble in water, and gave the ordinary reactions of pyrophospho-triamic acid.

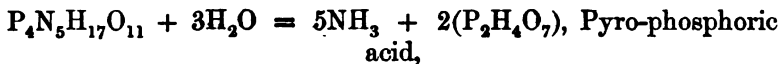
A comparison of the formulæ will show that these decompositions may be simple enough:



In practice there is always more or less of a further breaking down, such as,



The final result of the continuous breaking down of this liquid compound is probably in every case—



which, in its turn, assuming the elements of more water, becomes 4 molecules of  $PH_3O_4$ , Orthophosphoric acid.

This solid -tetramic acid combines with bases, and may be separated from its salts apparently unchanged.

The ammonium compound is solid, like the acid itself, and is also precipitable by alcohol from its aqueous solution. It seems to give up all its ammonia when dried in vacuo, but a specimen dried in the air gave 19.3 per cent. of nitrogen. The formula  $P_4(NH_2)_4H(NH_4)O_9$  requires 19.9 per cent. This seems also to have been very nearly the composition of one specimen of the solid white precipitate obtained by alcohol, though it had been dried for 4 or 5 days over sulphuric acid in vacuo. Ammonia added to a strong solution of the acid, produced at first a crystalline precipitate, which was re-dissolved on adding more of the alkali, from which it may be inferred that there are two ammonium compounds.

There certainly are two silver salts. If the aqueous solution be treated with nitrate of silver, a white or nearly white precipitate falls; if it be treated with the ammonio-nitrate, the precipitate is of a dirty yellow colour, very easily affected by light, and readily distinguishable from the bright yellow precipitate obtained from the liquid acid. These two salts were prepared from a small specimen of this acid, which was considered pure.

0.078 grm. of the dirty yellow salt gave 0.068 grm. of chloride of silver, and 0.073 grm. of ammonio-chloride of platinum.

This gives the following numbers:—

Nitrogen	..	..	..	5.90
Silver	..	..	..	65.63

showing that nearly 6 atoms of silver had combined with the acid, and indicating the composition  $P_4N_4H_4Ag_6O_9$ , a very likely formula, as the silver has replaced all the hydrogen which is theoretically possible in this kind of compound.

Phosphorus	.....	12.70
Nitrogen	.....	5.74
Hydrogen	.....	0.41
Silver	.....	66.40
Oxygen	.....	14.75
		<hr/>
		100.00

Two specimens of the lower silver-salt gave discordant results, but led to the belief that the white salt is the bibasic tetramate  $P_4(NH_2)_4Ag_2O_9$ , mixed with a small quantity of the higher compound.

#### AMIDE INSOLUBLE IN WATER.

If oxychloride of phosphorus be rapidly saturated with ammonia gas the temperature becomes very high, and on the addition of water, a white body remains, which is not pyrophosphotriamic acid, for it does not give a yellow compound when treated with ammoniacal nitrate of silver. In order to prepare this substance in a pure state, the compound of  $PCl_3O$  and  $4NH_3$ , produced without regard to temperature, should be heated for a while at rather above  $200^\circ C.$ , indeed at any temperature between that and what is required to volatilize the chloride of ammonium. Some molecular change is thus effected in the amidated oxychloride, and on the addition of water, little or none of the phosphorus finds its way into solution in any form, while there is produced a new insoluble acid.

The ultimate composition of this body was determined by the usual method of analysis.

I. 0.384 grm. gave 1.405 grm. of ammonio-chloride of platinum.

II. 0.059 grm., of another preparation, gave 0.208 grm. of ammonio-chloride of platinum.

III. 0.203 grm. of a third preparation, gave 0.280 grm. of pyrophosphate of magnesium.



IV. 0·261 grm. of a portion which had been washed with strong HCl before drying and weighing, gave 0·359 grm. of pyrophosphate of magnesium.

V. 0·249 grm. of the same, gave 0·871 grm. of ammoniochloride of platinum.

VI. 0·218 grm. dried at 100° C., gave 0·810 grm. of ammoniochloride of platinum.

VII. 0·218 grm. of the same, gave 0·303 grm. of pyrophosphate of magnesium.

These numbers give:—

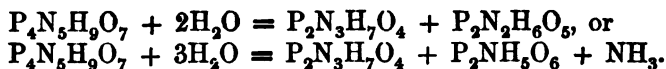
	I.	II.	III.	IV.	V.	VI.	VII.
Phosphorus	—	—	38·52	38·41	—	—	38·80
Nitrogen ..	22·4	22·12	—	—	21·95	23·29	—

These numbers indicate 5 atoms of nitrogen to 4 of phosphorus, and agree best with the formula  $P_4N_5H_9O_7$ .

Phosphorus .....	39·36
Nitrogen .....	22·22
Hydrogen.....	2·86
Oxygen.....	35·56
	100·00

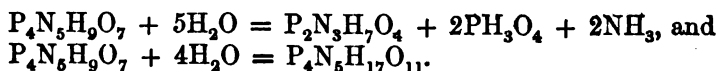
As this formula does not admit of each atom of nitrogen being satisfied with two atoms of hydrogen, we cannot look on the substance as a complete amide. I suggest as its name, simply, tetraphospho-pentazotic acid.

The body, however, though insoluble in water, is liable to be decomposed by it. When boiled with water, it is at once resolved into pyrophosphoric compounds, and without change of appearance, for the -triamic acid produced is white and insoluble, like the original compound, while -diamic and -amic acids enter into solution.



A similar change also takes place, slowly, at the ordinary temperature. Specimens which had been set aside for a few days, were generally found to give a yellow compound, with ammoniacal nitrate of silver; and those which had been placed in bottles after having been dried only in the air, were found, after a few months, to be resolved mainly into pyro-triamic and

-diamic acids. In one case a large quantity of orthophosphate of ammonium was found; in another, some tetrammoniated tetraphospho-pentamic acid. The formation of these additional bodies is also easily explained:—



This substance resembles pyrophospho-triamic acid in combining readily with alkalis, and in decomposing metallic salts, forming, in every instance, insoluble, or nearly insoluble compounds. There were considerable difficulties attending the preparation of pure salts, besides the suspicion that the specimen of acid itself might not be always definite in composition. The following observations, however, may be worth recording:—

*Ammonium Salt.*—0.505 grm. of the acid, treated with strong aqueous ammonia, gave a solid compound, which, when dried at 100° C., showed an increase in weight of 0.028 grm., or 5.5 per cent. The formula  $P_4N_5H_8(NH_4)O_7$ , would give an increase of 5.1 per cent.

That the original substance is not an ammonium salt, in the ordinary sense of the term, is proved by the fact that it may be produced from the amidated oxychloride in the presence either of strong hydrochloric acid or of strong potash.

*Potassium Salt.*—If the acid be washed repeatedly with a solution of hydrate of potassium, a white insoluble compound is formed. A specimen was analysed:—

I. 0.203 grm. gave 0.253 grm. of pyrophosphate of magnesium.

II. 0.220 grm. gave 0.150 grm. of potassio-chloride of platinum, and 0.726 grm. of ammonio-chloride.

The numbers deduced from this are sufficiently close to those calculated from the formula  $P_4N_5H_8KO_7$ , to leave little doubt that this is the composition of the salt.

	Calculated.	Found.
Phosphorus . . . . .	35.12	34.80
Nitrogen . . . . .	19.82	20.69
Hydrogen . . . . .	2.27	—
Potassium . . . . .	11.07	10.89
Oxygen . . . . .	31.72	—
	<hr/> 100.00	

*Copper Salt.*—This acid decomposes chloride of copper dissolved in water, but a specimen so prepared was found to be imperfect; at least, it yielded on analysis 21·52 per cent. of nitrogen, and 6·12 per cent. of copper, whereas  $P_4N_5H_8CuO_7$  would require 9·14 per cent. of the metal. When treated with an ammonio-copper salt, this first compound took up more copper, more in fact than one equivalent, for the new compound contained 11·49 per cent.

*Lead Salt.*—Three different specimens of this salt were prepared by the action of acetate of lead on the solid acid. They were found to contain respectively 30·3, 34·6, and 38·0 per cent. of metal, the last being associated with 11·86 per cent. of nitrogen. This also indicates more than one atom of lead, but the formula  $P_4N_5H_7Pb_2O_7$  requires 39·8 per cent.

*Silver compounds.*—The action of silver salts on this acid appeared worthy of study, and has led to unexpected results.

If it be treated with ammoniacal nitrate of silver, it gives a heavy compound of a pale yellowish brown colour.

This analysed in the usual way gave:—

	First preparation.			Second preparation.	
Phosphorus . . . .	18·65	—	—	18·41	—
Nitrogen . . . . .	—	11·32	11·05	—	10·05
Silver . . . . .	54·59	54·19	54·18	54·20	54·48

These results do not agree with any formula.

If this acid be treated with neutral or slightly acidulated nitrate of silver, a heavy compound, also of a pale yellowish brown colour, is formed, but its composition is quite different from that of the preceding.

I. 0·352 grm., analysed in the usual way, gave 0·196 of chloride of silver.

I. 0·521 grm. of a second preparation gave 0·293 of chloride of silver, and 0·428 of pyrophosphate of magnesium.

III. 0·452 grm. of the same gave 0·257 of chloride of silver, and 0·367 of pyrophosphate of magnesium.

IV. 0·492 grm. of a third preparation gave 0·275 of chloride of silver, and 0·870 of ammonio-chloride of platinum.

V. 0·485 grm. of the same gave 0·272 of chloride of silver, and 0·424 of pyrophosphate of magnesium.

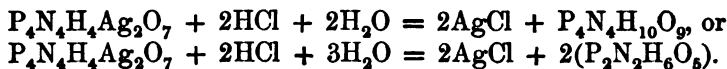
Which give the following percentages:—

	I.	II.	III.	IV.	V.
Phosphorus . . .	—	22·94	22·67	—	24·41
Nitrogen . . . . .	—	—	—	11·09	—
Silver . . . . .	41·91	42·33	42·80	41·98	42·21

This seems to show that the nitrate of silver had effected what the hydrochloric acid had failed to accomplish—the removal of a portion of the ammonia, and that the new compound was in fact  $P_4N_4H_4Ag_2O_7$ .

Phosphorus . . . . .	24·22
Nitrogen . . . . .	10·94
Hydrogen . . . . .	00·78
Silver . . . . .	42·19
Oxygen . . . . .	21·87
	100·00

This may be regarded as the normal  $P_4N_5H_8AgO_7$ , in which one molecule of ammonium has been subsequently replaced by silver. But for the purposes of nomenclature, it may be better to view it as containing 4 molecules of  $NH_3$ , when it may be called *Tetraphospho-tetramate of Silver*. It is clear that the pentazotic acid cannot be regained from it by simply decomposing the salt with an acid. On trying the experiment both with hydrochloric and with nitric acid, it was found that no insoluble acid was produced, but that the solution contained tetraphospho-tetramic and pyrophospho-diamic acids. The formation of either of these is very natural.



As this new acid seemed to be deserving of further study, an attempt was made to prepare a large quantity of the silver salt from a new specimen of oxychloride of phosphorus; but the salt was lighter in colour and different in composition, though the silver and nitrogen proved to be in the same ratio. As the oxychloride was possibly not pure, it was re-distilled from an

additional quantity of boracic acid, but a similar result was obtained. The only known difference in the manner of preparation was that the amidated oxychloride had not been heated so long at a high temperature. A portion was therefore exposed to 230° C. for about ten hours, and a silver salt was prepared from it. The result was somewhat intermediate between those formerly obtained.

I. 0.380 grm. of silver salt gave 0.223 grm. of chloride of silver, and 0.720 grm. of ammonio-platinum salt.

II. 0.356 grm. gave 0.210 grm. of chloride of silver, and 0.311 of pyrophosphate of magnesium, which give:—

	I.	II.
Phosphorus ..	—	24.39
Nitrogen ....	11.88	—
Silver .....	44.17	44.40

The ratio of atoms of nitrogen and silver is still 2 : 1 or 4 : 2, but the salt cannot contain as much as seven atoms of oxygen.  $P_4N_4H_2Ag_2O_6$  would require:

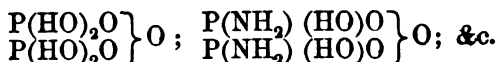
Phosphorus .....	25.71
Nitrogen .....	11.24
Hydrogen .....	00.41
Silver .....	43.37
Oxygen .....	19.27
	100.00

This silver compound also gave some tetraphosphodiamic acid, when decomposed by nitric acid.

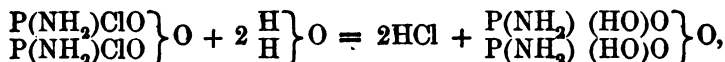
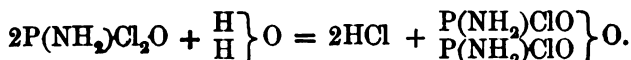
It is very evident that the investigation of these tetraphosphoric amides is still incomplete; but the difficulty of separating one from another, the apparent capriciousness of their formation, and the generally unsatisfactory character of compounds that will not crystallise, have induced me to leave the subject in its present condition. I think, however, that the existence of compounds analogous to the pyrophosphoric amides, but containing  $P_4$ , is proved; but whether those containing  $P_4N_5$  may not, after all, be mixtures, may be a matter of doubt. It will not be difficult to extend to these compounds the same method of reasoning by which I have previously endeavoured to explain the building up of the less complicated bodies.

*Theoretical Constitution.*

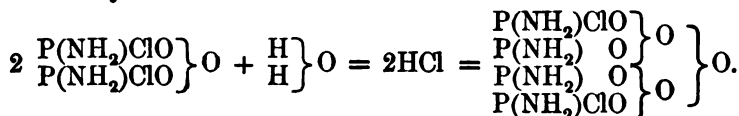
In previous communications I have regarded pyrophosphoric acid and its amide as bodies constituted on the water type, with the rational formulæ—



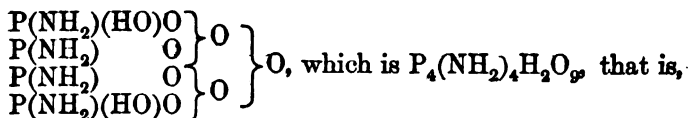
and the following was given as the probable process by which the -diamic acid is formed, when the amidated oxychloride of phosphorus attacks water:



the two reactions being perhaps simultaneous. But it does not follow that when two molecules of the amidated oxychloride have attacked one of water to form  $\left. \begin{array}{l} \text{P}(\text{NH}_2)\text{ClO} \\ \text{P}(\text{NH}_2)\text{ClO} \end{array} \right\} \text{O}$ , the remaining chlorine should be replaced by HO. The process of attacking both atoms of hydrogen in water may be repeated by the freshly formed chloride, thus—

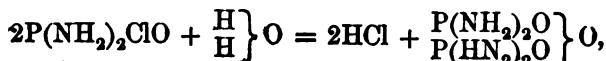


which, when acted upon by water in the usual way, gives 2HCl and

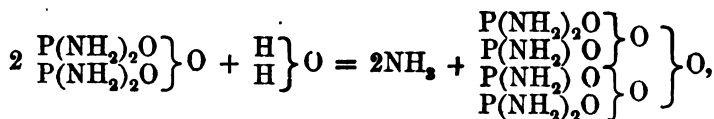


*Tetraphospho-tetramic acid.*

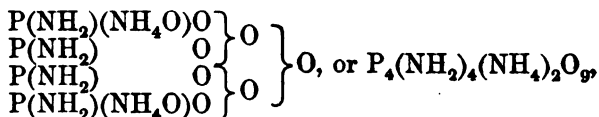
This acid may be prepared, like the pyro-diamic, from the higher amidated oxychloride  $\text{P}(\text{NH}_2)_2\text{ClO}$ . The first stage of the reaction, in both cases, will be—



and the second attack upon a molecule of water will give—



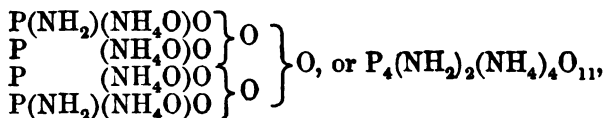
or *tetraphospho-hexamide*, a hypothetical body, to which I shall again refer, and which has simply to acquire the elements of  $2\text{H}_2\text{O}$  to be converted into



*Tetraphospho-tetramate of ammonium.*

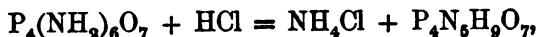
Now, this *-tetramic acid* must be the fourth amide of a *tetra-phosphoric acid* of the composition  $\text{P}_4(\text{HO})_6\text{O}_7$ ; and this is no hypothetical substance, for it is known in its salts. It is in fact Fleitmann and Henneberg's phosphoric acid.

It is difficult to assign satisfactory rational formulæ to the two compounds containing  $\text{P}_4\text{N}_8$ . The fact that the atoms of nitrogen are uneven in number, destroys the symmetry, and seems to point to their being products of decomposition of substances containing  $\text{P}_4\text{N}_8$ . That they both belong to the tetraphosphoric series, is evidenced by their easily giving rise to tetraphospho-tetramic acid. The genesis of the liquid  $\text{P}_4\text{N}_8\text{H}_{17}\text{O}_{11}$  from the hexamide, requires the assumption of  $\text{H}_2\text{O}$  by each phosphoric element, when it will be converted into



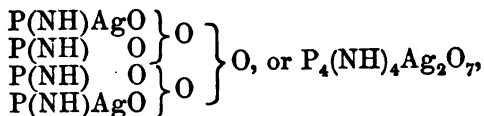
an *ammoniated tetraphospho-diamic acid*, which seems, I know not why, to part with one of its molecules of ammonia more readily than the other three.

The acid,  $\text{P}_4\text{N}_8\text{H}_9\text{O}_7$ , is easily derivable, theoretically speaking, by the action of free acid or hydrate of potassium on the hexamide



and this will account for its being monobasic. The action of

nitrate of silver on this pentazotic acid removes another molecule of  $\text{NH}_3$ , and restores the symmetry, producing



*Tetraphospho-tetrimate of silver.*

If the view of the mutual action of water and the chlorides of phosphorus, given in this and preceding papers, be correct, we obtain the following rational formulæ for the four known phosphoric acids:—

Ortho-phosphoric acid . . . . .  $\text{P}(\text{HO})_3\text{O}$ .

Meta-phosphoric acid . . . . .  $\text{P} \left\{ \begin{array}{c} \text{HO} \\ \text{O} \end{array} \right\} \text{O}$ .

Pyro-phosphoric acid . . . . .  $\left\{ \begin{array}{c} \text{P}(\text{HO})_2\text{O} \\ \text{P}(\text{HO})_2\text{O} \end{array} \right\} \text{O}$ .

Tetra-phosphoric acid (Fleitmann and Henneberg's) . . . . .  $\left\{ \begin{array}{c} \text{P}(\text{HO})_2\text{O} \\ \text{P}(\text{HO})\text{O} \\ \text{P}(\text{HO})\text{O} \\ \text{P}(\text{HO})_2\text{O} \end{array} \right\} \text{O} \left. \right\} \text{O}$ .

XXXI.—*On the occurrence of Organic Appearances in Colloid Silica obtained by Dialysis.*

By W. CHANDLER ROBERTS, Associate of the Royal School of Mines.

IN the following paper, it is proposed to give a brief account of the microscopical examination of colloid silica, obtained by dialysis.

It will be remembered that in Mr. Graham's papers on liquid diffusion, the method of preparing soluble silicic acid is detailed. It may be briefly stated as follows:—

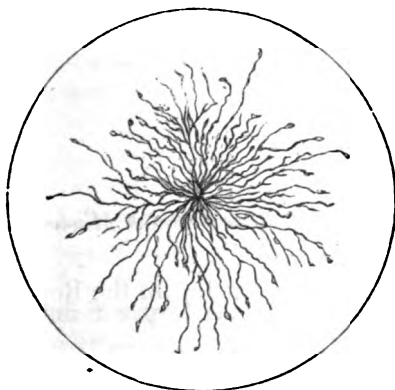
By bringing together 112 grms. of silicate of soda, 67.2 grms. of dry hydrochloric acid, and 1 litre of water, and dialysing for four days, a solution of soluble silica (containing 4.9 per cent. of



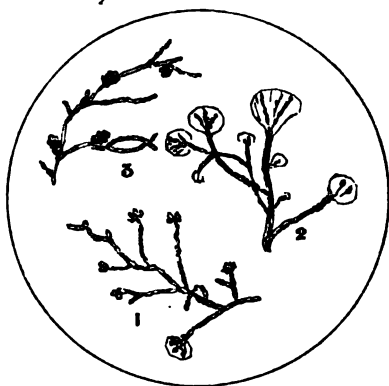
silicic anhydride) remains on the parchment paper, the chloride of sodium and excess of hydrochloric acid having diffused away. This solution becomes pectous somewhat rapidly, forming a solid jelly, which may be dried into a lustrous hydrate by two days' exposure to vacuum over sulphuric acid, or by a more protracted evaporation in air. The solid thus obtained is remarkably similar to opal from Zimapan, but contains 21.4 per cent. of water.

The specimens upon which the following observations were made were prepared in Mr. Graham's laboratory, and the microscopic examinations were made by his kind permission.

All the specimens of jelly dried in air contained dendritic forms, varying in size from 0.2 millimetre to 0.5 mm. At first, it seemed probable that they might be indications of the passage of colloid into crystallised silica, but when magnified to 90 linear, they appeared as radiating fibres, and when magnified 700 times, each fibre resolved itself into a series of elongated, beaded cells, with clusters of circular cells at intervals.



COLLOID SILICA (90 Linear).



COLLOID SILICA (700 Linear).

1. The most Common Form of the Organic appearances.
2. From a Thin Section.
3. Apparent Fructification.

From the fact that the air-dried jelly contained the structures, while they were wanting in the solid hydrate obtained by evaporation in vacuo, it was evident they might be organic.

On submitting them to Mr. Slack, he at once indicated their remarkable analogy to the common blue mould, or mildew.

The cells appear to be hollow; they do not blacken with sulphuric acid. An attempt to render their structure more apparent, by injecting with isinglass and vermilion, met with only partial success. In many cases the ends of the fibres are surrounded by an apparently vacuous space; it is therefore probable that the fungi actually grew after the partial solidification of the jelly; observations are, however, being continued in this direction. In natural mocha stones, the dendritic forms are not dissimilar, but when examined microscopically, they are distinctly angular and crystalline. It is possible that in natural agates many cellular structures may have been produced, as indicated above, and subsequently filled in with mineral matter. As early as 1814, Dr. M'Culloch described some undoubtedly organic forms in the agates of Dunglas.

Dr. Carpenter has also recorded the *growth* of fungi in the shells of the anomia.

I should apologise for bringing so small a matter before the Society, but I considered it might be of interest at a time when the microscope is becoming an indispensable aid in petrological research.

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### XXXII.—*Chemical Researches on New and Rare Cornish Minerals.*

By A. H. CHURCH, M.A., Professor of Chemistry in the Royal Agricultural College, Cirencester.

#### V. *Cornwallite.*

Is cornwallite a good species? The experiments given below were undertaken in order to see whether chemical analysis could afford an answer to this question.

Cornwallite was named by Zippe, basing the species on two analyses by Lerch, which gave the following percentages:—

	CuO.	As <sub>2</sub> O <sub>5</sub> .	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.
I. ....	55·00	29·78	2·54	12·68
II. ....	54·22	30·65	1·77	13·36

From these numbers the generally accepted formula  $\text{Cu}_3\text{AsO}_4 \cdot 2\text{CuH}_2\text{O}_2, 3\text{Aq.}$  was deduced.

The physical characters of cornwallite, as originally given, are quite distinctive. It is by no means a common mineral. I have obtained a few small specimens in Cornwall at different times, but my two best and largest pieces were purchased in London, and had formerly been in an old Cornish collection of minerals. Occasionally, specimens have been offered to me as cornwallite, which were merely varieties of the cupric *phosphate* known as *prasine*, in which a portion of the  $\text{P}_2\text{O}_5$  had been replaced by  $\text{As}_2\text{O}_5$ . One of these gave, on analysis, the following percentages:—

CuO .....	68·44
$\text{P}_2\text{O}_5$ .....	20·38
$\text{As}_2\text{O}_5$ .....	2·42
$\text{H}_2\text{O}$ .....	8·20
	99·44

Now this specimen was accompanied by torberite, while the true cornwallite, as noticed by Zippe, is associated with olivenite. The two specimens of which I now purpose giving an account, were partially coated on their surface and in their cavities with very delicate, nearly white, silky prisms of olivenite. In other respects also, as will be seen presently, they corresponded very closely with the original description of this species.

The hardness of my specimens was 4·5; the density of one of them was found to be 4·17. The colour is a very rich verdigris green, passing into a blackish green. The fracture of the more compact parts of the specimen is distinctly conchoidal. The minute botryoidal character of some portion of the mass is, however, very marked, and then the minute chains of bead-like globules serve to show the translucency and characteristic colour of the mineral very clearly.

The new analyses, given below, of cornwallite, were made with every care. The copper was always determined *finally* by Brown's volumetric method; it is probably slightly in excess of the truth, in consequence of a trace of iron in the solutions experimented with.

## ANALYSES OF CORNWALLITE: Synopsis of Results.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Substance taken ..	·5675	1·703	·5605	·5305	·511	·6005	·171	1·5395	·4187
SiO <sub>2</sub> .....	·004	·0115	·004	·002	·004	·006	·002	·023	·0035
Hygroscopic H <sub>2</sub> O .	·0065	·0195	·006	·006	·0058	·01	—	·0085	0065
H <sub>2</sub> O .....	—	—	—	—	—	·048	—	—	—
CuO .....	·3354	1·01182	·33084	·31246	·29776	·34922	·10109	—	—
MgNH <sub>2</sub> 2AsO <sub>4</sub> ·H <sub>2</sub> O	·284	—	—	—	—	—	—	·746	·206
Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	·024	—	—	—	—	—	—	—	—

Analyses I to VI were made with one sample; analyses VII to IX with another sample of cornwallite. When these results are calculated into percentages, after deduction of the intruding silica and the hygroscopic water, they give very accordant numbers. In a carefully prepared sample for analysis the silica does not exceed half a per cent., and is shown by microscopic examination to be an accidental admixture, due to minute veins of quartz in the mineral. I have considered the water lost at 100° C. merely hygroscopic, because it varies from day to day with the dampness of the atmosphere, and because in vacuo over oil of vitriol, the same loss of moisture ultimately occurs as at 100° C.

The following are the percentages deduced from the above analyses:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	Mean.
CuO ..	60·21	60·52	60·09	59·80	59·40	59·85	59·76	—	—	59·95
As <sub>2</sub> O <sub>3</sub> .	30·86	—	—	—	—	—	—	29·98	30·58	30·47
P <sub>2</sub> O <sub>5</sub> ..	2·71	—	—	—	—	—	—	—	—	2·71
H <sub>2</sub> O ..	—	—	—	—	—	8·23	—	—	—	8·23

It will be seen that the above analyses differ from the older ones of cornwallite only in the percentages of CuO and H<sub>2</sub>O. In fact, I find 5 per cent. more cupric oxide, and 5 per cent. less water; a comparison of the old and new theoretical and experimental percentages will at once show, either that the old view of the constitution of cornwallite is untenable, or that the mineral now under review is a new species. But I have already pointed out why my mineral seems to be the true cornwallite, and, if so, to some accidental cause must be attributed the larger amount of water given in the former analyses. It is evident that in Lerch's analyses one ingredient was determined by difference; if this constituent should have been either the

cupric oxide or the water, the discrepancy alluded to admits of explanation.

Here are the old and new analytical results translated into mean percentages, and placed for comparison beside the theoretical numbers:—

	Lerch.		Church.	
	Experiment. (Mean.)	Theory. ( $5\text{CuO} \cdot \text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ .)	Experiment. (Mean.)	Theory. ( $5\text{CuO} \cdot \text{As}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ .)
CuO ..	54.61	55.42	59.95*	58.33*
As <sub>2</sub> O <sub>5</sub> .	30.21	32.06	30.47	33.75
P <sub>2</sub> O <sub>5</sub> ..	2.16	—	2.71	—
H <sub>2</sub> O ..	13.02	12.54	8.23†	7.92†
	<hr/> 100.00	<hr/> 100.02	<hr/> 101.36	<hr/> 100.00

The formula for cornwallite may then be written  $\text{Cu}_3\text{2AsO}_4 \cdot 2\text{CuH}_2\text{O}_2 \cdot \text{aq.}$ , making this species stand to erinite,  $\text{Cu}_3\text{2AsO}_4 \cdot 2\text{CuH}_2\text{O}_2$ , among the arseniates, as ehrlite,  $\text{Cu}_3\text{2PO}_4 \cdot 2\text{CuH}_2\text{O}_2 \cdot \text{aq.}$ , stands to dihydrite  $\text{Cu}_3\text{2PO}_4 \cdot \text{CuH}_2\text{O}_2$ , among the phosphates. But, in fact, many of the hydrated native arseniates and phosphates require a most searching re-investigation. A complete classification of this group of minerals is not yet possible.

### XXXIII.—*On the Regenerative Gas Furnace as applied to the Manufacture of Cast Steel.*

[A Lecture delivered before the Fellows of the Chemical Society, May 7th, 1868.]

By C. W. SIEMENS, F.R.S., Mem. Inst. C.E.

IN responding to your call to deliver a lecture to your Society, on a subject of applied chemistry, I feel that I have undertaken a very responsible task, a responsibility which is only balanced by the honorary distinction conferred by your call.

It is a hopeful sign of the advancement of science that your

\* The greater part of the excess of the experimental over the theoretical percentage of CuO is due to the partial replacement of As<sub>2</sub>O<sub>5</sub> by P<sub>2</sub>O<sub>5</sub> in this mineral; of course cupric phosphate contains a much higher percentage of CuO than the arseniate.

† The water in the experiment is rather high; in other and subsequent determinations the percentages obtained were 7.45 and 8.16.

Society puts itself into intellectual communication with engineers and others, whose mission it is to apply and practise that pure science cultivated within your body. It would be presumptuous on my part to reason with you upon a purely chemical subject, for although many years ago I had the advantage of receiving instruction from Wöhler and Himly, I can in no way lay claim to be a chemist of the present day. Yet I can safely affirm that of all the instructions I received in early life, there is none that has been a more useful guide to me in my professional pursuits.

The subject to which I wish to call your attention this evening is one that has occupied my mind for many years, and which I hope may engage your interest, involving as it does the generation of intense heat by means essentially differing from those in general use, and the application of that heat to the production of cast steel in large masses, and directly from the ore or scrap metal.

The regenerative gas furnace, which is the joint production of my brother, Frederick Siemens, and myself, is already known through its application to nearly all those branches of industry in which furnace heat is employed. It was described by Faraday, to the members of the Royal Institution, in the last public lecture delivered by that great philosopher in 1862, and has since been the subject of several publications. I need not, therefore, bring before you all the features of this mode of producing intense heat for the various purposes to which it has been applied, but shall confine myself to its description as applied only to the production of cast steel in large masses, which is the principal subject of my present communication.

*Nature of Steel.*—Before proceeding with this description I shall briefly remark upon the nature of steel and the methods by which it has hitherto been produced.

*Steel.*—Steel is generally regarded as a *compound of iron and carbon, possessing the remarkable quality of becoming exceedingly hard when heated and suddenly cooled.* The proportion of carbon determines the degree of hardness of which the steel is capable, or what is termed its *temper.*

The following table of the percentage of carbon in steel suited to different purposes, is prepared from analyses made in my laboratory by Mr. A. Willis, unless another authority is mentioned.

Description.	Carbon per cent.	Authority.
Wootz.....	1·34	T. H. Henry
Steel for flat files .....	1·2	A. Willis
„ for turning tools .....	1·0	„
„ (Huntsman's) for cutters .....	1·0	„
„ for cutters.....	·9	„
„ for chisels.....	·75	„
Die steel (welding) .....	·74	„
Double shear steel.....	·7	„
Welding steel .....	·68	„
Quarry drills .....	·64	„
Mason's tools .....	·6	„
Ramrods .....	·6	„
Common steel for stamping..	·42	„
Steel for magnets (containing tungsten) .....	·4	„
„ spades.....	·32	„
„ hammers.....	·3	„
Bessemer steel for rails.....	·25 to ·3	various
Homogeneous metal armour plates .....	·23	Percy
Very mild steel from open furnace .....	·18	A. Willis
Sample before Spiegel was applied .....	·05	„
Bessemer iron (pure).....	trace	Abel

Cast-steel containing less than 0·3 per cent. of carbon is no longer capable of being hardened, and should be classed rather as homogeneous or melted iron than as steel, while on the other hand an excess of carbon above 1·4 per cent. again deprives the metal of the quality of taking a temper, and it must then be regarded as approaching in character rather to white cast-iron.

It is, however, a contested question between chemists whether the presence of a third substance may not be necessary to produce steel. Frémy, in his celebrated controversy with M. Caron before the French Academy, maintains that nitrogen or cyanogen is a necessary constituent of steel; the investigations of other chemists appear to confirm this theory and the old Sheffield practice of mixing leather and other animal substances with the charcoal used in the converting

furnace would also seem to corroborate it. M. Frémy's theory probably admits of great extension, and it may be that we should regard steel as a triple combination of iron with carbon and with another substance, taken from a series comprising nitrogen, sulphur, phosphorus, silicon, manganese, tungsten, titanium, tin, silver, and probably many other elementary bodies, each of which entering, in an exceedingly small proportion, into combination with the iron and carbon is capable of imparting to the steel distinctive physical properties.

*Nitrogen.*—Nitrogen has been found invariably in the steel produced by the ordinary processes.

*Sulphur and Phosphorus.*—Sulphur and phosphorus are commonly regarded as the worst enemies to steel, the one rendering it "*red-short*," or incapable of being forged, and the other "*cold-short*," or brittle at ordinary temperatures. It is owing to the presence of these impurities in nearly all British irons, that the highest qualities of tool steel are still made entirely from Swedish or other charcoal-iron of high quality, produced from the purest ores. If phosphorus exists in steel in quantities exceeding 0.1 per cent., its presence is indicated, on breaking the sample, by peculiarly bright and distinct faces of crystallisation on the fractured surface, but the steel admits of being forged and welded, and though somewhat brittle when cold, it is remarkable for hardness. It would, therefore, not be safe to maintain that phosphorus in small quantities is objectionable in steel under all circumstances. Steel containing above 0.2 per cent. of *sulphur* breaks under the hammer at a low red heat, and is, therefore, only applicable to the production of *steel castings*: for this purpose the presence of a small amount of sulphur is unquestionably a positive advantage imparting increased fluidity to the molten metal and toughness to the casting when cold. This effect is so well understood in Sweden as regards cast-iron, that in casting ordnance sulphur is added to the metal.

*Manganese.*—Manganese possesses the remarkable property of counteracting to a great extent the effect of sulphur (or red-shortness) in steel. Its application for this purpose is due to Josiah Marshall Heath (1839), and must be classed among the most important discoveries in modern times; for it is only in consequence of the addition of manganese (in the form of oxide, mixed with carbon) to the steel melted in pots,



that the Sheffield melters have been enabled to use English puddled iron for the commoner qualities of steel in place of the purer and more costly Swedish iron; and again it is only in consequence of the addition (by Mushet) of manganese in the form of ferro-manganese or *spiegeleisen* to the liquid bath produced in the Bessemer converter that the better qualities of English pig-iron have been made available for the production of malleable Bessemer metal. It is distressing to think that the author of this invaluable discovery was deprived of the fruits of his labour by an unjust combination among the manufacturers chiefly benefited by him, who contested the validity of Heath's patents upon trivial grounds, relying for their success upon their financial power to crush his unquestionable claims. The specific chemical action of manganese has never been clearly demonstrated. It is certain that only traces of metallic manganese are ever found in cast-steel, and that the bulk of the manganese added is found combined with oxygen, silica, and alumina, in the form of slag; yet it follows, from experiments which I have had occasion to make, that on adding manganese to a bath of liquid steel in an open reverberatory furnace, its beneficial action ceases if the metal is retained in the furnace, exposed to the flame for any length of time, say more than half-an-hour. This is the case quite independently of any sensible reduction in the proportion of carbon in the steel, and indicates that the effect of manganese is not due to the removal of sulphur or other substances with which it may enter into combination, but it is inseparable from the presence of metallic manganese in the steel, in however small a quantity. A further confirmation of the view, that the addition of manganese removes no impurity from the steel, is supplied by the fact, that if cast-steel from English iron which has been rendered perfectly malleable at a red-heat, by the addition of manganese, is re-melted *without* adding manganese, it becomes as red-short as ever. According to Parry, the presence of manganese in sensible quantity in steel tends to render it brittle when cold.

*Silicon.*—Silicon in small quantity seems to increase the hardness of steel without taking away from its malleability or toughness when cold, and the presence of a trace of silicon appears to have the singular effect of preventing that violent evolution of gas from fluid steel at the moment of solidifica-

tion, which renders the ingot so frequently unsound. Steel containing above 0·5 per cent. of silicon breaks up under the hammer if heated above low redness.

*Titanium, &c.*—The effect of titanium, tin, arsenic, silver, and other metals upon steel, is stated to produce *increased hardness*, but I have not myself made any experiments upon this subject, nor been able to find very reliable observations of others.

*Tungsten* has a very remarkable effect upon steel, first observed by Dr. Werner Siemens, in 1853, in increasing its power of retaining magnetism when hardened. Being specially interested in this question, I have determined, by careful experiments, the extent of the increase; and the practical result is, that whereas a horse-shoe magnet of ordinary steel, weighing 2 lbs., is considered of good quality when it bears *seven times* its own weight, and the famous Haarlem magnet of the same weight, supports about 13 times its weight, I am now able to produce a similar horse-shoe magnet carrying 20 times its weight, suspended from its armature.

The chief difficulty besetting experiments on the effects of these various admixtures upon the quality of steel, consists in the unavoidable presence of other substances in variable proportions; but the effects of these other substances could be eliminated if the experiments were accompanied by exhaustive analyses, and it is impossible to over-estimate the advantages that would result from such a course.

*Processes.*—Dr. Percy, in his truly invaluable metallurgical work, has made us acquainted with the various known processes for obtaining steel which have been followed from the earliest times; but no method of producing steel can be considered admissible at the present day which does not pass the metal through the condition of entire liquefaction, for it is only by fusion that foreign admixtures can be thoroughly separated, and that flaws and fissures can be avoided; inasmuch however as the steel obtained by them may be subsequently fused, I shall briefly refer to them. The principal processes of this class are:—

1. The *direct process* of making steel, or steely iron, from the ore in the Catalan forge, by employing a large excess of charcoal. The steel is obtained without fusion in the form of a ball of spongy metal, and is drawn out into bars.

2. The *cementation process*, in which bar-iron is converted into

steel by prolonged contact at a comparatively low temperature either with liquid cast-iron, as formerly practised in Styria and elsewhere,\* or with crushed charcoal—a method extensively employed in Sheffield at the present day for the manufacture of steel for railway and carriage springs, and for the production of bar-steel from Swedish iron, which, when subsequently melted in pots, makes the finest quality of steel for tools and cutlery.

3. The *decarburization process*, in which steel is made from cast-iron by the removal of part of the carbon in the puddling furnace, or by the partial application of any of the older methods of decarburizing cast iron in an open hearth in direct contact with the fuel. A modified form of the decarburization process has been recently introduced to some extent by Messrs. Heaton and Hargreaves. They remove the carbon of the pig-iron by the action of oxydizing salts, principally nitrate of soda, and either fuse the crude metal obtained, producing cast steel, or work it up into blooms under the hammer.

The Bessemer process, now so well known, is also a method of producing steel by the decarbonization of cast iron; but it presents a vast advantage over those just named, in the fact that the steel is obtained in the liquid state, and may be cast, free from flaws, into homogeneous ingots of any size. As Bessemer steel is produced much more cheaply than the cast steel obtained by any other process yet extensively in use, its introduction has opened out a vast field for the application of steel where iron alone could formerly be thought of. Thus many parts of steam and other machinery, railway plant, boiler-plates, and even rails, are now made of Bessemer steel, and are found to be cheaper in the end when made of that material rather than when made of iron, although their absolute cost is fully twice as great.

*Cast Steel.*—The remaining methods of producing cast steel, are those in which it is obtained by the fusion either of steel already made by other processes, or of its component materials, iron or iron-ore, on the one hand, and carbon, either as charcoal or already combined in the form of cast iron, on the other.

The oldest known steel of high quality, the Indian Wootz, is obtained by the fusion of compact iron and carbonaceous substances in small crucibles, but it is only in the course of the last century that the manufacture of cast-steel was first introduced in Europe.

\* Percy, Metallurgy, II, 790, 807.

Réaumur states, in his work on the conversion of forged iron into steel, published in 1722, that he had succeeded in producing steel by the fusion together of cast and wrought iron in a common forge; but steel melting was first practically carried out in the latter half of the century by Huntsman, of Sheffield; the process he employed consisting in "*the fusion in closed crucibles of steel already made by cementation in charcoal,*" is still universally in use for the production of the finest qualities of steel for tools and cutlery. The Hindoo process has, however, been revived within the last twenty years, by Heath, Price and Nicholson, Gentle Brown, Attwood, and others, and large quantities of steel are now made in Sheffield and elsewhere, by the fusion of puddled iron or puddled steel with charcoal, or with pure pig-iron (Canadian or Spiegeleisen), in such proportions as to form steel of the required quality. The Uchatius process is somewhat similar to these in principle; it consists in effecting the partial decarburization of granulated pig-iron by fusing it in contact with iron-ore, but the temper obtained is said to be irregular, and, together with the process just mentioned, it labours under the disadvantage of involving the expensive operation of *fusion in pots*.

*Open Hearth.*—Some method of effecting the fusion of steel more cheaply than in crucibles, as well as in larger masses, has long been a desideratum. Heath, the discoverer of the beneficial action of manganese, was the first (in 1845) to conceive that cast-steel might be produced in large quantities by fusing wrought and cast-iron together upon the open hearth of a reverberatory furnace. The *modus operandi* he proposed, consisted in melting pig-metal in a cupola, and running it into the heated furnace. The wrought-iron was introduced into another part of the furnace, forming a bank between the bath of fluid metal and the chimney, to be there heated by the waste heat of the flame, previously to its being pushed forward into the liquid in order to be dissolved. Fearing the effect of the ashes from a common fire-place, Heath proposed to heat his furnace by jets of gas, and there is every probability that his experiments would have been crowned with success, if he had possessed the means of imparting to his flame the intensity of heat and, at the same time, the absence of cutting draught, which are essentially necessary. Since the date of Heath's patent, the fusion of steel in an open furnace has formed the subject of an

extensive series of experiments, by Sudre, in France. The experiments of M. Sudre were made at the Montataire Iron Works, at the expense of the Emperor of the French, and were superintended, on his behalf, by three members of the French Institute; MM. Sainte-Claire Deville, Treuille de Beau-lieu, Colonel of Artillery, and Caron, Captain of Artillery, who have made an able report on the subject, showing that it is just possible to raise the heat of an ordinary furnace by means of a fan-blast, sufficiently to effect the fusion of tool-steel upon the open hearth in protecting the metal by a layer of glass, but that the rapid destruction of the furnace, the cost of fuel, and other difficulties attending the operation, were such as to render the process, commercially, of doubtful value.

*Regenerative Gas Furnace.*—The regenerative gas furnace is so manifestly suitable for the operation of melting steel, both in pots and on the open hearth, that my attention was directed from the first towards this object. The early experiments conducted by my brother and myself at Sheffield failed, however, partly on account of certain irregularities, arising from defects in the furnace which have since been removed, but chiefly in consequence of the want of determination on the part of the manufacturers and their workmen to persevere with us to the attainment of the proposed results.

*Attwood.*—In 1862, Mr. Charles Attwood took a licence to apply the regenerative gas furnace to the melting of steel upon the open hearth in connection with certain chemical processes or mixtures of his own. I supplied the design of a furnace which answered the purpose, except that the quality of steel produced was not such as Mr. Attwood desired. This circumstance decided him to carry out his process in closed pots heated in the same furnace.

*Le Chatelier.*—In 1863, my friend, M. Le Chatelier, Ingénieur en Chef des Mines, elaborated a process for producing steel from cast-iron by puddling, and melting the hot puddled blooms in a bath of cast-iron prepared in a regenerative gas furnace, upon a bed of *bauxite* of the following composition:—

Silica. . . . .	13 to 17 per cent.
Alumina . . . . .	60 to 65 „
Peroxide of iron. . . .	4 to 8 „
Water in combination	15 to 17 „

This material presents the advantage of being exceedingly infusible and of containing no materials that could impart hurtful ingredients to the steel. A furnace of great heating power was constructed by Messrs. Boigue, Rambour, and Co., at their works near Montluçon, in France, under my superintendence and would certainly have accomplished the desired object if the company had displayed the least determination to succeed. The furnace-bottom of bauxite did not succeed, as it was not solidified by the heat, and rose to the surface of the liquid bath,—but this defect was soon rectified by the substitution of a white sand bottom. Through some carelessness, however, the covering arch of the furnace was damaged by excess of heat; and this slight accident, which proved nothing except an ample sufficiency of heating power, sufficed to deter the company from pressing on to the attainment of that success which was so nearly within their reach. In the meantime I had granted a licence to Messrs. Emile and Pierre Martin, of the Sireuil Works, to melt steel, both in pots and on the open hearth, and a furnace was erected by them in 1864 which was chiefly intended for a heating furnace, but was at the same time constructed of such materials (Dinas brick) and in such a form as to be also applicable for melting steel.

With this furnace, which was really less suitable than those previously erected, MM. Martin have succeeded in producing cast-steel of good quality and of various tempers, and their produce was awarded a gold medal at the great French Exhibition of last year. MM. Martin have since patented various arrangements of their own, such as the employment of particular *fluxes* to cover the surface of the molten metal, the application of a *separate furnace* for heating the iron before charging it into the melting furnace, and the employment of particular brands of cast and wrought-iron, which may be useful under special circumstances, but which form no essential part of the general solution of the problem.

Having been so often disappointed by the indifference of manufacturers and the antagonism of their workmen, I determined, in 1865, to erect experimental or "Sample Steel Works" of my own at Birmingham, for the purpose of maturing the details of these processes, before inviting manufacturers to adopt them. The first furnace erected at these works, is one for melting the higher qualities of steel in closed pots, and

contains 16 pots of the usual capacity. The second, erected in 1867, is an open bath furnace, capable of melting a charge of 24 cwt. of steel every 6 hours. Although these works have been carried on under every disadvantage, inasmuch as I had to educate a set of men capable of managing steel furnaces, the result has been most beneficial, in affording me an opportunity of working out the details of processes for producing cast-steel from scrap-iron of ordinary quality and also directly from the ore, and in proving these results to others.

I shall now proceed to describe the construction and working of the regenerative gas furnaces (similar to those at Birmingham) which are now at work, or in course of erection, in this country and abroad for the production of cast-steel, both by the old method of fusion in pots, and by the new system of making cast-steel on a large scale and on an open furnace bed, from *scrap iron* and from the *ore*.

The regenerative gas furnace consists of two essential parts ;

The Gas Producer, in which the coal or other fuel used is converted into a combustible gas ; and

The Furnace, with its " regenerators " or chambers for storing the waste heat of the flame, and giving it up to the in-coming air and gas.

Any combustible gas might be burned in the regenerative furnace ; I have used ordinary lighting gas very successfully on a small laboratory scale, but it is far too costly to be employed in larger furnaces, and the only gas generally available is that generated by the complete volatilisation of coal, wood, or other fuel, with admission of air in a special " gas producer." Any description of carbonaceous matter may be worked in a suitable gas producer, and will afford gas sufficiently good for the supply of even those furnaces in which the highest heat is required. Coal is the fuel chiefly used for gas furnaces in England ; small coke has been employed in some cases, as in gas-works, where it is to be had at a cheap rate ; wood is used in France, Bohemia, and Spain ; sawdust in Sweden, furnishing gas for welding and other high-heat furnaces ; lignite in various parts of Germany ; and peat in Italy and elsewhere ; this last being applicable with the greatest relative advantage.

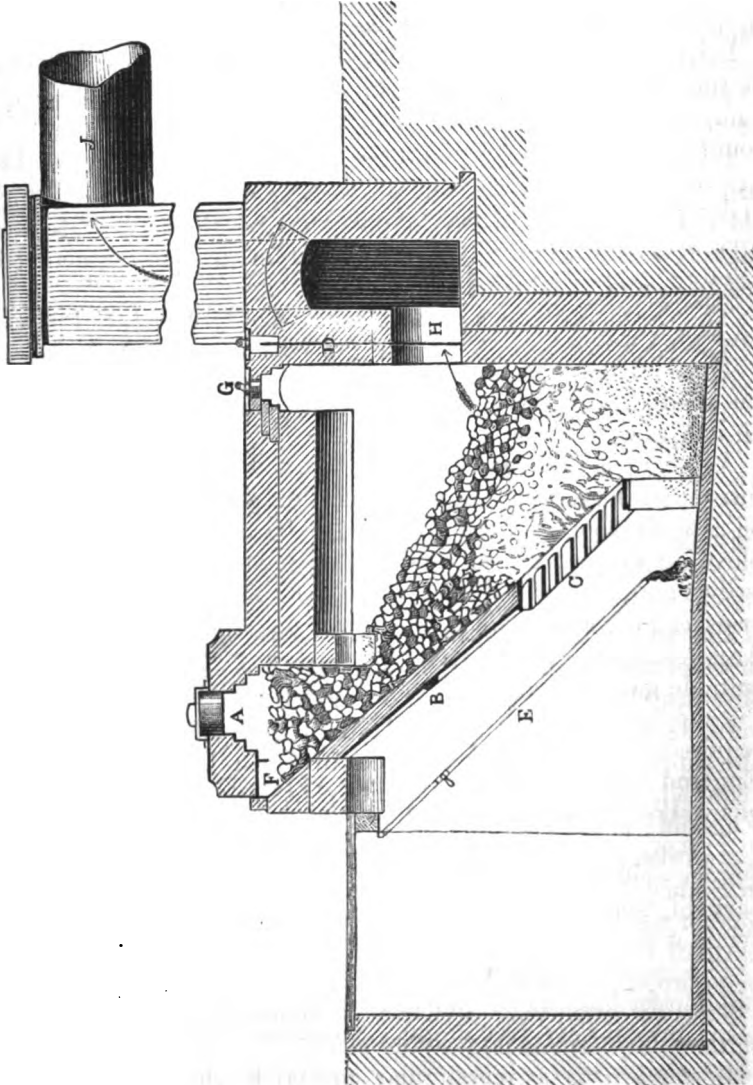
The accompanying illustration represents a gas-producer suitable for burning non-caking slack.

In form it is a rectangular fire-brick chamber, one side

of which, B, is inclined at an angle of from  $45^{\circ}$  to  $60^{\circ}$ , and is provided with a grate, C, at its foot. The fuel is filled in

SECTION OF GAS PRODUCER.

(Scale  $\frac{1}{4}$  inch to a foot.)





at the top of the incline at A, and falls in a thick bed upon the grate. Air is admitted at the grate, and as it rises slowly through the ignited mass, the carbonic acid, first formed by the combination of the oxygen with the carbon of the fuel, takes up an additional equivalent of carbon, forming carbonic oxide, which diluted by the inert nitrogen of the air and by a little unreduced carbonic acid, and mixed with the gases and vapours distilled from the raw fuel during its gradual descent towards the grate, is led off by the gas flue to the furnace. The ashes and clinkers that accumulate on the grate are removed at intervals of one or two days.

The composition of the gas varies with the nature of the fuel used, and the management of the gas producer. That of the gas from the producers at the Plate Glass Works, St. Gobain, France, burning a mixture of  $\frac{3}{4}$  caking coal and  $\frac{1}{4}$  non-caking coal is as follows, by an analysis dated July, 1865:—

	Volumes.
Carbonic oxide .....	23·7
Hydrogen .....	8·0
Carburetted hydrogen .....	2·2
Carbonic acid .....	4·1
Nitrogen .....	61·5
Oxygen .....	0·4
	99·9

The trace of oxygen present is no doubt due to carelessness in collecting the gas, or to the leakage of air into the flue, and allowing for this, the corrected analysis will stand as under:—

	Volumes.	
Carbonic oxide .....	24·2	}
Hydrogen .....	8·2	
Carburetted hydrogen ....	2·2	
Carbonic acid .....	4·2	}
Nitrogen .....	61·2	
	100·0	

Only the first three of these constituents, say 35 per cent. of the whole, are of any use as fuel, the nitrogen and carbonic acid present only diluting the gas. It is the presence of this

large proportion of inert gases, which must be heated to the full temperature of the flame, that renders it so difficult to maintain a high heat by gas of this description burned in the ordinary way. In using such gas in a regenerative furnace the presence of so large an amount of nitrogen is not objectionable, as the heat it carries off is given up again to the air and gas coming in.

The gas as it passes off from the fuel contains also more or less aqueous vapour, which is got rid of by cooling it, with some tar and other impurities, and a small quantity of suspended soot and dust.

Any air drawing in unburned through a hole in the mass of fuel, reduces the value of the gas, by burning the carbonic oxide again to carbonic acid. To prevent the indraught of air in this way at the side of the grate, I have found it very advantageous to set the side walls of the gas producer back, forming a broad step, about nine or ten inches above the grate; any air creeping up along the wall is thus thrown into the mass of fuel and completely burned. The effect of this feature in the form of the producer on the quality of the gas has been very striking.

Three-tenths of the total heat of combustion of solid carbon are evolved in burning it to carbonic oxide; but in the gas producer, a small portion only of this heat is really lost, because it is in a great measure taken up and utilized in distilling the tar and hydrocarbon gases from the raw fuel; and it may be still further economised, especially in burning a fuel, such as coke or anthracite, which contains little or no volatile matter, by introducing a regulated supply of steam with the air entering at the grate. This is effected very simply by keeping the ash-pit always wet. The steam is decomposed by the ignited coke, and its constituents, hydrogen and oxygen are re-arranged as a mixture of hydrogen and carbonic oxide, with a small variable proportion of carbonic acid. Each cubic foot of steam produces nearly two cubic feet of the mixed gases, which, being free from nitrogen have great heating power and form a valuable addition to the gas. The proportion of steam that can be advantageously introduced into the gas producer is, however, limited, as it tends to cool the fire, and if this is at too low a heat, much carbonic acid is produced instead of carbonic oxide, causing waste of fuel.

From the high temperature of the gas, as it rises from the

fuel (1000° F. to 1300° F.), and from its comparatively low specific gravity, it is considerably lighter than atmospheric air, and ascends into the upper part of the producer with a slight outward pressure. It is necessary to maintain this pressure through the whole length of the gas flue, in order to ensure a free supply of gas to the furnaces, and to prevent its deterioration in the flue, through the indraught of air at crevices in the brickwork. The slight loss of gas by leakage, which results from a pressure in the flue, is of no moment, as it ceases entirely in the course of a day or two, when the crevices become closed by tar and soot.

Where the furnace stands so much higher than the gas producer, that the flue may be made to rise considerably, the required plenum of pressure is at once obtained; but more frequently the furnaces and gas producers are placed nearly on the same level, and some special arrangement is necessary to maintain the pressure in the flue. The most simple contrivance for this purpose is the "elevated cooling tube." The hot gas is carried up by a brick stack to a height of eight or ten feet above the top of the gas producer, and is led through a horizontal sheet-iron cooling tube, J, of not less than 60 square feet of surface per gas producer, from which it passes down either directly to the furnace, or into an underground brick flue.

The gas rising from the producer at a temperature of about 1100° F., is cooled as it passes along the overhead tube, and the descending column is consequently denser and heavier than the ascending column of the same length, and continually over-balances it. The system forms, in fact, a syphon in which the two limbs are of equal length, but the one is filled with a heavier fluid than the other. The height of cooling tube required to produce as great a pressure in the flue as would be obtained by placing the gas producers, say *ten feet* deeper in the ground may be readily calculated. The temperature of the gas as it rises from the producers has been taken as 1100° F., and we may assume that it is cooled in the overhead tube to 100° F., an extent of cooling very easily attained. The calculated specific gravity, referred to hydrogen, of the gas of which I have quoted the analysis, being 13·14, we obtain the following data:—

	lb.
Weight of the gas per cube foot at 1100° F.	= ·022
"                    "                    "                    100° F.	= ·061
Weight of atmospheric air per cube foot at 60° F.	= ·076

and from these we have, on the one hand, the increase of pressure per foot of height, in a flue rising directly from the gas producer,

$$= \cdot076 - \cdot022 = \cdot054 \text{ lb. per square foot;}$$

and on the other hand, the excess of pressure at the foot of the downtake from the cooling tube, over that at the same level in the flue, leading up from the gas producer (for each foot in height of the cooling tube)

$$= \cdot061 - \cdot022 = \cdot039 \text{ lb. per square foot.}$$

The height of the cooling tube above the level of the flue that will be sufficient to produce the required pressure, equal to 10 feet of heated gas column, is therefore,

$$\frac{\cdot054}{\cdot039} \cdot 10 \text{ ft.} = 13' 10'', \text{ or say } 14 \text{ feet.}$$

This method of obtaining a pressure in the gas-flue by cooling the gas, has been objected to as throwing away heat that might be employed to more advantage in the furnace, but this is not the case, because the action of a regenerator is such, that the initial temperature of the gases to be heated has no effect on the final temperature, and only renders the cooling of the hotter fluid more or less complete. The only result, therefore, of working the furnace with gas of high temperature is to increase the heat of the waste gases passing off by the chimney flue. The complete cooling of the gas results, on the other hand, in the great advantage of condensing the steam that it always carries with it from the gas producer; and in the case of iron and steel furnaces, in burning wet fuel, it is absolutely necessary to cool the gas very thoroughly, in order to get rid of the large amount of steam that it contains, which, if allowed to pass on to the furnace, would oxidize the metal.

There is, undoubtedly, a certain waste of heat, which might

be utilized by surrounding the cooling tube with a boiler, or by otherwise economising the heat it gives off, as, for instance, in drying the fuel; but the saving to be effected is not very great, for as 100 volumes of the gas require for combustion about 130 volumes of air, including 20 per cent. above that theoretically required, the heat given off in cooling the gas 1000° is no more than would be lost in discharging the products of the complete combustion of the fuel, at a temperature 435° in excess of the actual temperature of 200°, and this loss is greatly diminished if a richer gas is obtained.

In erecting a number of gas producers and furnaces, I generally prefer to group the producers together, leading the gas from all into one main flue, from which the several furnaces draw their supplies. The advantages of this are saving of labour and convenience of management, from the gas producers being all close together, and greater regularity in working, as the furnaces are seldom all shut off at once; nor is it likely that all will require at the same time an exceptional amount of gas.

From the fact that the gas producers may be at any distance from the furnaces that they supply, if they are only at a lower level, it would be perfectly practicable to erect them in the very coal mine itself, burning the slack and waste coal *in situ* (in place of leaving it in the workings as is now often done), and distributing the gas by culverts to the works in the neighbourhood, instead of carrying the coal to the different works and establishing special gas producers at each. In rising to the mouth of the pit, the gas would acquire sufficient pressure to send it through several miles of culvert.

In the regenerative furnace the gas and air employed are separately heated by the waste heat of the flame, by means of what are termed "regenerators," placed beneath the furnace. These are four chambers, filled with fire-bricks, stacked loosely together, so as to expose as much surface as possible; the waste gases from the flame are drawn down through two of the regenerators, and heating the upper rows of bricks to a temperature little short of that in the furnace itself, pass successively over cooler and cooler surfaces and escape, at length, to the chimney flue nearly cold. The current of hot gases is continued down through these two regenerators until a considerable depth of brickwork, near the top, is uniformly heated

to a temperature nearly equal to that of the entering gas, the heat of the lower portion decreasing gradually downwards, at a rate depending on the velocity of the current, and the size and arrangement of the bricks. The direction of the draught is then reversed; the current of flame or hot waste gases is employed to heat up the second pair of regenerators; and the gas and air entering the furnace are passed in the opposite direction through the first pair, and coming into contact, in the first instance, with the cooler brickwork below, are gradually heated as they ascend, until, at some distance from the top, they attain a temperature nearly equal to the initial heat of the waste gases, and, passing up into the furnace, meet and at once ignite, producing a strong flame, which, after passing through the heating-chamber, is drawn down through the second pair of regenerators to the chimney-flue. The temperature attained by the ascending gas and air remains nearly constant, until the uppermost courses of the regenerator brickwork begin sensibly to cool; but by this time the other two regenerators are sufficiently heated, and the draught is again reversed, the stream of waste gases being turned down through the first pair of regenerators, re-heating them in turn, and the gas and air which enter the furnace being passed up the second.

By thus reversing the direction of the draught at regular intervals, nearly all the heat is retained in the furnace that would otherwise be carried off by the products of combustion, the temperature in the chimney-flue rarely exceeding 300° F., whatever may be the heat in the furnace. The proportion of heat carried off in an ordinary furnace by the products of combustion is generally far greater than that which can be utilized, as all the heat of the flame below the temperature of the work to be heated is absolutely lost. The economy of fuel effected in the regenerative gas furnace, by removing this source of loss, and making all the heat of the waste gases, however low its intensity, contribute to raise the temperature of the flame, amounts in average practice to fully 50 per cent. on the quantity used in an ordinary furnace, and the saving is greater the higher the heat at which the furnace is worked. In addition to this economy in the amount of fuel used, a much cheaper quality may generally be burned in the gas producer than could be used in a furnace working at the same heat, and in which the fuel is burned directly upon the grate in the ordinary way.

When the heat of the furnace is not abstracted continually by cold materials charged into it, the temperature necessarily increases after each reversal, as only a very small fraction of the heat generated is carried off by the waste gases. The gas and air, in rising through the regenerators, are heated to a temperature nearly equal to that at which the flame had been passing down, and when they meet and burn in the furnace the heat of combustion is added to that carried up from the regenerators, and the flame is necessarily hotter than before, and raises the second pair of regenerators to a higher heat. On again reversing, this higher heat is communicated to the gas and air passing in, and a still hotter flame is the result.

The temperature that may be attained in this way by the gradual accumulation of heat in the furnace and in the upper part of the regenerators appears to be quite unlimited, and the heat at which a suitably designed furnace can be worked is limited in practice only by the difficulty of finding a material sufficiently refractory of which it can be built.

Welsh Dinas brick, consisting of nearly pure silica,\* is the only material, of those practically available on a large scale, that I have found to resist the intense heat at which steel-melting furnaces are worked; but though it withstands perfectly the temperature required for the fusion of the mildest steel, even this is melted easily if the furnace is pushed to a still higher heat.

As the gas flame is quite free from the suspended dust which is always carried over from the fuel by the keen draught of an ordinary furnace, the brick-work exposed to it is not fluxed on the surface and gradually cut away, but fails, if at all, only from absolute softening and fusion throughout its mass. A Stourbridge brick, for example, exposed for a few hours to the heat

\* Analysis of Dinas "clay" from Pont-Neath-Vaughan, Vale of Neath (Percy's Metallurgy, vol. i, p. 237).

Silica .....	98.81
Alumina .....	0.72
Protoxide of iron .....	0.18
Lime.....	0.22
Potass and soda .....	0.14
Water combined.....	0.35

99.92

The "clay" is mixed with 1 per cent. of lime in making the bricks.

of the steel-melting furnace, remains quite sharp on the edges, and is little altered even in colour; but it is so thoroughly softened by the intense heat, that on attempting to take it out, the tongs press into it and almost meet, and it is often pulled in two, the half-fused material drawing out in long strings. It results from this perfect purity of the flame, that where the heat is not sufficient to effect the absolute fusion of the bricks employed, the length of time is almost unlimited, during which a gas furnace will work without repairs.

Another advantage in employing the fuel in the manageable form of gas is that the rate of combustion may be regulated at pleasure to produce an active heating flame of any length, from little more than two feet, as in the pot steel-melting furnaces, to thirty feet in the largest furnaces for the fusion of plate glass; and the most intense heat may be thrown exactly upon the charge, the ends of the furnace and the apertures through which the gas and air are introduced being actually protected from the heat by the currents of unburned and comparatively cool gases flowing through them, and only mixing and burning at the very point at which the heat is required, and where it is taken up at once by the materials to be fused or heated. This is of especial importance in the case of those furnaces in which a very intense heat is employed.

The amount of brickwork required in the regenerators to absorb the waste heat of a given furnace is a matter of simple calculation. The products of the complete combustion of one pound of coal have a capacity for heat equal to that of nearly 17 pounds of firebrick,\* and (in reversing every hour) 17 pounds of regenerator brickwork at each end of the furnace per pound

\* Taking the analysis by Vaux of the celebrated ten-yard coal of South Staffordshire (Watts' Dictionary of Chemistry, i, 1081), the exact calculation is as follows:—

Composition of the coal.		Oxygen required.	
Carbon .....	·7857	x $\frac{8}{3}$ =	2·0952
Hydrogen.....	·0529	x 8 =	0·4232
Sulphur.....	·0039	x 1 =	0·0039
			<hr/>
Nitrogen .....	·0184		2·5223
Oxygen.....	·1288	..... less.....	0·1288
Ash .....	·0103		<hr/>
		net oxygen required	2·3935
	1·0000	20 per cent. excess	0·4737
			<hr/>
		Total Oxygen .....	2·8721



of coal burned in the gas-producer per hour would be theoretically sufficient to absorb the waste heat, if the whole mass of the regenerator were uniformly heated at each reversal to the full temperature of the flame, and then completely cooled by the gases coming in; but in practice by far the larger part of the depth of regenerator chequer-work is required to effect the gradual cooling of the products of combustion, and only a small portion near the top, perhaps a fourth of the whole mass, is heated uniformly to the full temperature of the flame; the heat of the lower portion decreasing gradually downwards nearly to the bottom. Three or four times as much brickwork is thus required in the regenerators, as is equal in capacity for heat to the products of combustion.

The best size and arrangement of the bricks is determined by the consideration of the extent of opening required between them to give a free passage to the air and gas, and by the rule, deduced from my experiments on the action of regenerators in 1851-2,\* that a surface of six square feet is necessary in the regenerator to take up the heat of the products of combustion of one pound of coal in an hour.

By placing the regenerators vertically and heating them from the top, the heating and cooling actions are made much more uniform throughout than when the draught is in any other direction, as the hot descending current on the one hand passes down most freely through the coolest part of the mass, while the ascending current of air or gas to be heated, rises chiefly

Corresponding Nitrogen ..	9·616
Nitrogen in the fuel .....	·018
	9·634
Total Nitrogen .....	9·634

Gases produced from 1 lb. of coal.	Specific heats.	Equivalent weight of water.
Carbonic acid = 2·881	·217	·625
Water (Steam) = 0·476	·480	·228
Sulphurous acid = 0·004	·154	·001
Oxygen in excess = 0·479	·218	·104
Nitrogen = 9·634	·244	2·350
		8·308
Total equivalent weight of water.....		8·308
"                    "          firebrick (sp. heat = 0·2) ....		16·540

\* Proceedings of the Institution of Civil Engineers, 1852-3, page 571, On the Conversion of Heat into Mechanical Effect.

through that part which happens to be hottest, and cools it to an equality with the rest.

The regenerators should be always at a lower level than the heating chamber; as the gas and air are then forced into the furnace by the draught of the heated regenerators, and it may be worked to its full power, either with an outward pressure in the heating chamber, so that the flame blows out on opening the doors, or with the pressure in the chamber just balanced, the flame sometimes blowing out a little, and sometimes drawing in. The outward pressure of the flame prevents that chilling of the furnace, and injury to the brickwork, from the in-draught of cold air through crevices, which is otherwise unavoidable in any furnace worked without blast.

The action of the furnace is regulated by the chimney damper, and by valves governing the supply of gas and air, and the draught is reversed by cast-iron reversing valves, on the principle of the common four-way cock.

*Fusion of Steel in Crucibles.*—In the application of the system to the fusion of steel in closed pots or crucibles, the melting chamber, containing generally 24 pots, is constructed in the form of a long trench, 3 feet 6 inches wide at the bottom, and gathered in to under 2 feet at the top. The sides of the melting-chamber are arched both horizontally and vertically, to keep them from sinking together in working, and the work is strengthened by cross walls at intervals. The pots are set in a double row along the centre of the melting-chamber, and the flame passes from side to side, the gas and air from the regenerators being introduced alternately from one side and from the other, opposite to each pair of pots. The melting chamber is closed above by loose firebrick covers, which are drawn partly off in succession by means of a lever suspended from a pulley above the furnace, when the pots are to be charged or drawn out. The pots stand in a bed of finely ground coke-dust, resting on iron plates. The coke dust burns away only very slowly, if it is made of hard coke and finely ground, and it presents the great advantage of remaining always in the form of a loose dry powder, in which the pots stand firmly, while every other material that I have tried either softens at the intense heat, or sets after a time into a hard, uneven mass, in which the pots do not stand well.

The process of melting carried out in this form of gas furnace

is the same in all respects as that in the small air furnaces or melting-holes fired with coke which are commonly employed, but a great saving is effected in the cost of fuel, and in the number of crucibles required.

The ordinary consumption of hard coke, costing 22s. per ton in Sheffield, is between three and four tons per ton of steel fused, while in the gas furnace the same work may be done by the expenditure of 15 to 20 cwt. of common coal slack (worth only 5s. to 8s. per ton), at a cost that is of only 5s. against 75s. per ton of steel melted. There is a further saving in the number of crucibles required, as they may be used in the gas furnace four or five, and sometimes even ten times, while in furnaces heated by coke, two or three casts are as much as are ever obtained. The lining of the furnace lasts at least 15 to 20 weeks without repair (in working day and night), while 4 to 5 weeks is the longest duration of the ordinary coke-fired holes.

*Fusion of Steel on the Open Bed.*—The furnace employed for the fusion of steel on the open bed is similar in shape to a reheating or puddling furnace; the direction of the flame is from end to end; and the regenerators are placed transversely below the bed, which is supported on iron plates, kept cool by a current of air. The air enters beneath the bed plates in front, and escapes by two ventilating shafts at the back of the furnace near the ends. This cooling of the bed is very necessary to keep the slag or melted metal from finding its way through into the regenerator chambers. The upper part of the furnace is built entirely of Dinas brick.

There are three doors in the front of the furnace, one in the centre immediately over the tap-hole, and two near the bridges, through which the bed can be repaired when necessary, and ingot ends or other heavy scraps may be charged in. Sloping shoots are provided at the back of the furnace, through which long bars, such as old rails, may be conveniently charged, and beneath these are openings for charging the pig-iron. The upper end of the shoots is on a level with an elevated charging platform behind the furnace.

The bottom of the furnace is formed of siliceous sand, which answers exceedingly well if properly selected and treated.

Instead of putting moist sand into the cold furnace, as is usually done in preparing the bottoms of furnaces for heating or melting iron or copper, I dry the sand, and introduce it into the hot

furnace, in layers of about 1" thickness. The heat of the furnace must be sufficient to fuse the surface of each layer, that is to say, it must rather exceed a welding heat to begin with, and rise to a full steel-melting heat at the end of the operation, in order to impart additional solidity to the uppermost layers. Care must be taken that the surface of the bath assumes the form of a shallow basin, being deepest near the tap-hole. Some white sands, such as that from Gornal, near Birmingham, will set under these circumstances into a hard impervious crust, capable of surviving from 20 to 30 charges of liquid steel, without requiring material repairs. If no natural sand of proper quality is available, white sand, such as Fontainebleau sand, may be mixed intimately with about 25 per cent. of common red sand, to obtain the same results.

In tapping the furnace, the loose sand near the tapping-hole is removed, when the lower surface of the hard crust will be reached. The lowest point of this surface is thereupon pierced by means of a pointed bar, upon the withdrawal of which the fluid metal runs out from the hottest and deepest portion of the bath into the ladle in front of the furnace.

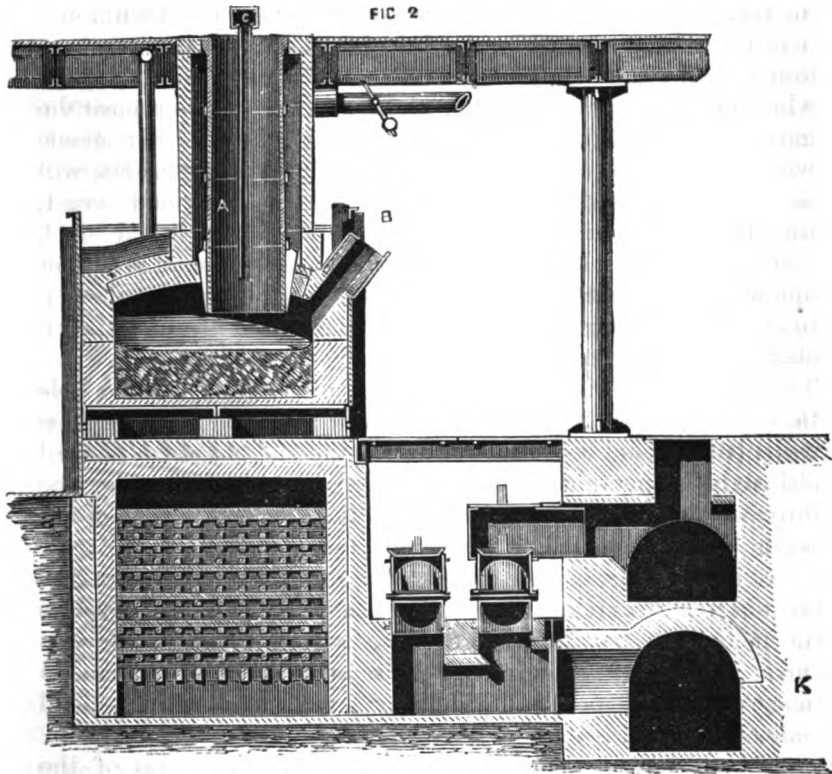
M. Le Chatelier now proposes to mix the natural Bauxite, of which the bottom of the experimental furnace at the works of MM. Boignes, Rambourg and Co., near Montluçon was first made, with about 1 per cent. of chloride of calcium in solution, to calcine the mixture, and to form it into moulded masses of highly refractory material.

A hard bottom being thus prepared, and the heat of the furnace being raised to whiteness, it is ready to receive the materials to be melted.

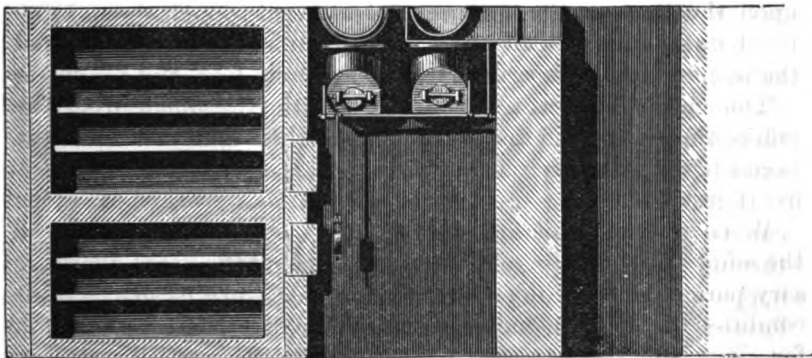
If these materials consist of bar iron, or of old iron and steel rails, they are cut into lengths of about six feet, and are introduced into the furnace through slanting hoppers from the elevated platform at the back, so that their ends rest upon the sand bottom forming the bath.

If the capacity of the furnace is such, that charges of 3 tons can be formed, about 6 cwt. of grey pig-iron is introduced through the ports or short hoppers, below the main charging hoppers before-mentioned. As soon as a bath of pig metal is formed, the heated ends of the rails or bars begin to dissolve, causing the bars gradually to descend. By partially closing the mouths of the charging hoppers, a regulated quantity of

THE REGENERATIVE GAS FURNACE AS APPLIED TO THE PRODUCTION OF CAST STEEL DIRECTLY FROM THE ORE.



Transverse section on line C D.



Half plan through the regenerator chamber and main gas flue.

Scale  $\frac{1}{4}$  inch to a foot.

- AA Charging shoots for the ore.
- BB Charging shoots for the pig iron.
- C Tube conveying reducing gas into the mass of ore.

flame is allowed to escape from the furnace, in order to heat the descending bars of metal previous to their entry into the melting-chamber, the object being to maintain the high temperature of the furnace, notwithstanding the constant introduction of cold metal. The escaping products of combustion, which are thus withdrawn from the regenerators, are a positive gain to the heat of the furnace, because, having been in contact with comparatively cold metal, they would be at a heat inferior to that of the upper portions of the regenerators, and would therefore only lower their temperatures.

As the bars sink in the hoppers by their gravity, they are followed up by additional bars until the metal charged amounts to about three tons, all of which will be rendered fluid within about four hours from the time of commencing the charge. The metallic bath is tested from time to time by the introduction of a bar through one of the front doors of the furnace, and if the bath should become thick before the end of the operation, although the heat has been maintained, it will be necessary to introduce an additional quantity of pig-metal. All the metal being liquid, a sample is taken out by means of a small iron ladle, and plunged into cold water while still red-hot. In breaking this sample upon an anvil, the temper and quality of the metal may be fairly judged. Its fracture should be bright and crystalline, betokening a very small proportion of carbon (not exceeding .1 per cent.), and the metal should be tough and malleable, notwithstanding its sudden refrigeration. From 5 to 8 per cent. of Spiegeleisen (containing not less than 9 per cent. of manganese), is thereupon charged through the side openings upon the bank of the furnace, and allowed to melt down into the bath, which is then stirred and made ready for tapping in the manner before described.

The amount of carbon introduced with the Spiegeleisen determines the temper of the steel produced, the manganese being necessary to prevent redshortness, unless Swedish or Styrian iron is used.

When old iron rails or scrap of inferior quality are charged, the addition of manganese does not suffice to effect the necessary purification of the steel produced; but the perfectly liquid condition of the bath, together with the unlimited time available for chemical reaction, offer extraordinary advantages for the introduction of such materials as may be found to combine with

sulphur, phosphorus, silicon, or arsenic, which are the usual antagonists to be dealt with.

The experiments which I have been able to institute in this direction, are by no means complete;—nevertheless, I have obtained most beneficial results from the introduction into the bath of litharge, in conjunction with oxidising salts containing strong bases, such as the alkaline nitrates, chromates, chlorates, stannates, titanates, &c.

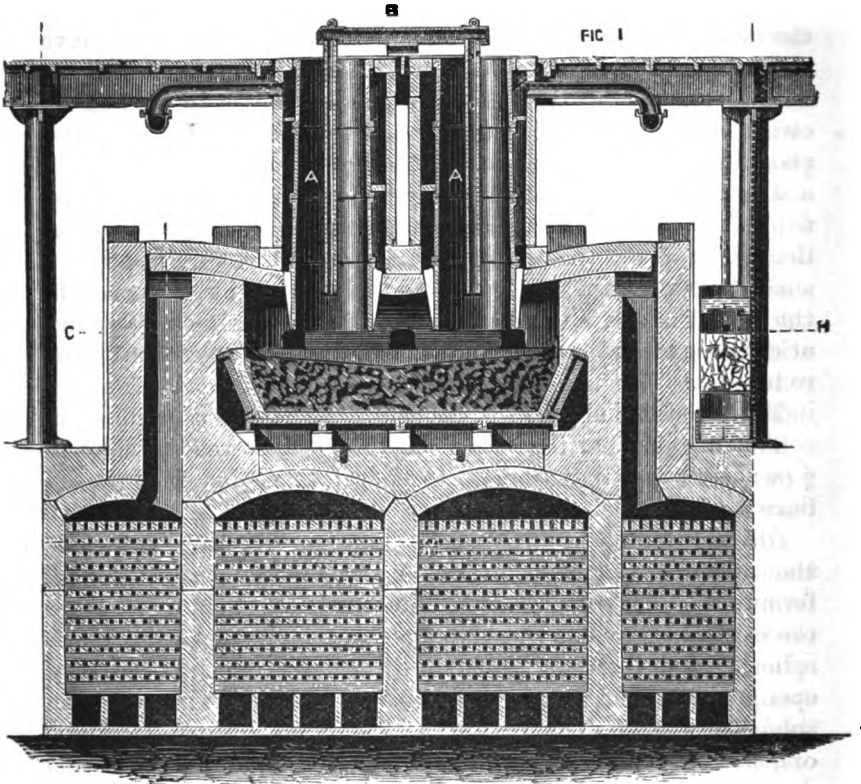
The choice of the reagents and the quantity to be employed depend, naturally, upon the quality and quantity of objectionable matter to be removed.

By the aid of the process just described, it will be possible to convert old iron rails into steel rails of sufficiently good quality at a cost scarcely exceeding that of re-rolling them into fresh iron rails. The non-expensive nature of the process may be judged by the fact that extremely little labour is required in conducting it; that the loss of metal does not exceed from 5 to 6 per cent., and that from 10 to 12 cwt. of coal suffices to produce a ton of cast steel.

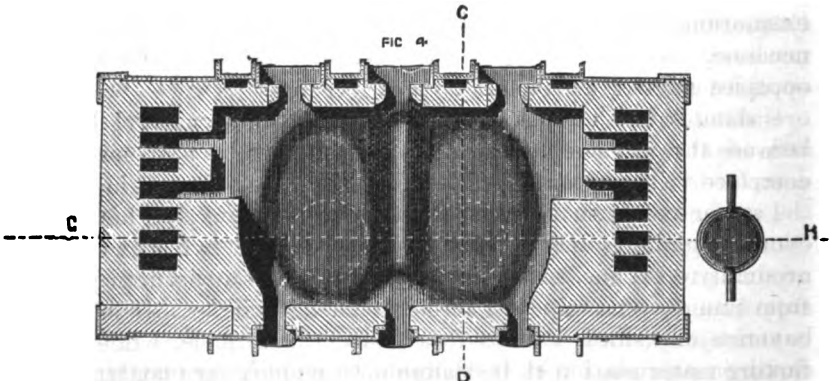
*Ore.*—Although I have succeeded in producing malleable steel from ordinary English iron by this process, it would be unreasonable to expect steel of really high quality, in using those materials which are already contaminated in the blast-furnace; and I am sanguine in the expectation of producing cast steel superior in quality, and at a low cost, directly from the better description of ores, such as the hæmatites, magnetic oxides, and the spathic carbonates. My experiments in this direction extend over several years; and last year I sent a few bars of steel produced from hæmatite ore, to the French Exhibition, which had stood a high test in Kirkcaldy's machine. A "grand prix" was awarded for this and other applications of the regenerative gas furnaces.

Having tried various modifications of the furnace, I have arrived at a form of apparatus not dissimilar to the one just described. The furnace and tapping arrangements are, indeed, the same, except that for the slanting hoppers, vertical hoppers over the middle of the bath, are substituted, in which the ore gradually descends. Each hopper is formed of a cast iron pipe, supporting a clay-pipe, which is attached to it by means of a bayonet-joint, and reaches down into the furnace, while the cast-iron pipe rests with its flange on the charging platform.

THE REGENERATIVE GAS FURNACE AS APPLIED TO THE PRODUCTION OF CAST STEEL DIRECTLY FROM THE ORE.



Longitudinal section on the line G H.



Section of plan through the melting chamber.  
Scale  $\frac{1}{4}$  inch to a foot.



A fire space is provided surrounding each hopper, through which flame ascends from the furnace, and is allowed to escape in regulated quantities near the upper extremity of the retort, the object being to heat the latter and the ore contained in it to a red heat. A wrought iron pipe descends into each hopper from a general gas-tube above, through which a current of ordinary producer gas is forced in amongst the heated ore. The propulsion of the gas is effected most conveniently by means of a steam-jet in the gas-tube leading from the main gas-channel to the top of the furnace, care being taken to effect a total condensation of the steam by passing the gas finally through a small scrubber, in which water trickles over pieces of coke. In this way the gas is at the same time purified from sulphurous acid, the sulphur of which might otherwise combine with the reduced ore.

The furnace is charged in the following manner:—

The hoppers and gas-pipes being placed in position, about  $\frac{1}{4}$  cwt. of charcoal is charged through each hopper to form a basis for the ore with which these are afterwards filled.

About 10 cwt. of pig-metal is charged through the ports at the back or front of the furnace, which, upon being melted, forms a metallic bath below the hoppers. In the meantime, the ore in the lower parts of the hoppers, being heated in an atmosphere of reducing gas, has become partially reduced into metal sponge, which, in reaching the metallic bath, is readily dissolved in it, making room for the descent of the superincumbent ore, which is likewise reduced in its descent and dissolved in due course, fresh ore being continually supplied on the charging platform. The dissolution of the reduced ore proceeds with extraordinary rapidity, but is practically limited by the time necessary to effect the reduction of the ore in the hopper which occupies several hours. It is, however, not essential that the ore should be thoroughly reduced before reaching the bath, because the carbon contained in the cast metal serves also to complete the operation.

I prefer to employ a mixture of hæmatite and spathic ore, containing the elements for forming a fusible slag, which will accumulate on the surface of the metallic bath, and may be from time to time removed through the centre door. If the ore contains any silica, it is necessary to add some lime or other fluxing materials, but it is desirable to employ ores containing

little gangue, in order not to encumber the furnace with slag, reserving the poorer ores for the blast furnace. The ore should moreover, be in pieces ranging from the size of a pea to that of a walnut, in order to be pervious to the reducing gases. If ores in the form of powder are employed, it is necessary to mix them with about 10 per cent. by weight of light carbonaceous materials, such as dry peat, wood, or charcoal.

The metallic bath having sufficiently increased in the course of from three to four hours, the supply of ore is stopped, and that contained in the hoppers is allowed to sink. Before the hoppers are empty, a false cover of cast iron, lined with clay at its under side, is introduced, being suspended from above by a strong wire, in order to prevent the access of flame to the interior of the empty hoppers. Charcoal and ore are filled in upon the top of this false cover, and, on cutting the wire, afterwards form the commencement of the succeeding charge.

When all the ore has disappeared, the metallic bath is tested as before described in reference to the melting of scrap. If it should be partially solidified, cast iron is added to re-establish complete liquefaction; but if, on the other hand, the bath contains an excess of carbon, oxidising agents may be added as before described, in requisite proportion. From 5 to 8 per cent. of Spiegeleisen is then added, and the furnace is tapped as already described.

The quality of the steel produced is chiefly dependent upon the quality of the ore, but considering that ores of great freedom from sulphur, phosphorus, or arsenic can be had in large quantities, this process contains all the elements for producing steel of high quality.

Having tried a variety of ores, I do not attach much importance to their precise composition, so long as they are comparatively free from gangue, and from sulphur and phosphorus, the heat being sufficient to reduce the most refractory. My experience is, however, as yet limited to experimental working.

I hoped to have been in a position to have given you the temperature of this furnace, as determined by an electric resistance pyrometer, which I have constructed for this purpose, but have not yet been able to obtain satisfactory results, owing to the destruction of the coil of platinum wire, which has to be exposed to the heat. My efforts were baffled moreover by the fact, interesting in itself, that platinum wire produced by fusion

# PROCEEDINGS

AT THE

## MEETINGS OF THE CHEMICAL SOCIETY.

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Anniversary Meeting, March 30th, 1868.

Mr. Warren De la Rue, F.R.S., President, in the Chair.

The following report was read by the President :—

The President and Council on this, as on many previous anniversary meetings, are able to congratulate the Society upon the gradually increasing number of its Fellows, upon the prosperous state of its finances, and above all upon the continuance of its activity and usefulness.

The number of Fellows at the last anniversary was 499 : at present the number is 510. The particulars of alteration are as follows :—

Number of Fellows, March 30th, 1867 .. ..	499
Since elected and paid admission fees .. ..	34
	<hr/>
	533
Removed on account of arrears .. ..	8
Withdrawn .. .. .	5
Deceased .. .. .	10
	<hr/>
	23
Number of Fellows, March 30th, 1868 .. ..	<hr/>
	510
Number of Foreign Members, March 30th, 1867	40
Deceased .. .. .	1
	<hr/>
Number of Foreign Members, March 30th, 1868	<hr/>
	39

Number of Associates, March 30th, 1867	..	0
Since elected	.. .. .	2
		<hr/>
Number of Associates, March 30th, 1868	..	2

The names of the Fellows who have withdrawn are:—

C. N. Ellis, Anselm Odling, Dr. F. V. Paxton, Edward Rea, W. V. Russell.

During the past season the subject of the admission of new Fellows into the Society has been specially considered by the Council. The report of a Committee appointed for inquiring into the matter having been adopted by the Council and circulated among the Fellows, the by-law relating to the election of Fellows was, after due notice, amended in accordance with the recommendation of the Committee's report, at an extraordinary general meeting of the Society, held on December 5th, 1867.

The by-law now stands as follows:—

Every candidate for admission into the Society shall be proposed according to a form of recommendation (see No. 1 Appendix) subscribed by five Fellows of the Society, to three, at least, of whom he shall be personally known; and such certificate shall be read and suspended in the Society's rooms, or place of meeting, for three Ordinary Meetings.

The following is the List of Papers read at the meetings of the Chemical Society between March 30th, 1867, and March 30th, 1868:—

1. "Note on Solidified Glycerin:" by Dr. Gladstone.
2. "Experiments on Oxidation by means of Charcoal:" by Prof. Crace Calvert.
3. "Observations on the Weathering of Copper Ores:" by Mr. J. Spiller.
4. "On the Oxidation of the Acids of the Lactic Series:" by Messrs. E. T. Chapman and Miles H. Smith.
5. "On Limited Oxidation with Alkaline Permanganate:" by Messrs. E. T. Chapman and Miles H. Smith.
6. "On the Presence of Soluble Phosphates in Cotton Fibre, Seeds, &c.:" by Prof. Crace Calvert.

7. "Observations on Combination by the Alleged Saturation of Atomicities:" by Dr. Odling.
8. "On the Constitution of the Phosphites:" by Professor Rammelsberg.
9. "On the Changes in the Proportion of Acid and Sugar in Grapes during the Process of Ripening:" by Dr. Dupré.
10. "On the Addition of Plaster of Paris to Must:" by Dr. Dupré.
11. "On an Adapter to Absorb Sulphuretted Hydrogen:" by the Rev. B. W. Gibson.
12. "On the Practical Loss of Soda in the Alkali Manufacture:" by Mr. W. C. Wright.
13. "On some new Derivatives of Hydride of Salicyl:" by Mr. W. H. Perkin.
14. "On Pyrophosphoric Acid:" by Dr. Gladstone.
15. "On Water Analysis and the Determination of Organic Matter in Water:" by Messrs. Wanklyn, Chapman, and Smith.
16. "Analysis of a Biliary Concretion:" by Dr. Phipson.
17. "On the Action of Chloride of Iodine on Picric Acid:" by Dr. Stenhouse.
18. "On the Chloride of Carbon of Julin:" by Mr. H. Bassett.
19. "On the Estimation of Compound Ethers in Wine:" by Dr. Dupré.
20. "On the Action of Acetic Anhydride upon the Hydride of Salicyl, Ethyl-Salicyl, &c.:" by Mr. W. H. Perkin.
21. "On Nitrous and Nitric Ethers:" by Messrs. E. T. Chapman and Miles H. Smith.
22. "On the part taken by Oxide of Iron and Alumina in the Absorptive Action of Soils:" by Mr. R. Warrington, Jun.
23. "Analysis of the Water of the Holy Well, at Humphrey Head, North Lancashire:" by Mr. T. E. Thorpe.
24. "On the Action of Permanganate of Potash on Urea, Ammonia, and Acetamide, in strongly Alkaline Solutions:" by Messrs. J. A. Wanklyn and Arthur Gamgee.
25. "Verification of Wanklyn, Chapman and Smith's Process of Water Analysis:" by Prof. J. A. Wanklyn.
26. "On the Relation between the results of Water Analysis and the Sanitary Value of the Water:" by Mr. E. T. Chapman.
27. "On the Pyrophosphoric Amides:" by Dr. Gladstone.

28. "On the Artificial Production of Coumarin and Formation of its Homologues:" by Mr. W. H. Perkin.
29. "On Turacin, a New Animal Colouring Matter:" by Prof. Church.
30. "Note on the Preparation of Urea:" by Mr. John Williams.
31. "On the Freezing of Water and Bismuth:" by Mr. Alfred Tribe.
32. "On the Isomeric Forms of Valeric Acid:" by Mr. Alexander Pedler.
33. "On a Simple Apparatus for Determining the Gases incident to Water Analysis:" by Dr. Frankland.
34. "On the so-called Thioformic Acid:" by Dr. Debus.
35. "On a New Galvanic Battery:" by Mr. Warren De la Rue and Dr. Hugo Müller.
36. "On Gas Analysis:" by Dr. J. W. Russell.
37. "On the Reduction of Carbonic Acid to the State of Oxalic Acid:" by Dr. Dreschel.
38. "On some New Benzylic Derivatives of the Salicyl Series:" by Mr. W. H. Perkin.
39. "On the Action of Oxidizing Agents on Organic Compounds in Presence of Excess of Alkali:" by Messrs. Wanklyn and Chapman.
40. "Note on Dr. Frankland's Process of Water Analysis:" by Mr. E. T. Chapman.
41. "Note on the Estimation of Nitric Acid in Potable Waters:" by Mr. E. T. Chapman.
42. "On the Hydride of Aceto-Salicyl:" by Mr. W. H. Perkin.
43. "On the Absorption of Vapours by Charcoal:" by Mr. John Hunter.
44. "On the Occurrence of Prismatic Arsenious Acid:" by Mr. T. Claudet.
45. "On the Action of Nitric Acid on Picramic Acid:" by Dr. Stenhouse.
46. "On Chloranil:" by Dr. Stenhouse.
47. "On the Action of Zinc-ethyl on Nitrous and Nitric Ethers:" by Messrs. E. T. Chapman and Miles H. Smith.
48. "On the Direct Transformation of Carbonate of Ammonia into Urea:" by Professor Kolbe.

The following lectures also have been delivered:—

“On Ideal Chemistry:” by Sir Benjamin C. Brodie, Bart.

“On Water Analysis:” by Dr. Frankland.

“On Chemical Geology:” by Mr. David Forbes.

“On the Manufacture of Glass:” by Mr. Henry Chance.

### *Progress of Chemistry.*

Without pretending to give an account of the extraordinary activity in chemical investigation, and the important additions made to the science of chemistry since you were last addressed from this chair, I may, nevertheless, bring briefly to your recollection some of the most important work which has been accomplished during the past year.

Although organic chemistry still receives the larger share of attention, inorganic chemistry has, nevertheless, latterly gained in popularity, and bids fair to gather a continually increasing number of votaries. In purely theoretical chemistry, the appearance of Sir Benjamin Brodie's chemical calculus has given a new impulse to abstract speculation on a subject which goes to the very foundation of the true philosophy of our science. Whatever may be the ultimate verdict of chemists with respect to the views propounded by Sir Benjamin, it cannot be disputed that the publication of his monograph will have initiated a most valuable and suggestive discussion.

On account of its important bearing on the physics of chemistry, I will recall, in the first instance, the remarkable results obtained by Professor Graham, in the pursuance of his researches on dialysis. You will remember that MM. Deville and Troost had observed the permeability of platinum and iron to hydrogen at a high temperature; also that Professor Graham had pointed out the power which a septum of india-rubber possesses in separating gases. Following up this train of thought, he has been more recently induced to study the action of metallic septa at different temperatures, and has found that the permeability is different for different gases, and that even an approximate separation of gases mixed together can be effected by this means. The extraordinary power of condensation and occlusion of some gases, possessed by several metals, among which palladium is so especially distinguished,

may be regarded as one of the most striking phenomena which have been brought under the notice of chemists.

Messrs. Frankland and Duppa, in continuation of their researches in synthetical chemistry, have given a very important contribution to the long list of new bodies with which the method used by themselves and Geuther, had already enriched chemistry, and which, by the light they throw upon isomerism, are justly deserving of the high appreciation of chemists.

In the same direction may be cited the results of the important researches of Fittig, and his associates, on the synthesis of the aromatic hydrocarbons, which have been considerably augmented during the last year.

The transformation of aromatic monamines into acids richer by one increment of carbon, effected by Hofmann, by subjecting the monamine to distillation in the presence of oxalic acid, whereby a certain portion of the corresponding nitrile is obtained, constitutes a valuable method for preparing certain aromatic acids which until now existed only in theory. The discovery by Hofmann of a new series of isomers of the hydro-cyanogen series, also promises to afford a fertile field of chemical research.

Passing on to another branch of synthesis, it is gratifying to notice, that the number of instances of the artificial production of organic substances, formerly known only as products of organised life, is also steadily on the increase. Perkin, during his researches on hydride of salicyl, has effected the artificial formation of coumarin, whereby the exact association of this interesting substance with the salicylic series has been established.

Liebreich, some years ago, discovered an interesting organic base, neurine, a direct derivative of protogan, a constituent of brain. Baeyer has since shown that this substance has the composition and constitution of hydrate of oxethyl-trimethyl ammonium, thereby suggesting the possibility of the synthetical production of neurine. Wurtz has quite recently carried the suggestion into effect, and has actually produced this complex organic body by artificial means. I cannot pretend to assert that our modern theory of chemistry is not destined to be substituted by other hypotheses, but I think the artificial production of so complex a substance as neurine may be adduced as evidence of our being able to form a good working theory, and of the general soundness of modern chemical reasoning.



Urea, the artificial production of which furnished the first proof of the identity of chemical and vital action, has been quite recently produced by a new process, which, like so many other processes of Kolbe, startles us by its simplicity and boldness. Finally, in drawing attention to the synthetical production of oxalic acid carried out by Drechsel, in Kolbe's laboratory, I conclude the list of recent additions to the number of artificially produced substances—results which must always be regarded as triumphs of mind over matter.

In physiology, it will suffice to record here the recent unlooked-for results obtained by Pettenkofer and Voit, in their experiments with the celebrated respiration apparatus at Munich, by which it appears that during sleep animals store up oxygen, a fact which seems to throw important light on the functions of sleep.

Friedel and Ladenberg, by the discovery of the silicium-mercaptan, have brought more prominently to light the chemical resemblance of carbon and silicium.

The recent researches on gun-cotton by Abel, have completed the chemical history of this remarkable substance, an instalment of which was given by him in his former memoir on the subject. He has now cleared away all doubts respecting its stability and adaptability for use as an explosive.

In the branch of analysis, it is hardly necessary to refer to the zealous prosecution of the important subject of the analysis of potable water, further than to prognosticate that, out of the active investigations which have recently so much engaged our attention, we may look forward to an early solution of the problem.

In concluding this very brief review of the progress of chemistry, I must not omit to mention the interest which has been re-awakened in the chemical investigation of geological phenomena; and we look forward with interest to the new views which we may expect to be developed.

During the past year we have lost, by the hand of death, nine Fellows and one Foreign member of our Society; death has also removed a distinguished chemist, who, although he withdrew from the Society some years ago, will be recollected by many as one of the original members; I mean Dr. Thomas Clark.

List of Fellows deceased, since the last Anniversary, March, 1867:—

Walter Crum, Esq., F.R.S., Dr. Daubeny, F.R.S., Dr. Faraday, F.R.S., W. H. Gossage, Esq., William Herapath, Esq., Alfred Noble, Esq., Rev. H. M. St. Aubyn, John Tennent, Esq., Robert Warington, Esq., F.R.S., J. Pelouse, Membre de l'Acad. Imp. des Sciences, Paris; William Winsor, Esq., died the 1st of November, 1865.

Thomas Clark, one of the original members of the Chemical Society, was born in Ayr, on the 31st March, 1801. His father, a man of singular energy, integrity, and circumspection, was captain of a merchantman, and, during a long career, sailed in every sea, without encountering a disaster. His mother was also a woman of uncommon cast; she originated the well-known Ayrshire needlework. All the children that grew up to maturity were marked with strength of character, in different ways. Thomas was educated at the Ayr Academy, a school then famous in the west of Scotland, numbering upwards of 400 pupils. The course of instruction was extensive and complete, including French, classics, and mathematics; and the rector (Mr. Jackson, afterwards Professor of Natural Philosophy in St. Andrew's University), gave occasional lectures in experimental science. Clark was considered a heavy, dull boy; his progress was slow, till about 13, when he began mathematics, and became one of the distinguished boys of the Academy. He was fond of propounding school-boy schemes, and got the *sobriquet* "Philosopher Tom." Many men of eminence have proceeded from the same school.

In 1816, he went to Glasgow, and entered the counting-house of Charles Macintosh and Co., the inventors of the waterproof cloth. The main portion of the business of the firm at that time was preparing a material known as "cudbear," which was used as a scarlet dye, more especially in the manufacture of cloth for the army. While Clark was still in the employment of the firm, they began the manufacture of the India-rubber cloth. Macintosh also, from a mineral found in the margin of the coal formation, created an extensive alum manufacture.

It was in this connexion that Clark first had his mind turned to mineralogy and chemistry, and their applications in the arts.

Although he often remarked that his training in the counting-house was of value to him in the diagrammatic representation of scientific facts, he was by no means an apt accountant, and he did not remain very long at the work. The Macintoshes discovered the true bent of his mind; and, on their recommendation, he obtained the situation of chemist, in Tennant's Chemical Works, at St. Rollox.

In 1826, he was appointed Lecturer in Chemistry to the Glasgow Mechanics' Institution, having then left St. Rollox. About this date, he began his career of original investigation. In the programme of his lectures for 1826, he gave his table of chemical elements and formulæ, from which may be inferred the state of advancement of his views on the atomic theory, and the theory of salts.

That theory of the constitution of salts in which they are represented as uniformly consisting of a metal or hydrogen united with a radical, simple or compound, no doubt originated in Davy's discovery of the composition of chloride of sodium; and the credit of the generalization is generally ascribed to that philosopher. But it does not appear that Davy ever expressed the view in precise terms. In objecting to the rival view—of the presence of acids and oxides in salts like the sulphate of potash, and in illustrating his binary theory of certain other salts,—he looked upon the former class as triple compounds of metalloids, metals, and oxygen. He admits, though with inaccurate numbers, that the atomic weight of hydrogen is 1, of oxygen 16, of carbon 12, and of sulphur 16; water being composed of two atoms of hydrogen and one of oxygen. But the new theory, particularly in its relation to the function of hydrogen in the hydrated acids, appears to have been first properly appreciated and fully developed by Dr. Clark in his early chemical lectures of 1826. It was sagaciously applied by him to explain the proportion of acids in salts of peroxides, like sulphate of alumina, and was a manifest advance upon the canon of Berzelius, that the oxygen of the acid is always a multiple of the oxygen in the base. Dr. Clark also interpreted the atomic theory less rigidly than most of his English contemporaries, and more in accordance with modern views. He allowed portions of an equivalent to be represented, as  $\frac{3}{4}$  Fe, the quantity of iron united with one equivalent of oxygen in the peroxide, which he could thus assimilate to a protoxide in con-

stitution. He exercised also a free judgment in fixing the atomic weights of elements, and we find in his table of 1826, carbon made 12, and oxygen 16, in reference to hydrogen as 1.

In an early essay shown to friends privately, but never printed, he established the fact that bisulphate of potash consists of sulphate of potassium combined with sulphate of hydrogen. Thence he assumed that all the acid salts are similarly constituted, for example, the bichromate of potash. On experiment, he found that this salt contained no hydrogen, and belonged to a class containing more than one equivalent of acid without the elements of water. He, consequently, lost faith in his theories, and shrunk from their consequences.

In 1826, he published his papers, entitled (1.) "On the Pyrophosphate of Soda," (2.) "On the Arseniate of Soda," and (3.) "On a New Phosphate of Soda." Probably the most durable of Clark's contributions to chemistry is the discovery of the pyrophosphate of soda, considering the support given by that discovery to the then struggling doctrine of isomerism, and the important part played by the phosphoric acids in leading to the more recent ideas of polyatomicity. The establishment of so new and characteristic a substance as pyrophosphate of soda is likely always to hold a place in chemical history. Sir John Herschel in his "Introduction to the Study of Natural Philosophy," pronounced this research as one of the most felicitous examples of a successful induction.

It was with a view to teaching chemistry in a medical school, and not to medical practice, that, in 1827, he entered the University of Glasgow, as a medical student, and, after passing through the medical course, took the Doctor's degree, in 1831. In 1829, he became apothecary to the Glasgow Infirmary. While in this office, he made three contributions to Pharmacy: (1.) On the Pharmaceutical Preparation of the Precipitated Carbonate of Iron; (2.) A Chemical Examination of Singleton's Golden Ointment, with an improved formula for preparing the Red Precipitate Ointment; (3.) On a new Process for preparing medicinal Prussic Acid. (Glasgow Medical Journal, Nos. 11, 12, 14.)

In 1832, he published, in the "Westminster Review," an exceedingly elaborate enquiry into the whole system of existing weights and measures. It attracted great attention, and the value of it is not yet exhausted. He had collected materials

for a second article, which would have probably been full of curious interest, "On the Lost History of English Weights and Measures." Neither this, nor another enquiry that occupied him for a considerable time,—on the Law of Patents—was ever published.

The Professorship of Chemistry in Marischal College having become vacant by the death of Dr. French, in October, 1833, Clark became a candidate for the office, which had to be filled up by competitive examination. The other candidates were Dr. Henderson, and Dr. Laing. The examiners (Dr. Thomson, of Glasgow, the Rev. Mr. Forsyth, of Belhelvie, Professors Davidson and Skene, of Marischal College), reported in favour of Dr. Clark, and he was elected and admitted accordingly.

As a chemical lecturer, he had strongly marked peculiarities. Applying his thoroughly original and independent mind to chemistry, as to every thing else, he took nothing on trust himself; and it was his aim to bring before the students whatever doubts and difficulties attended the subject, and to exhibit the evidence, experimental or theoretical, for each position. He also paid great attention to the manner of stating and expounding his science. Instead of commencing with the generalities of the atomic theory, he described in detail a few of the leading elements—as oxygen, hydrogen, carbon, sulphur, stating, as matter of fact, the proportions of each in the several compounds, water, carbonic acid, &c., without making any references to the theory of combination. He next took up the atomic theory and expounded it minutely, showing how far it was hypothetical, and how far an expression of experimental truth. Then followed the usual detail of the elements and their compounds, interspersed with discussions of leading points, as the constitution of the salts and acids, the theory of muriatic acid, the theory of the prussiates, &c. He devoted occasional lectures to leading processes in the arts, as the manufacture of coal-gas. His method of describing these was carefully studied, but was chiefly resolvable into the practice of starting from known and familiar elements, and showing how they became transformed in the course of the operation to the more recondite products. Many of his students probably remember, to this hour, the manufacture of sulphuric acid, as depicted by him from his acquaintance with the works at St. Rollox.

There was what many parties considered a want of order in his course. He did not proceed by following out a systematic and exhaustive classification of the elements, as in an ordinary chemical text book. He rather selected important and typical bodies, making them the representative of general classes and doctrines. This was especially his way with organic chemistry, under which he merely adverted to a few important substances. Neither was he systematic in dealing with the chemistry of drugs; a few substances that he had thoroughly mastered being all that he took notice of. Indeed, system was never his strong point; he disliked the empty vagueness often disguised under a systematic array, and preferred the minute and thorough investigation of single and isolated facts. The accurate determination of any fact, however limited its place in a system, or even its utility, was always to him an intense satisfaction.

At the time of his going to Aberdeen, he had thoroughly investigated at least two subjects. The first of these was the theory of hydrometry, and the practice of hydrometer-making. The practical outcome was the construction of an instrument which at once gave, by its own readings, the true specific gravity, instead of requiring a calculation by a formula.

The other subject was the detection of arsenic. This he had studied with reference to the soda and mineral acid manufactures, and he had found methods of detecting the slightest quantities of arsenic in all the different products of these manufactures. At that time, an account of these methods would have been of the greatest value; but he never prepared any paper on the subject. The practical results were the improved methods employed in his own laboratory, for purifying the sulphuric and hydrochloric acids, and for testing arsenic in poisonings.

His practical turn of mind, and his experience in chemical manufactures, would have probably led him into extensive practice as a commercial chemist, had not his Aberdeen professorship removed him to a distance from the seats of the great manufactures. He acted for several successive summers, as adviser to a chemical company in Staffordshire, but the business was interrupted by disputes among the proprietors.

In 1835 was published his paper On the Application of the Hot Blast in the Manufacture of Cast Iron; in which he gave the true explanation of the benefits arising from the process.

He had also been occupied in making investigations on the subject for the inventors.

In 1836 appeared his letter to Mitscherlich, "On a Difficulty in Isomorphism, and on the Received Constitution of the Oxygen Salts;" of which no notice was ever taken by the Berlin chemist. Although, in this paper, he still prefers the new to the old view of the salts, he speaks in very measured language, and considered that both ways must remain open to the choice of chemists, until some discovery be made, inconsistent with one, and compelling the adoption of the other; and he thought that the subject he was then considering would be found to yield the desired solution.

Clark is best known by his water tests, and his process for softening hard waters. The specification of his patent for the softening process (October, 1841) described the three tests employed—the soap test, the acid test, and the silver test. In a circular addressed to his "chemical friends" (1847), he entered into a more minute description of the tests for hardness and for alkalinity, but was embarrassed by the discordance of his own experiments to fix the degrees of hardness corresponding to the soap test measures. He did not get over the difficulty, until, in June, 1849, when he had to report to the General Board of Health, on certain specimens of water proposed to be supplied to the town of Birmingham. He then found that the action of magnesia on the soap test was peculiar. At a certain degree of dilution, its hardening effect is partially disguised, or latent, and is brought out only after further dilution. In one of the Birmingham specimens, the actual hardness of the water was 8·3°, while dilution brought out a farther hardness of 8·5°. This result suggested to him the true cause of the irregularity of his table of soap-test measures, namely, the presence of a small quantity of magnesia in the ordinary chalk waters. On preparing artificially a solution of carbonate of lime, he found that the correspondence of the degrees of hardness and the soap-test measures was exact and numerical throughout.

The softening process has been hitherto declined by the London companies, although in the invention, he had chiefly in view the water supplied by them. It was first applied at Plumstead, Woolwich; next at Castle Howard, the seat of the Earl of Carlisle; then, at Caterham, Surrey; and recently at the Chitern Hills, in all cases with perfect success. Our colleagues,

Professors Graham, Miller, and Hofmann in reporting in 1851, to the Government, as to "the chemical quality of the waters supplied, and proposed to be supplied to the Metropolis," remarked with reference to the process, "it is no longer possible to disregard the chemical means of removing hardness, or to represent them as impracticable on a great scale; they place the question of water supply upon an entirely new footing."

At the beginning of the session 1843-4, the question of the abolition of University Tests was taken up by the Senatus of Marischal College, in a series of resolutions moved by Dr. Clark. In the preparing and correcting of these resolutions he spent, as usual, enormous labour, and was very much excited by the subject. In the course of that session he became seriously ill of disease in the brain, which interrupted his lecturing; and he never again was able for the work of his class. For several years he was wholly absent from Aberdeen, and resided in his mother's house, first at Glasgow, and afterwards at Rothesay. So obstinate was the derangement, that his life was a constant series of headaches, and his days were often spent in bed. In the beginning of 1848, after four years of such disablement, he was induced to try a course of the hydropathic treatment, then coming into notice, and obtained a degree of benefit not amounting to a radical cure, but changing entirely his whole course of life. His headaches became rare; he was no longer obliged to be in bed in the day-time; he took regular exercise, and was fit for consecutive study. In 1849 he married, and in the same year resumed his residence in Aberdeen. He had hopes of being able to teach his class again, but found that his strength, though improved, was unequal to unbroken task work; and he made himself useful to the College in the struggles that ended in the union of the Aberdeen Universities in 1860, which led to his being superannuated.

In all the discussions connected with medical education he always took a leading part. He was the chief promoter of the scheme of examinations pursued at Marischal College, which was a great advance in strictness and severity. He was deputed by the Senatus to watch over the medical Bills introduced in 1844 and 1845, and spent many weeks in London on that object.

His earliest publication connected with university reform was



a pamphlet (in 1833) entitled "Reform in the University of Glasgow," containing a complete university constitution, with a new governing body, somewhat akin to the recently constituted university courts in the Scotch universities. There is also a minute examination of Mr. Oswald's Bill for the University of Glasgow.

The question of the union of the Aberdeen universities had been agitated at various times, and was brought up, soon after Dr. Clark's appointment, by Mr. Bannerman's Bill, and again by the Royal Commission of 1836. Dr. Clark studied the whole subject carefully, and his letter to the Commission is a very able document, which may, one day, be looked back to with interest.

A pamphlet appeared in January, 1850, challenging the right of Marischal College to grant degrees in divinity, law, or medicine, and the official circular of King's College for 1851, contained a sentence implying the same want of authority on the part of Marischal College. This was the occasion of a pamphlet by Dr. Clark, in which he argued the question from a decision of the House of Lords, under Lord Chancellor Hardwicke, in 1745. His reasoning was forcible and conclusive, and was couched in his peculiar style of elaborate and studied statement. Both language and typography had their powers tasked to the utmost to give explicitness and force to the arguments.

The introduction of the Scotch Universities' Bill of Lord Advocate Inglis necessarily involved discussions and negotiations in the several universities. The Bill contained clauses for uniting the two separate Aberdeen universities—King's College and Marischal College—into one university. Dr. Clark took part in opposing the union, and was the author of numerous memorials and statements with reference to it. His opposition turned upon the very strong views entertained by him as to the effective teaching of the classes. It was the distinction of the Aberdeen Colleges to possess classes of manageable dimensions, with thorough examination and discipline, and he was strongly apprehensive that this advantage must cease with the fusion.

When Mr. John Stuart Mill became Lord Rector of the University of St. Andrews, he chose for assessor Dr. Clark, being intimately and personally acquainted with his general ability, as well as his great aptitude and experience in university matters.

Clark was, throughout life, an ardent politician of the liberal school, and formed decided opinions on all passing public measures. He was a frequent contributor of leading articles to the journals, and on those occasions wrote with rapidity, and with no small pungency of manner, as well as pertinency in the matter. In all the various controversies that he found himself involved in, he made free use of the editorial pen in support of his side.

A much more extended notice would be necessary to give an adequate impression of Clark's various labours and many-sidedness. His industry between the ages of twenty and forty must have been enormous. His intellectual faculties belonged to the highest class. His strongest feature may be expressed by sagacity, and his delight was to attain his ends by the simplest and often the seemingly most unlikely means. He had essentially a practical mind; his originality and his sagacity took the direction of practical suggestions. His love of minute accuracy, so valuable in itself, was carried to a pitch of extravagance, which was perhaps his chief foible, as an investigator. He never knew when to have done refining and improving: hence the unfinished state of so many of his inquiries. His attention to style was an additional source of embarrassment and delay, when he had any work to publish.

The energy and vehemence of all his determinations made him urgent and imperious; and, while increasing his sway over others, often excited no small hostility and dislike. He was furious in his onslaught when roused by opposition, yet he could also control himself and employ all the resources of his cultivated expression in suavity, courtesy, and conciliation. His loves and his hates were alike on a large scale, but his amiable side greatly preponderated. His generosity and sympathy were manifested both in public spirit and in private benefits. He was looked up to and beloved by the whole circle of his intimate friends.

His death was somewhat sudden. On the morning of the 27th November last he was unable to get up as usual. He soon became insensible, and expired at two o'clock the same day.

His last years were made sorrowful, and his widow's grief is now deepened, through the loss of an amiable and gifted boy, their only child.

The name of Walter Crum occupies a high rank among those cultivators of science of whom England is justly proud; men actively engaged in arduous business or professional pursuits sufficient to engross the intellectual energy of the most industrious, who nevertheless find leisure to contribute materially to the stock of human knowledge. Mr. Walter Crum, who died on the 5th of May, 1867, was born in Glasgow in 1796, and educated in that city. In 1818 and 1819 he was a distinguished student of practical chemistry under the late Dr. Thomas Thomson, and from this period devoted much time and energy to the cultivation of science. For upwards of forty years he took a leading part in the improvement of calico printing, by the application of chemical discoveries, and has been long recognized as the scientific head of that interesting art in this country. Mr. Crum, indeed, gained for the house of which he was the principal, a place in the front rank, not only for the excellence of its products, but also for the high character of its transactions. In February, 1823, Mr. Walter Crum communicated to the *Annals of Philosophy* his first and well-known paper, entitled "Experiments and Observations on Indigo, and on certain Substances which are produced from it by means of Sulphuric Acid." This paper is remarkable for a facility in expedients and for accuracy in analysis; it not only gained for him a European reputation, but will remain an enduring monument to his fame as one of the early pioneers in accurate organic research.

Among the chemical discoveries of Mr. Walter Crum may be noted the formation of a new oxide of copper, analogous in composition to peroxide of iron. The paper containing an account of this substance was published in the *Mem. of the Chem. Soc.*, vol. ii, p. 387. In the *Journal of the Chem. Soc.* for 1854 he described an isomeric variety of alumina which is incapable of combining with colouring matter. In an early investigation of gun-cotton he described a method for determining nitrogen, lately revived in the analysis of potable waters. Mr. Crum showed that a large class of colouring matters are fixed in cotton by the passage of their constituents, while in a soluble state, into the cavity of the fibre, and their subsequent precipitation therein as a solid pigment; as in the case of dyeing with acetate of lead and chromate of potash. Almost the last communication of Mr. Crum's was a short

memoir on the stalactitic sulphate of baryta found in Derbyshire.

Mr. Crum will hereafter be remembered as one of those who have mainly contributed to establish dyeing and calico printing on a secure scientific basis. He was most highly respected in the scientific circles of his native city, and by all those who had business or social relations with him; and it has been said of him "that he has not left behind him one enemy."

Dr. Charles Giles Bridle Daubeny was born February 11, 1795, at Stratton, in Gloucestershire; third son of the Rev. Jas. Daubeny. He entered Winchester School in 1808, and was elected to a demyship in Magdalen College, Oxford, in 1810. In 1814, at the age of nineteen, he took the degree of B.A. in the second class. In 1815 he won the Chancellor's Prize for the Latin essay. Destined for the profession of medicine, he proceeded to London and Edinburgh as a medical student (1815-18). Although he subsequently took the title of M.D. at Oxford, and became a Fellow of the College of Physicians, his career as a medical man was very brief. He, however, throughout his life took a lively interest in the progress of medical science, and in 1845 delivered the Harveian Oration before the College of Physicians; for a short time he was attached to the Radcliffe Infirmary.

While a medical student in Edinburgh, the lectures of Professor Jameson on geology and mineralogy attracted his earnest attention, and strengthened a desire for the cultivation of natural science, which had been awakened by the teaching of Dr. Kidd at Oxford. In Dr. Kidd's class room under the Ashmolean Museum the future historian of volcanoes had frequently met Buckland and the Conybeares, Whately and the Duncans, men of vigorous minds and various knowledge. At that time Daubeny entered keenly into the discussion then going on with great animation between the Plutonists and Neptunists; and after quitting the University of Edinburgh, proceeded, in 1819, on a leisurely tour through France, everywhere collecting evidence on the geological and chemical history of the globe, and sent to Professor Jameson, from Auvergne, the earliest notices which appeared in England of that remarkable volcanic region. From the beginning to the end of his scientific career, volcanic phenomena occupied the

attention of Dr. Daubeny, and by frequent journeys through France, Italy, Sicily, Germany, Hungary, and Transylvania, he had extended his knowledge of that subject, and laid the foundation for his great work on volcanoes, which appeared in 1826. This work contains careful descriptions of all regions affected by igneous eruptions, and a chemical hypothesis of the cause of the thermic disturbance, namely, water coming into contact with the metallic bases of the earths and alkalis below the crust of the earth. In later years Dr. Daubeny freely accepted, as at least very probable, a higher interior temperature of the earth, but was unwilling to allow that the admission of water to a heated interior oxidized mass would account for the chemical effects which accompany and follow an eruption.

Four years previously to the publication of his "Description of Volcanoes," Dr. Daubeny succeeded Dr. Kidd as Aldrichian Professor of Chemistry, and took up his abode under the Museum founded by Ashmole.

Professor Phillips remarks, in his obituary notice of Dr. Daubeny, of which this account is mainly an epitome, "I well remember the zealous activity with which Dr. Daubeny entered into all investigations which had a bearing on the principal subject of his thoughts. Mineral waters, as indications of chemical processes going on below the surface of various countries, attracted his earnest attention. He carried about a considerable apparatus for examining these waters in their freshest attainable state, and would busy himself for days in evaporating and analysing on a large scale. Thus he worked in his quarters at one of the hotels in York, just as if he were in his own laboratory at home. By his busy scrutiny of waters in the volcanic country of Central France and the South of Italy, he provoked the suspicious credulity of the natives, who thought he was poisoning their springs, and endangered his personal safety."

Dr. Daubeny was extremely, possibly too methodical in his chemical teaching. Every lecture had its specific apparatus duly arranged, which was put away carefully into a compartment duly allotted to it after the lecture was delivered, so as to be ready when this part of the course came round again. His biographer says of him, that "he was not a dexterous manipulator of chemical instruments, though a diligent practical analyst." His knowledge of chemistry was considerable and

varied. In 1831 appeared his "Sketch of the Atomic Theory." His other published writings are very numerous; many are scattered through various periodicals, but the following is a list of works which contain the principal results of Dr. Daubeny's scientific and literary labours:—

1. "Description of Active and Extinct Volcanoes." 8vo., London, 1826. Second edition, 1848. Several supplements.
2. "Tabular View of Volcanic Phenomena." Fol., thick, 1828.
3. "Notes of a Tour in North America" (privately printed). 8vo., 1838.
4. "Introduction to the Atomic Theory." 8vo., 1852.
5. "Lectures on Roman Husbandry." 8vo., 1857.
6. "Lectures on Climate." 8vo., 1863.
7. "Trees and Shrubs of the Ancients." 8vo., 1865.
8. "Miscellanies on Scientific and Literary Subjects." Two vols., 8vo., 1867.

Those who desire to know Dr. Daubeny's views on the various subjects which engaged his attention, will find them fully set forth in these works. The last on the list was published only a very short time before his death.

So soon as the arrangements were made for the location of chemistry in its new abode, Dr. Daubeny resigned the chair of chemistry, and used all his influence to increase the efficiency of the office, and secure the services of the present eminent Professor.

Dr. Daubeny was not only Professor of Chemistry, but also occupied the Chair of Botany, to which he was appointed in 1834. He then migrated to the "Physic Garden," which had been founded in the early part of the reign of Charles I. (1621-1632), by Henry Lord Danvers, afterwards created Earl of Danby. Here he instituted many experiments on vegetation, under different conditions of soil; on the effect of light on plants; on the distribution of potash and phosphates in leaves and fruits; on the conservability of seeds; on the ozonic element in the atmosphere, and the effect of varied proportions of carbonic acid on plants analogous to those of the coal-measures. Several of his researches in these matters formed the subjects of communications made to the Chemical Society. Although during a long

and active career, Dr. Daubeny's studies were extensive and varied, chemistry was the thread which bound together all his researches.

Professor Phillips says of him that "in his whole career Dr. Daubeny was full of that practical public spirit which delights in co-operation, and feeds upon the hope of benefiting humanity by the associations of men. The same earnest spirit was manifested in all his academic life. No project of change, no scheme of improvement in University Examinations, no modification in the system of his own college, ever found him indifferent, prejudiced, or unprepared. On almost every such question his opinion was formed with rare impartiality, and expressed with as rare intrepidity. Firm and gentle, prudent and generous, cheerful and sympathetic, pursuing no private ends, calm amid jarring creeds and contending parties—the personal influence of such a man on his contemporaries for half a century of active and thoughtful life fully matched the effect of his published works."

In 1856 he became President of the British Association, at Cheltenham, in his native county, amidst numerous friends, who caused a medal to be struck in his honour, the only occurrence of this kind in the annals of the Association.

Dr. Daubeny died after a few weeks' severe illness, which he endured patiently, on December 13th, 1867, in his 73rd year.

Among our many losses, we have to deplore the removal by death of one of the greatest and most noble of men, whose genius has enriched science, and contributed to the well-being and advancement of civilized man. Michael Faraday was so prolific and original, not only in chemical science, which more especially concerns us, but also in physical science, that it would be quite impossible within the scope of this notice to give such an account of his discoveries, as would do justice to his memory; for, without question, he was the greatest experimental philosopher that has ever lived. Fortunately, pens much more eloquent than that of the writer of this notice have already placed before the world an account of the man and of his works; but even the vivid portraiture of a De la Rive and a Tyndall fail to present such a picture of Faraday, as is reverently cherished in the memories of those who had the advantage of his personal acquaintance, and listened to him

as a teacher. Few men have ever taken so much pains as Faraday did to improve great natural endowment, and to train an impulsive though kindly spirit to a habitual veneration of all that is truthful, good and pure; there never existed a more unselfish encourager of contemporaries, or a more kindly adviser of the youthful aspirant in science. The charm of unfolding the hidden laws of Nature so entirely engrossed him, that he invariably declined the tempting sources of gain continually brought within his easy reach. If Faraday had so desired it, he might have accumulated great wealth. In all the relations of life, Faraday was respected and beloved; he was very fond of children, entering into their sports most keenly, and aiding them with his knowledge and resources; nothing ever gave him more sincere pleasure than to lecture to the young. He had the highest sense of justice, was possessed of great firmness, and although ever ready to consider with tenderness any palliation of a fault, he never allowed wrong to be done without reproof; he was consequently always well served. His sense of justice was so keen, that a casual wrong witnessed in the streets, would rouse his indignation, and elicit his active interference on the side of the offended. He was eminently charitable, and discriminating in his aid.

Michael Faraday was born September 22, 1791, at Newington Butts, Surrey. His father James was a whitesmith of Clapham Wood Hall, Yorkshire. After receiving an elementary education, Michael was apprenticed in 1804 to Mr. Riebau, a bookseller and bookbinder in Blandford Street, Marylebone, and thereby, not only came in contact with the means of gratifying his thirst for knowledge, by books, but gained the acquaintance of Mr. Dance, a Member of the Royal Institution, who enabled him to hear several of Sir Humphry Davy's last lectures in that establishment. The notes which Faraday made of these lectures, he submitted to Sir Humphry, with an application for any employment connected with science, and in March, 1813, Faraday entered the service of the Royal Institution as assistant in the laboratory, of which he eventually became the director. In October, 1813, he resigned his situation in order to accompany Davy in a tour through France, Switzerland, and Italy, during which they met with the most eminent philosophers of Europe, and already Faraday attracted



their notice, and laid the foundation of enduring friendships. He was re-engaged at the Royal Institution on his return to England in 1815; and then he commenced those researches, which are the history of his life, written by himself in the four volumes of his "Experimental Researches." On June 12, 1821, he married Miss Sarah Barnard, the daughter of Mr. Edward Barnard, a silversmith, who survives him. The union was eminently a happy one.

While young, he gave several lectures on science at the room of the City Philosophical Society in Dorset Street, Fleet Street; but it was not till February 3, 1826, at the first of the celebrated Friday evening meetings, that he lectured at the Royal Institution—his subject being Caoutchouc, abundantly illustrated by specimens in the raw and manufactured states, furnished by the late Mr. Thomas Hancock. His courses of lectures at the Institution commenced with one in April, 1827, on Chemical Philosophy, and terminated with a Christmas course on the Chemical History of a Candle, at the close of 1860.

As a lecturer, he was long regarded as *facile princeps* in regard to his manner, matter, and successful experimental illustrations. His last Friday evening discourse, on gas furnaces, was delivered on June 20, 1862, when his enthusiasm resembled the brilliant flash from an expiring fire. As he became aware of his gradually failing mental and bodily powers, he gracefully withdrew from duties which he desired to fulfil only in the very highest manner; and on August 25th, 1867, he peacefully closed a laborious life at Hampton Court Green, in a house which had been granted to him by the Queen in 1858, and which had been a source of much pleasure to him in the summers of his later years. He was interred at Highgate Cemetery on the Friday following, in a most unostentatious manner, in conformity with his expressed desire.

Faraday's merits as an investigator in science were early recognized abroad and at home. In 1823 he was elected Corresponding Member of the Academy of Sciences at Paris, and in 1844 one of the eight Foreign Associates. He was elected F.R.S. in 1824, and in after years successively received the Copley, Rumford, and Royal Medals, awarded by the Society. He was nominated D.C.L. by the University of Oxford, in 1832, at the same time as Brewster, Dalton, and Robert Brown; and, in course of time, was elected a member of all the great

scientific bodies in Europe and America. In 1833 he was nominated the First Fullerian Professor of Chemistry in the Royal Institution, by John Fuller, Esq., no lectures being required from him; and he held the Professorship of Chemistry at the Royal Military Academy, Woolwich, from 1829 to 1853. His first paper, printed by the Royal Society (On Two New Compounds of Chlorine and Carbon), was read in December, 1820. In 1829 he gave his Bakerian Lecture, on the Manufacture of Glass for Optical Purposes; in 1831 he published his Discovery of Magneto-Electricity; in 1833, the Great Law of Electro-Chemical Decomposition; in 1845, the Discovery of the Magnetisation of Light, Dia-magnetism, and the Magnetic Condition of all Matter; in 1847, the Magnetism of Flame and Gases; in 1848, the Magneto-crystallisation of Bismuth; in 1850, Researches in Atmospheric Magnetism.

Among Faraday's most remarkable chemical discoveries were the condensation of chlorine and other gases, in 1823; and the production of some new compounds of hydrogen and carbon, including benzol, since so important as the start point of the aniline colouring matters. His first printed paper appeared in the Quarterly Journal of Science, in 1816; it is an account of his Analyses of native caustic lime in the water of ancient baths in Tuscany.

Faraday had naturally a great love of literature; especially of fiction and the drama. In early life he acquired some knowledge of Latin and of several modern languages; and he was well read in the great English classics, Spenser, Shakspeare, and Milton.

Many have speculated on the advantages which Faraday might have derived from a mathematical training; but Dr. Whewell appreciated him correctly when he said that he was a *natural* mathematician.

Although Faraday was not one of the founders of the Chemical Society, he joined it the year after its formation, and always expressed a great interest in its development and welfare.

William Herapath was the son of a maltster in St. Philips, Bristol, and succeeded to his father's business. He studied chemistry at first in connection with the trade in which he was engaged, and, eventually as the profession of his life. It was

as a toxicologist that he was principally known to the public, but throughout the west of England he was constantly referred to as the leading analytical and consulting chemist. From time to time he contributed several papers, chiefly on toxicological subjects, to the medical and scientific journals, and his opinions and experience as a toxicologist are frequently quoted in works on medical jurisprudence. The first important medico-legal case in which he was engaged was that of Mrs. Burdock, tried in 1835 at Bristol for poisoning Mrs. Smith with arsenic, when his evidence attracted considerable attention, and was much appreciated. More recently he was one of the principal witnesses for the defence of the celebrated William Palmer, tried in 1856 at London for poisoning John Parsons Cook with strychnia. He was one of the founders of the Bristol medical school in 1828, and its first lecturer on chemistry and toxicology, a position which he held to the last. He was also one of the original members of the Chemical Society. In early life he took a very active part in the politics of his native town, and was a leader of the extreme liberal party. He fulfilled several municipal appointments, and at the period of his death was the senior magistrate of the city. For some years past he had suffered from diabetes; but till a few days previous to his death he persevered in his professional pursuits, and exhibited his usual activity and readiness. Mr. Herapath died on the 13th of April at his residence, the Manor House, Old Park, Bristol, in the 73rd year of his age.

Jules Théophile Pelouze was born at Valognes (in the department of Manche) in France, on the 26th February, 1807. In commencing life he had little else to rely upon than the advantages of a solid education, an active and intelligent mind, and great energy of character. His father was a native of Saint Lucia, in the Island of Martinique; during the wars he was taken prisoner by the English. He turned to account the knowledge of English acquired during his captivity, by teaching that language, and became successively a manufacturer of porcelain, a director of works in the plate glass manufactory of Saint Gobain, subsequently the director of several iron works, amongst others the well-known works of Creusot; but in spite of all his energy and varied knowledge, he never accumulated any fortune; his son Jules derived no inheritance from him, but

had to rely solely upon his own force of character to make his career. His start in life was anything but encouraging, indeed he had for some time to endure the hardships of penury.

M. Pelouze first turned his attention to pharmacy, and was for eighteen months a student at La Fère. In 1825 he went to Paris, hoping there to find greater scope for his activity. He in the first instance engaged himself to M. Chevalier, a member of the Academy of Medicine; but a year later he was received as house-pupil in pharmacy of the Hospital de la Salpêtrière. Notwithstanding the duties of his office, he directed his attention to pure chemistry, and in order to gratify his desire to follow this science, he gave up the emoluments of his appointment and entered the laboratory of M. Wilson, which was under the direction of MM. Gay Lussac and Lassaigne. From this moment his chemical studies entirely engrossed his mind, and became the sole object of his life. His enthusiasm gained for him the friendship of his master, Gay Lussac, and friendship became a strong affection which bound together those sympathetic natures. In his turn Pelouze did for many a young aspirant what Gay Lussac had done for him, and it would be difficult to name any one who contributed more than M. Pelouze to the advancement of those who were worthy of such aid. When Pelouze first became an assistant to Gay Lussac, he slept in a garret in the Rue Copeau, but he lived really in the laboratory, where a piece of bread and a glass of water were his frequent repasts. In the pursuit of his favourite science, however, he felt more than compensated for lack of worldly comforts. In order that he might add to his resources, Gay Lussac suggested that he should give lessons; but he refused, because he was disinclined to lose any opportunity of acquiring knowledge.

In 1830, the municipality of Lille created a chair of chemistry to which Kuhlmann was appointed titular Professor, and Pelouze was chosen associate Professor. From this period Pelouze's name began to be known; he turned his attention to the perfecting of the processes for extracting sugar from beetroot, and he showed that beetroot contains 10 per cent. of its weight of crystallisable sugar, in every way identical with cane sugar. He proved by his researches, that the alleged inferiority of beetroot sugar to cane sugar was solely attributable

to defects of manufacture, or to the cultivation of the beetroot not being understood.

On his return to Paris, in 1832, he became a candidate for the office of Assayer to the Mint of Paris, and entered into a competitive examination, in which he was so eminently successful, that M. Thénard, the president of the jury appointed to examine the candidates, passed the highest eulogium on him, concluding his report in the following words:—"If you appoint him to the place, of which he has proved himself publicly so highly deserving, he will far exceed all your most sanguine expectations of the services to be desired from a public officer."

Pelouze was at this period twenty-five, and he had already made a name by important works. He was unanimously appointed a tutor in chemistry and Deputy Professor to assist Gay Lussac in the Ecole Polytechnique. His numerous published papers from this time placed him in the front rank of chemists. About this period he travelled in Germany, and entered into scientific relations with Liebig, of whom he had been the co-disciple, and had not ceased to be the friend; several discoveries resulted from this alliance, one of the most remarkable being that of Ceanthic Ether.

In the month of June, 1837, M. Pelouze was elected a member of the Academy of Sciences in the place of M. Deyeux, deceased. At the same time he was deputy to Thénard in the College of France, and at a later period he succeeded to the Chair.

M. Dumas, in his funeral oration on the occasion of the interment of M. Pelouze, speaks in terms of the warmest eulogy of his lectures at the Ecole Polytechnique, and at the Collège de France. He characterises them as remarkable for their correctness of method, and for their measured and quiet style of delivery, which, however, became heightened and impassioned when the importance of a new product, a new experiment, or the description of a discovery emanating from one of the numerous laboratories of Europe, drew forth his eloquence.

It is not possible here to give an account of the very numerous published memoirs of M. Pelouze. Besides those printed in the Comptes Rendus, are several contributions to the Dictionary of Technology, the Annales de Chimie et de Physique, La Revue des deux Mondes, &c. But, besides these published

papers, it must not be forgotten that his unpublished correspondence contributed greatly to the advancement of practical chemistry. Pelouze was one of the earliest and principal contributors to organic chemistry.

Besides cenanthic ether, of which mention has been just made, may be cited his researches on butyric acid and berberine. In 1867, he published a memoir on glycerin. His researches on woody fibre or cellulose, led to the discovery of nitroxylose, the prototype of gun-cotton, and nitro-compounds in general. Pelouze has given a process for the extraction of tannic acid from leather. In connection with M. Cahours, he made a chemical examination of the American petroleum; he has given several processes for obtaining pure chemicals, notably pure sulphuric acid, on a large scale. He is the author of many analytic methods, held in high repute; for example, the assay of nitre by means of protochloride of iron, the determination of copper by means of a standard solution of sulphide of sodium. He determined the quantity of iron in blood (about  $\frac{1}{100000}$ ths); and jewellers hold in high estimation a sort of green aventurine with a base of chromium, which he discovered.

Pelouze made an exhaustive study of the composition of glass, and has explained the phenomenon of devitrification by the presence of an excess of silica. During the latter years of his life he studied the action of the solar rays in producing the coloration of glass, with the object of explaining the cause which he succeeded in discovering. These investigations were made with the glass of St. Gobain, to which establishment Pelouze was consulting chemist, and were the source of important benefit to its manufacture.

The work written conjointly by himself and his former pupil, M. Fremy, the "Traité de Chimie Générale, analytique, industrielle et agricole," which has passed through three editions, will ever remain a monument to his memory.

In 1848, Pelouze founded a laboratory, where were educated several distinguished chemists. One of them, M. Fremy, says of him: "Who has known so well as he how to join to the lustre of a high and legitimately acquired scientific position, such amenity of character, or such thorough goodness of heart? One could scarcely make his acquaintance without loving him."

In 1848, Arago, who had the highest feeling of friendship for

Pelouze, proposed him as President of the "Commission des Monnaies et Médailles" to succeed M. Persil. In this new and important position he evinced all those high qualities which characterize an administrator. The most important monetary operations have been accomplished during his presidency. He carried out with great ability the recoinage of the silver and copper money. Latterly, with M. de Parien, he represented France in the monetary convention settled between France, Italy, Belgium, and Switzerland.

Although Pelouze did not run after honours or fortune, it may be said that they came to him as the natural recompense of merit and earnest work. In 1838, he was nominated Chevalier de la Légion d'Honneur, Officier in 1850, and Commandeur in 1854. Moreover, he had received decorations from most countries of Europe, and was a member of nearly all the scientific societies.

Since 1849 M. Pelouze was a member of the Municipal Council of the town of Paris; during his connection with that body, he was very influential in doing much for the sanitary condition of the great metropolis of Europe; and, leaving to his colleagues the charge of the embellishment of the city, he devoted his great knowledge to those important questions on which the health and comfort of its inhabitants depend. He was untiring in searching out the causes of insalubrity or discomfort, and in finding means for removing them.

Pelouze owed his high scientific position entirely to his great energy of character, his rectitude and unswerving reliance on the value of experimental research; he was willing to leave to others the development of theory. He died in June, 1867, after more than forty years' devotion to chemistry, and was buried with great honours. M. Dumas on that occasion delivered a funeral oration, full of eloquence, and characterized by much feeling and a just appreciation of the man.

John Tennent, one of the original Fellows of this Society, was born at Well Park, in Glasgow, in the year 1813. He was educated at the Grammar School of that city. At an early age he was employed at the silk factory of the Messrs. Pollack, at Govan; and while thus engaged, devoted the whole of his leisure time to the cultivation of physical and chemical science. Leaving the factory about the year 1833, he entered the labora-

tory of Dr. Macconochie, in Glasgow, with a view to the more systematic study of chemistry, &c.; and afterwards pursued the same course of study in the College laboratory, where he acted as assistant to Dr. Thomas Thomson.

In the year 1837 Mr. Tennent became acquainted with Mr. Charles Macintosh, and was employed by him in experimenting upon the artificial production of ultramarine, and also at the Cudbear Works at Dunchattan. In the autumn of this year he accepted the proposal of Mr. Macintosh to go to the Mauritius and Madagascar in search of superior qualities of lichen for the Cudbear manufacture. Sailing from Liverpool in October, he suffered shipwreck on the coast of Ireland, and returned to Glasgow, with loss of everything but life. In December he again started from London, and was absent about eighteen months, visiting and exploring the accessible parts of the Mauritius, Madagascar, Bourbon, and the Cape. He succeeded, with much difficulty, in collecting numerous specimens of lichens, gums, india-rubber, and other milky juices; amongst these latter, gutta-percha, unknown before that time as an article of commerce, and only applied to useful purposes several years later. Mr. Tennent sent home considerable quantities of several of these products, accompanied by analyses and descriptions of practical trials of their commercial value: but owing to the high price of labour in some of these colonies, and the impossibility in others of getting the recently emancipated natives to work, the main object of the expedition was frustrated, and did not prove commercially successful.

On Mr. Tennent's return to Scotland in 1839, he became practical manager of the Alum and Prussiate of Potash Works belonging to Mr. Macintosh, at Campsie, where he remained until the year 1845.

In that year he undertook the management of the Chrome works, belonging to Messrs. J. and J. White, at Shawfield, but remained there only about one year. In 1847 Mr. Tennent entered into a partnership with Mr. John Tennant, of St. Rollox, to work, at Bonnington, the gas-tar and ammoniacal liquor produced at the Edinburgh and the Edinburgh and Leith gas-works, and personally superintended these works till the year 1853, when he was requested to join the firm, and take the active management of the large bleaching powder and alkali works of Messrs. Charles Tennant and Co. at St.



Rollox, Glasgow. This he did till the date of his death, planning and superintending the large branch work erected by Messrs. Tennant and Co. in the year 1863, at Hebburn on the Tyne.

Mr. Tennent has left no published records of his skill as a chemist. His field lay in the application of chemical and physical science to the manufacture of the most largely used chemical products, in the purest mercantile form, and upon the largest practicable scale; and in this field, and with a wider scope than it falls to the lot of most men to encounter, he was eminently successful. The object of his ambition was to have the largest chemical work under his control, and he obtained it.

During the last twenty years of his life Mr. Tennent suffered constantly and most severely from chronic rheumatism, which painfully racked and crippled his body, but appeared to have no influence upon his mind, which retained its vigour to the last. He died at Glasgow, from an attack of diarrhoea, at the age of 54 years.

We have now to speak of one of our deceased members to whom was mainly due the founding of this Society; for although it must have occurred to many minds that Chemistry would be promoted by the closer association of its votaries, yet it is well known that the zeal of Robert Warrington contributed chiefly to this end, and that he filled for many years the post of Secretary, during a period requiring the greatest devotion of all its officers to the interests of the Society, in order to ensure an ultimate success.

Robert Warrington, the third son of Thomas Warrington, was born at Sheerness, on the 7th September, 1807, his father being at that time a victualler of ships. When ten years of age he was entered at Merchant Taylors' School, where he remained four years. On leaving school, he became a home pupil of Mr. J. T. Cooper, then well known as a lecturer on Chemistry, and was articled for five years from November, 1822. Mr. Cooper lectured at that time on Chemistry at the Medical Schools of Aldersgate Street and Webb Street; he also manufactured the more rare chemical substances, was the only maker of potassium and sodium\* in Great Britain, and for some time enjoyed a monopoly of the manufacture of iodine.

\* Sodium at that time was sold at 12 guineas per ounce.

On the opening of University College, in 1828, Mr. Warington was chosen by Dr. E. Turner, as his assistant, in conjunction with Mr. W. Gregory, afterwards professor of chemistry at Edinburgh. Mr. Warington remained three years as assistant to Dr. Turner, and took charge of the practical classes. While at University College, he communicated to the "Philosophical Magazine" his first published research, entitled, "Examination of a Native Sulphuret of Bismuth."

In 1831, Mr. Warington entered the service of Messrs. Truman, Hanbury, and Buxton, the well-known brewers, and remained at the brewery until 1839. In 1835, he married Elizabeth, the daughter of the late Mr. George Jackson, a surgeon and skilful amateur mechanist, well known for his many improvements in the construction of the microscope. Mr. Warington's connection with the brewery did not prevent the pursuit of chemistry in his leisure; his papers during the period were "On the establishment of some perfect system of Chemical Symbols, with remarks on Professor Whewell's paper on that subject."—*Phil. Mag.*, Sept., 1832. "On the action of Chromic Acid upon Silver, and its combinations with the oxide of that metal."

About the year 1839, Mr. Warington canvassed for the formation of the Chemical Society, and on the 23rd of February, 1841, convened a meeting at the rooms of the Society of Arts, which resulted in the formation of our Society. Mr. Warington was appointed one of the Secretaries of the Society, and held the office for ten years. On his retirement he received a testimonial of plate, subscribed for by the Fellows of the Society.

The papers published by Mr. Warington up to 1842, were: "On the Coloured Films produced by Electro-chemical Influence and by Heat," *Phil. Mag.*, 1840; "On the Preparation of Chromic Acid," *Mem. Chem. Soc.*, 1841; "On a Re-arrangement of the Molecules of a Body after Solidification," *Mem. Chem. Soc.*, 1842; "On the change of Colour in the Biniodide of Mercury," *Mem. Chem. Soc.*, 1842; "Some additional observations on the Red Oxalate of Chromium and Potash," *Mem. Chem. Soc.*, 1842.

On the death of Mr. Hennell, in 1842, Mr. Warington was appointed chemical operator to the Society of Apothecaries, a position which he held until within a year of his death. His professional engagements became very numerous during his

connection with the Apothecaries' Society, and he was often employed as scientific adviser in important actions at law; he nevertheless found leisure for scientific investigations and for the promotion of chemistry. He took part in the formation of the Cavendish Society, in 1846, and held the office of Secretary for three years. He also was one of the promoters of the Royal College of Chemistry, and was for some time a member of the Council. Besides contributions to chemistry, Mr. Warrington commenced experiments on the relations of animal and vegetable life in stagnant water, which resulted in the establishment of the "Aquarium." The result of his first experiments in this line of investigation was presented to the Chemical Society in 1850; and he followed up the subject in several papers, communicated to various journals.

Mr. Warrington's other published researches were chiefly the following:—"On the action of Alkalies on Wax;" "On a curious change in the Molecular structure of Silver;" "On a curious change in the Composition of Bones taken from Guano;" "On some Commercial Specimens of Green Glass;" "Observations on the Action of Animal Charcoal;" "On the Green Teas of Commerce;" "On the Preparation of Turnbull's Blue;" and "On the Production of Boracic Acid and Ammonia by Volcanic Action;" which will be found in the publications of our Society.

Mr. Warrington was a juror in the International Exhibition of 1862, and was elected a juror for the Paris Exhibition of 1867, though unable to attend. He was elected a Fellow of the Royal Society in 1864.

In 1851, Mr. Warrington revised the translation of the Pharmacopœia, left unfinished by Mr. Phillips; he was also much engaged in the construction of the British Pharmacopœia of 1864, and was one of the editors of the 2nd edition of this work, in 1867. He was, moreover, one of the editors of the abridged edition of "Pereira's Materia Medica."

In the autumn of 1865, Mr. Warrington's lungs became seriously affected, and he passed the winter at Hastings; the following winter he went to Worthing, and ultimately died at Budleigh-Salterton, in Devonshire, on the 17th November, 1867.

Mr. Warrington's career was marked by an unflagging zeal in the promotion of the interests of chemistry, and by success in a variety of pursuits; for he was not only well known as a chemist, but was an excellent microscopist and an ardent culti-

vator of natural science. He was much respected, both in public and private life, and evinced a sincere pleasure in aiding the researches of others.

The late Mr. William Winsor, one of the founders of the well-known house of Winsor and Newton, was born in 1804, and until within twelve months of his decease personally superintended the business operations of the house. Possessing an extremely accurate eye for colour, and an extensive knowledge of practical chemistry, he brought the manufacture of many pigments used in the fine arts, to a high state of perfection. The rapid growth and wide diffusion of taste for painting, which has shown itself during the last thirty years, caused a largely increased demand for material, which his knowledge of chemistry and mechanics enabled him to devise means of supplying.

When the late Sir Charles Eastlake was writing his work "Materials for the History of Painting," Mr. Winsor, by his desire, and in immediate connection with the subject, made a series of experiments, and worked out to solution certain important questions in reference to colour. At the time of his decease he was engaged in revising that well-known standard work on colour, "Field's Chromotography."

Mr. Winsor was a sound musician, and during many years was the principal amateur double bass in London. He was an active member of the Sacred Harmonic Society. On the occasion of the Handel Festival of 1859, he officiated as one of the superintendents, and in musical matters generally took a warm interest.

He joined the Chemical Society in 1859; he was also a Fellow of the London and Middlesex Archæological Society, and a member of the Society of Arts.

Mr. Winsor died on the 1st of November, 1865, regretted by an extensive circle of friends, to whom he had endeared himself by his many estimable qualities and strict probity of character

Philip James Chabot was born in Spitalfields, on 27th November, 1801. His father was descended from a French refugee at the Revocation of the Edict of Nantes, and was the surviving partner of an old firm of grain-dyers, who for many

years had the contract of the East India Company to supply the scarlet wool for the clothing of their army.

The son, after receiving a fair classical education, joined his father in the business, for which his taste for chemistry seemed peculiarly to fit him; but having also a great literary turn he soon quitted the dye-house, and in 1820 entered himself at St. John's College, Cambridge, where he graduated B.A. in 1824, and M.A. in 1827.

He was called to the bar at Lincoln's Inn in 1830; but upon the death of his father in 1832, he was induced, by the earnest entreaties of his friends, although much against his own inclination, to give up the bar and take his father's place.

Whilst directing the works, he discovered sundry improvements in dyeing, especially in the several shades of blue. At length, Mr. Chabot, finding that the business had not answered his expectations, gave it up, and in a few years started the Silk-conditioning Company, of which he was the secretary and manager till his death. He gave a lecture at our Society on the subject of silk-conditioning, that is, the determination of hygrometric moisture and other extraneous substances accompanying raw silk which is sold by weight.

Mr. Chabot was a member of the Old Mathematical Society in Spitalfields, of the Cavendish, and Philological Societies, and a Fellow of the Royal Astronomical Society; he was also a member of the Board of Managers of the French hospital for the poor descendants of the French Refugees: a man extremely well read, interested in science and literature, of a kind and sociable disposition, ever ready to take any amount of trouble for his friends, and of the most scrupulous probity; he was trusted to an unlimited extent by all who knew him, and none had reason to regret a misplaced confidence.

Mr. Chabot joined our Society the year after its formation, and withdrew in 1864, he died on the 11th of January, 1868.



November 7th, 1867.

Mr. Warren De la Rue, President, in the Chair.

A resolution was passed, "That the Fellows of the Chemical Society request their President to convey to Mrs. Faraday their deep sense of the loss which science has sustained in the death of her highly distinguished and much esteemed husband, and to express their heartfelt sympathy with her in her own great loss."

The following papers were read:—

"On the Action of Acetic Anhydride upon the Hydrides of Salicyl, Ethyl-Salicyl, &c:" by Mr. W. H. Perkin, F.R.S.

"On Nitrous and Nitric Ethers:" by Messrs. E. T. Chapman and Miles H. Smith.

"On the part taken by Oxide of Iron and Alumina in the Absorptive Action of Soils:" by Robert Warington, Jun., Esq.

"Analysis of the Water of the Holy Well, a medicinal Spring at Humphrey Head, North Lancashire:" by Thomas E. Thorpe, Esq.

"On the Action of Permanganate of Potassium on Urea, Ammonia, and Acetamide in Strongly Alkaline Solutions:" by Messrs. J. A. Wanklyn and Arthur Gamgee.

"Verification of Wanklyn, Chapman, and Smith's process of Water Analysis on a Series of Artificial Waters:" by J. A. Wanklyn, Esq.

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November 21st, 1867.

Mr. Warren De la Rue, F.R.S., President, in the Chair.

The following papers were read:—

"On the relation between the results of Water Analysis and the Sanatory Character of the Water:" by E. T. Chapman, Esq.

"On the Pyrophosphoric Amides:" by Dr. J. H. Gladstone, F.R.S.

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December 5th, 1867.

Extraordinary General Meeting.

A resolution was passed that the first paragraph in the first bye-law be amended as follows:—

“Every candidate for admission into the Society shall be proposed according to a form of recommendation (No. I, in the Appendix), subscribed by five Fellows of the Society, to three at least of whom he shall be personally known, and such certificate shall be read and suspended in the Society’s rooms, or place of meeting, for three ordinary meetings.”

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Ordinary Meeting.

The following gentlemen were duly elected Fellows of the Society:—

Thomas Hall, B.A., City of London School; Charles Walter Maybury, King-street, Manchester; George Lunge, Ph.D., South Shields; F. J. R. Carulla, Sheffield; C. Meymott Tidy, M.B., Cambridge Heath, Hackney; Augustus A. Wood, Cheapside; Alfred Coleman, Plough Court, Lombard-street; Walter W. Fiddes, Sothernhay, Clifton; Robert R. Tatlock Kyles, of Bute; Wm. Phipson Beale, Stone Buildings, Temple; Alexander Crum Brown, M.D., D.Sc., Edinburgh.

The following papers were read:—

“On the Artificial Production of Coumarin and Formation of its Homologues:” by Mr. W. H. Perkin, F.R.S.

“On Turacin, a New Animal Colouring Matter:” by Prof. A. H. Church.

“Note on the Preparation of Urea:” by Mr. John Williams.

Dr. Hofmann gave a verbal account of his recent researches “On Methylic Aldehyde,” and “On a New Series of bodies homologous with Hydrocyanic Acid.”

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December 19th, 1867.

Mr. Warren de la Rue, F.R.S., President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Wm. Frank Smith, M.D., Sheffield; Alfred E. Fletcher, Esq., Prescott, Lancashire.

The following paper was read:—

“On the Freezing of Water and Bismuth:” by Mr. Alfred Tribe.

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January 16th, 1868.

Mr. Warren De la Rue, F.R.S., President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

G. W. Child, M.D., Oxford; Edward Chapman; W. G. Mason; Peter Griess, Burton-on-Trent; Captain Alexander Walker.

The following papers were read:—

“On the Isomeric Forms of Valeric Acid:” by Mr. Alexander Pedler.

“On the so-called Thioformic Acid:” by Dr. Debus, F.R.S.

Dr. Frankland delivered a lecture “On Water Analysis.”

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February 6th, 1868.

Mr. Warren de la Rue, F.R.S., President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Lieutenant J. W. Hozier, B.A., Staff College, Farnborough; Herbert McLeod, Bridge Street, Southwark; Robert Schenk, Ph.D., Hanover Place, Kennington; Thomas Charlesworth, Leicester.

The discussion upon Dr. Frankland's lecture on Water Analysis was resumed.

The following papers were read :—

“On a new form of Voltaic Battery :” by Mr. De la Rue, F.R.S., and Dr. Hugo Müller, F.R.S.

“On Gas Analysis :” by Dr. W. J. Russell.

“On the Reduction of Carbonic to Oxalic Acid :” by Dr. E. Drechsel.

“On some new Benzylic Derivatives of the Salicyl Series :” by Mr. W. H. Perkin, F.R.S.

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February 20th, 1868.

Dr. A. W. Williamson, F.R.S., Vice-President, in the Chair.

The following gentleman was duly elected as Fellow of the Society :—

Martin Murphy, College of Chemistry, Liverpool.

Mr. David Forbes, F.R.S., delivered a lecture “On Chemical Geology.”

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March 5th, 1868.

Mr. Warren De la Rue, F.R.S., President, in the Chair.

The following gentlemen were duly elected Fellows of the Society :—

Benjamin H. Paul, Ph. D., Gray's Inn Square; Thomas W. White, Ifield, Crawley, Sussex; Edward Dowson, M.D., Park Street, London.

Mr. Reinhold Richter was elected an Associate.

The following papers were read :—

“On the Action of Oxidising Agents on Organic Compounds in presence of excess of Alkali :” by Messrs. J. A. Wanklyn and E. T. Chapman.

“Note on Dr. Frankland's Process of Water Analysis :” by Mr. E. T. Chapman.

“Note on the Estimation of Nitric Acid in Potable Waters :” by Mr. E. T. Chapman.

“On the Hydride of Aceto-Salicyl :” by Mr. W. H. Perkin, F.R.S.

"On the Absorption of Vapours by Charcoal:" by Mr. John Hunter, M.A.

"On the Occurrence of Prismatic Arsenious Acid:" by Mr. Frederick Claudet.

"On the Action of Nitric Acid upon Picramic Acid:" by Dr. Stenhouse, F.R.S.

"On Chloranil:" by Dr. Stenhouse, F.R.S.

"On the Action of Zinc-ethyl on Nitrous and Nitric Ethers:" by Messrs. E. T. Chapman and Miles H. Smith.

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March 19th, 1868.

Mr. Warren, De la Rue, F.R.S., President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

R. Calvert Clapham, Newcastle-on-Tyne; B. Byramjee, M.D., Bombay Army.

Dr. Meuzel was elected an Associate of the Society.

Professor Kolbe gave a verbal account of the Transformation of Carbonate of Ammonia into Urea.

Mr. H. Chance delivered a lecture "On the Manufacture of Glass."

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March 30th.

Anniversary Meeting.

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April 2nd, 1868.

Mr. Warren De la Rue, F.R.S., President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

John Tyndall, LL.D., F.R.S., Royal Institution.

Frederick Guthrie, Ph.D., Royal College, Mauritius.

W. B. Giles, Old Swan, Liverpool.

The following papers were read:—

"On the constitution of Glyoxylic Acid:" by Messrs. W. H. Perkin, F.R.S., and B. F. Duppa, F.R.S.

"On a Glyoxalic Amide:" by Dr. Odling, F.R.S.

“On the occurrence of Organic appearances in Colloid Silica, obtained by Dialysis:” by Mr. W. Chandler Roberts.

“On the Solubility of Xanthine in Dilute Hydrochloric Acid:” by Dr. Bence Jones, F.R.S.

“Researches on New and Rare Cornish Minerals:” by Prof. A. H. Church.

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April 16th, 1868.

Mr. Warren De la Rue, F.R.S., President, in the Chair.

The following gentleman was duly elected a Fellow of the Society:—

Lieutenant Francis C. H. Clarke, Staff College, Farnborough.

The following papers were read:—

“On an improved Voltastat:” by Dr. Guthrie.

“On Graphic Formulæ:” by Dr. Guthrie.

“On the Tetraphosphoric Amides:” by Dr. J. H. Gladstone, F.R.S.

“On the Solubility of Plumbic Chloride in Water, and in Water containing Hydrochloric Acid:” by Mr. J. Carter Bell.

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May 7th, 1868.

Mr. Warren De la Rue, F.R.S., President, in the Chair.

The following gentleman was duly elected a Fellow of the Society:—

Thomas Bournes, St. Helen's, Lancashire.

Mr. C. W. Siemens, F.R.S., delivered a lecture “On the Regenerative Gas Furnace, as applied to the Production of Cast Steel.”

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May 21st, 1868.

Mr. Warren De la Rue, F.R.S., President, in the Chair.

The following papers were read:—

“Some Experiments on the Application of the Measurement of Gases to Quantitative Analysis:” by Dr. W. J. Russell.

“Observations upon the Combining Powers of Carbon:” by Mr. W. H. Perkin, F.R.S.

“On the Reducing Action of Peroxide of Hydrogen and Carboic Acid:” by Mr. John Parnell.

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June 4th, 1868.

Mr. Warren De la Rue, F.R.S., President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Henry Chance, M.A., Oldbury, Birmingham.

William Hustler, Esq., Rosemerryn, Falmouth.

Wm. Bourger Miller, Esq., Royal Mint, Sydney.

The following papers were read:—

Chemical notices. I. “Action of Chloride of Zinc on Oxalic Ether.” II. “On the Artificial Production of Pyridine.” III. “Isomerism in the Organic Cyanides:” by Messrs. E. T. Chapman and Miles H. Smith.

“On the Modes of Testing mineral Oils used in Lamps:” by Dr. B. H. Paul.

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June 18th, 1868.

Mr. Warren De la Rue, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

H. B. Riddel, Stratton Street, Piccadilly.

S. A. Saddler, Oldbury, Birmingham.

The following papers were read:—

“Additional Note on Tetraphosphoric Amides:” by Dr. Gladstone.

“On High Chemical Formulæ—the ground on which they rest:” by J. A. Wanklyn, Esq.

“On the Production of Saltpetre in India:” by Dr. W. J. Palmer.

“On an Instrument for Maintaining Constant Temperature:” by Dr. Guthrie.

“On Chalybite, Diallogite, and Woodwardite:” by Prof. A. H. Church.

## Donations to the Library, Session 1867-8:—

“New Experiments, Physico-mechanical, touching the Air: by the Hon. Robert Boyle: from the Rev. B. W. Gibson.

“Principles of Chemistry, founded on Modern Theories:” by A. Naquet: translated from the Second Edition, by W. Cortis, and revised by Dr. T. Stevenson: from the Publisher.

“An Introduction to Pharmaceutical Chemistry:” by John Attfield: from the Author.

“Supplement to the Mineral Resources of Central Italy:” by W. P. Jervis: from the Author.

“Catalogue of Scientific Papers (1800-1863):” compiled and published by the Royal Society of London: from the Royal Society.

“A Dictionary of Chemistry, and the Allied Branches of other Sciences:” by Henry Watts. Parts XLIII., XLIV., XLV.: from Messrs. Longman and Co.

“Chemical Notes for the Lecture-room:” by Thomas Wood: from the Author.

“An Essay on the Theory of Phlogiston:” by G. F. Rodwell: from the Author.

“Abridgements of Specifications relating to the Plating and Coating of Metals with Metals:” compiled by W. H. Walenn: from the Compiler.

“Abridgements of Specifications relating to Photography:” Part. II.: compiled by W. H. Walenn: from the Compiler.

“Experimental Investigations connected with the Supply of Water from the Hooghly to Calcutta:” by David Waldie: from the Author.

“On the proposed Water-supply of the Metropolis:” by E. Frankland: from the Author.

“Agricultural Pamphlets:” by Augustus Voelcker: from the Author.

1. Field Experiments on Root Crops.

2. The Composition and Nutritive value of *Anthyllis vulneraria* as a Fodder Plant.

3. Field Experiments of Crude German Potash-salts and Common Salt on Mangolds.

4. The changes which take place in the Field and Stack in Haymaking.

“Australian Vegetation, indigenous or introduced:” by Dr. Ferdinand Müller: from the Author.

Report on the Vegetable Products exhibited at the International Exhibition of 1866-7: by Dr. Ferdinand Müller: from the Author.

“On the Temperature of the Ancient World:” by C. Daubeny: from the Author.

“On the Existence of Rocks containing Organic Substances in the fundamental Gneiss of Sweden: by J. Igelström, A. E. Nordenskiöld, and F. L. Erman: from the Authors.

“On the Magnetic Attraction of Cosmical Bodies:” by J. A. R. Newlands: from the Author.

“A Sketch of a Philosophy.” Part. II. “Matter and Molecular Morphology:” from Messrs. Williams and Norgate.

“A programme of Atomechanics, or Chemistry as a Mechanics of the Panatoms:” by Gustavus Heinrichs: from the Author.

“Hydrologie Générale:” par A. A. Ferreira: from the Author.

“Etudes sur les Affinités Chimiques:” par E. M. Guldberg and P. Waage: from the University of Christiania.

“Recherches sur la Réduction du Niobium et du Tantale:” from C. Marignac: from the Author.

“Systematische Zusammenstellung der sogenannten unorganischen Verbindungen:” von C. Weltzien: from the Author.

“Kurzes Lehrbuch der Chemie, nach den neuesten Ansichten der Wissenschaft, von H. E. Roscoe. Deutsche Ausgabe, unter Mitwirkung des Verfassers, bearbeitet von C. Schorlemmer:” from Professor Roscoe.

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in Deville's furnace, does not increase in electrical resistance, with increase of temperature in the same ratio as that produced by the old process, owing probably to the presence of carbon or other alloy in fractional quantities.

Avoiding the use of fused platinum wire, I have measured temperatures by electrical resistance up to a full welding heat, which I estimate at  $1,600^{\circ}\text{C.} = 2,900^{\circ}\text{F.}$ ; and in judging the heat of the steel-melting furnace by comparison of effects, I should put it at not less than  $2,200^{\circ}\text{C.} = 4,000^{\circ}\text{F.}$  The effect of this degree of heat may be judged by the following:—

An ingot of rather hard cast-steel, weighing 6 cwt., was introduced into the furnace to be incorporated with the bath of steel. The ingot was nearly cold, and was allowed to remain fifteen minutes upon the bank before it was pushed into the bath, where it was completely dissolved in fifteen minutes, the time occupied in heating and melting the ingot being thirty minutes. A cube of wrought metal of nearly 8 inches, weighing 130 lbs., was also introduced cold into the furnace, and allowed to remain upon the bank during ten minutes to be heated externally to whiteness, before being pushed into the metallic bath, when twelve minutes sufficed to render it completely liquid. It must be borne in mind that these results are produced without a strong draught, the flame being indeed so mild, as not to oxidize the unprotected metal, which can be maintained for several hours as liquid steel in the furnace without adding carbon in any form.

It may be matter for surprise, that the material composing the furnace can be made to resist such a heat, and it must be admitted that best Dinas brick is the only brick capable of resisting for four to five weeks, by which time the thickness of the arch is reduced to about 2 inches, by the absolute fusion of the inner surface; but this excessive heat is confined to the heated chamber only, the regenerators being at such a moderated heat, that the chequerwork will stand for months, and the arches for years of constant working.

In conclusion, I wish to express to you my sense of the disproportion that exists between the magnitude of the task I have brought before you, and my ability to accomplish it in all its ramifications. It may be granted that the Regenerative Gas Furnace itself has passed beyond its experimental stage, but much is yet to be done in working out the applications of the

system to the useful arts, and the modifications and improvements in processes which it frequently involves.

Much, also, is yet to be done before the method of producing cast steel, in one direct process from the ore, can take its place as the recognized system of making steel on a large scale from the purer iron ores, a position that I firmly believe it will assume, sooner or later. It is my earnest hope that, in bringing the subject before your Society, I may induce some of its members to forward this result, by taking up particular branches of the scientific inquiries upon which I have only been able to touch lightly in my present communication. I have much pleasure in acknowledging the assistance I have received in working out this subject from Mr. William Hackney, my principal superintendent, and Mr. Willis, the chemist in charge at my experimental works.

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XXXIV.—*Some Experiments on the application of the Measurement of Gases to Quantitative Analysis.*

By W. J. RUSSELL, Ph.D.

THE following experiments were made to ascertain whether the gas given off in certain reactions could be so easily and accurately collected and measured, that it might form trustworthy data for quantitative determinations. The volume of a gas is capable of being determined with so much precision that this method of analysis would apparently have certain substantial advantages. The gas measurements were all made by the method described by Dr. Williamson and myself.

The form of apparatus drawn in my paper "On Gas Analysis,"\* was used, and in place of an ordinary eudiometer a somewhat larger graduated tube was employed; this is the only alteration that has to be made to the apparatus. The tube used in the following experiments was 29 inches long, and rather more than three-quarters of an inch in internal diameter. The top of it is drawn out to a comparatively narrow tube, which is bent

\* Chem. Soc. Journ., April, 1868.

at right angles and left open. The bent part should be only about half an inch long. Over this is pushed, as far as it will go, a piece of india-rubber tubing, which is to be bound tightly on with wire, and cemented all round with marine glue. The glue must be applied as hot as possible; it then adheres most firmly to the glass and makes a perfect joint. The india-rubber tubing must be of the best quality, and very thick: the diameter of the tube outside should be about half an inch, and inside only  $\frac{1}{4}$  to  $\frac{1}{8}$  of an inch. The inside should be well vulcanized, and the rest of the tube only slightly so. The length of it is about  $3\frac{1}{2}$  inches.

It is important that this tube should be as short as possible, or else when carbonic acid is being experimented with, a considerable error may arise from the absorption of the gas by the india-rubber. In one experiment in which the carbonic acid from 0.124 grm. of marble was collected in a glass tube, to the top of which was attached a piece of this thick india-rubber tubing some 8 or 9 inches long it was found that, although there was some air in the tube as well as the carbonic acid, the latter occupying 201.71 divisions, the gas, at the end of one hour, had diminished 7.7 divisions; at the end of two hours it had diminished 9.9 divisions; in three hours 11.5 divisions; in four hours, 13.3 divisions; and by the next day it had diminished as much as 30.3 divisions. With a short piece of india-rubber tubing, such as that above described, the amount of gas which disappears is about  $\frac{1}{10}$ th of a division of the tube every five minutes.]

The most convenient form of vessel to hold the substances which are to react, is a small flask, easily made by blowing a bulb on a piece of tubing. This tubing must be of such a size that the india-rubber tube will just fit into it; it thus forms a sort of stopper to the flask, and connects it in the simplest way with the measuring tube. Before introducing the india-rubber tube, it must be slightly wetted, and as long as this joint is kept wet, there is not the slightest fear of any leakage; if it becomes dry and there is a high column of mercury in the measuring tube, it will probably leak. This is the whole of the special apparatus required for collecting the gases. The manipulations are very simple. The measuring tube with the flexible tube attached to it is clamped to the end of the rod, just as a eudiometer would be; a drop of water is introduced into the tube,

and it is placed in its position within the glass cylinder of the apparatus. To fill the tube with mercury before commencing an analysis, a piece of strong glass tubing, about 2 feet in length, and slightly tapering at one end, is inserted into the end of the flexible tube; the measuring tube may now be depressed as far as it will go into the well of the trough. It is not necessary that the well be deep enough to receive the whole of the tube: for the mercury is easily sucked up to the height of several inches, if another piece of the thick india-rubber tubing is fastened to the end of the thick glass tube which reaches above the top of the glass cylinder. On applying the mouth to the end of this tube and sucking, the mercury may with the greatest ease be raised to the required height in the measuring tube. On removing the mouth, the tubing is compressed by the finger and thumb, and a piece of glass rod inserted into it prevents the entrance of the air. The mercury in the measuring tube should now stand some two or three inches from the top of the tube. The rod carrying it is now raised, so that the india-rubber tube fastened to the measuring tube comes above the top of the glass cylinder; a clamp is put over it and closed.\* The long glass tube is now withdrawn from the flexible tube, and the end of the flexible tube inserted into the neck of the flask containing the materials which are to react. This done, the clamp is removed, and the flask becomes in fact part of the measuring tube. By bending the flexible tube, the flask is brought within the glass cylinder, which of course is filled with water. A common india-rubber ring slipped over the iron rod conveniently holds the flask against the side of the measuring tube, so that they can be raised or lowered in the cylinder without difficulty. The next operation is to read off the volume of air contained in the tube and flask. This is done in the ordinary way; the tube is lowered into the well until the column of mercury within it is of the same height as the column in the pressure tube; this gives the amount of air in the apparatus before the reaction commences; the tube has now to be raised, the flask again brought outside the cylinder, and the action caused to take place. Another measurement when the reaction is completed gives the volume of gas produced. The substances to be used are prevented from coming in contact when intro-

\* The V-shaped clamp, drawn in fig. 7, page 241, vol. ii, N.S., of this Journal, answers exceedingly well.

duced into the small flask in the usual way, one of them being placed within a small tube, which is lowered into the flask containing the other substances which are to take part in the reaction. The flexible tube enables the flask to be bent about, so that the mixing can easily be effected, and heat can of course be readily applied when necessary. In order to ensure there always being moisture round the joining of the india-rubber tube and flask, a piece of cotton wick is wound round it at this point, and the ends allowed to dip into the water in the glass cylinder. This simple plan of using the india-rubber tube as a sort of cork to the flask has been found to answer admirably; as long as the joining is wet, there is not the slightest tendency to leakage, even under considerable pressure, and the joining is made and severed with the greatest ease. It was proved by direct experiment that the varying amount of bending which the india-rubber tube of the thickness above given will undergo when placed in the glass cylinder, does not appreciably alter the volume of air in the measuring tube.

In an ordinary gas analysis it is sufficient if we know the relative volumes of gas at the different stages of the analysis; but for the present purpose the necessary data for converting these relative volumes into absolute volumes, and for ascertaining their weight, must be determined.

The tube is calibrated in the usual way, and a table of volumes drawn up similar to one for an ordinary eudiometer. The volume of mercury which has been used in the calibration has to be weighed, and the temperature noted. By means of the following formula, quoted from Bunsen's Gasometry, the value of one volume in the table expressed in cubic centimetres,  $c$ , is determined:—

$$c = \frac{g \times (1 + 0\cdot0001815t)}{13\cdot596V}$$

where  $g$  is the weight, and  $t$  the temperature of the constant quantity of mercury which occupies the volume  $V$  used as the standard in the calibration.  $0\cdot0001815$  is taken as the co-efficient of expansion of mercury and  $13\cdot596$  as its specific gravity at  $0^\circ$  C. To find the weight of the gas evolved, it is further necessary to know the temperature and pressure at which the measurement has been made. When the measurements are made by means of a pressure-tube, it is only necessary to ascer-

tain once for all what is the temperature and pressure, at the same moment, of the air in the upper part of the pressure-tube, the mercury standing exactly at the mark which indicates the constant volume. The determination is easily made in the following way:—A linear measure—a eudiometer graduated to millimetres, if the scale go to the end, will do—is fixed in the clamp of the eudiometer-rod and lowered within the glass cylinder till it just touches the mercury in the trough. The following observations are all made by means of the telescope in the ordinary way: first the level of the mercury is raised or lowered so as exactly to bring it to the mark on the pressure tube; then, by means of the fine adjustment, the millimetre measure is made just to touch the surface of the mercury in the trough, the mark or pointer on the pressure tube extending behind it, and giving exactly the height of the column of mercury in the pressure-tube. Besides this it is only necessary to have a good thermometer hanging inside the glass cylinder against the pressure-tube; its height is easily read off after making the former observations; then, if the height of the barometer be noted, it completes the necessary data. Two or three observations should be made, and the mean of them taken. A perfectly simple calculation will then, from these data, give the weight of the dry gas occupying one tabular volume of the tube. In an analysis, after reading off the volume of gas before and after the reaction, the difference has merely to be multiplied by the constant, to give the weight of the gas evolved.

In the following calculations, the weights obtained by Regnault for carbonic acid and hydrogen are used, namely, 1.977414 grammes as the weight of one litre of carbonic acid at 0° and 760mm. pressure, and 0.089578 grammes the weight of a litre of hydrogen.

With regard to the following experiments, it is but fair to state that these are all the analyses which have been made in this way, that they have been made with different amounts of air in the pressure-tube, with different flasks, and many of them made very hurriedly. First, with regard to the reactions in which carbonic acid is evolved, one series of experiments was made with pure sodic carbonate, which had been prepared with great care, and another series with calc-spar. In the experiments with sodic carbonate, quantities of the salt were used,



which varied between 0·27 and 0·35. When the bulk of acid to be used is considerable, it is convenient to put it directly into the flask, and the carbonate into the tube; when small, the reverse is best. It will hardly be necessary to give the details of each experiment, but it will be sufficient to state the amount per cent. of carbonic acid obtained from the sodic carbonate, and the nature and quantity of the acid used.

In the following experiments 1·3 c.c. of a mixture of two parts of water and one part of pure sulphuric acid was used.

1st experiment	41·524	per cent. CO <sub>2</sub> .
2nd	„	41·524 „
3rd	„	41·571 „
4th	„	41·532 „
5th	„	41·607 „
6th	„	41·484 „
7th	„	41·517 „
8th	„	41·502 „

In the last experiment 1·4 c.c. of the acid was used.

The theoretical amount of carbonic acid in sodic carbonate is 41·509 per cent.

Dilute hydrochloric acid was substituted for the sulphuric acid. A mixture of one part of water and two parts of ordinary pure acid was made.

1st experiment	1·3 c.c. acid used	41·518
2nd	„ 1·5 „	41·491
3rd	„ „ „	41·495
4th	„ „ „	41·461
5th	„ 2·5 „	41·192

In the two following experiments a mixture of one part of water and three parts of hydrochloric acid was used, and 1·3 c.c. of it taken in each experiment.

1st experiment	41·378
2nd „	41·430

The following are the experiments with calc-spar. In this case of course sulphuric acid could not be used.

Commencing with the largest amount of acid used, and the most diluted, we have the following series—one part of hydrochloric acid, and one part of water:—

1st experiment	2.8	c.c. acid used,	43.520	CO <sub>2</sub> per cent.
2nd	2.4	„	43.550	„
3rd	„	„	43.596	„
4th	„	„	43.666	„
5th	„	„	43.555	„
6th	„	„	43.827	„
7th	2.0	„	43.719	„
8th	„	„	43.773	„
9th	1.6	„	43.854	„
10th	1.5	„	43.858	„
11th	„	„	43.836	„
12th	„	„	43.798	„
13th	„	„	43.796	„

The theoretical amount of carbonic acid in calcic carbonate is 44.00 per cent., but it has generally been found to contain a less amount.

A mixture of two parts of hydrochloric acid and one part of water was used in the following experiments:—

1st experiment	2.4	c.c. acid used,	43.731	CO <sub>2</sub> per cent.
2nd	„	„	43.714	„
3rd	1.5	„	43.581	„
4th	1.2	„	43.889	„
5th	„	„	43.901	„
6th	„	„	43.901	„
7th	„	„	43.842	„
8th	„	„	43.901	„
9th	„	„	43.850	„

The following five consecutive experiments were made under similar circumstances, 2.4 c.c. of acid used:—

0.2692	gram. calc spar gave	43.751	per cent CO <sub>2</sub> .
0.2706	„	43.744	„
0.2820	„	43.724	„
0.2634	„	43.741	„
0.2677	„	43.721	„

In the next experiments nitric acid was used instead of hydrochloric, two parts of the pure nitric acid were diluted with one part of water.

0·3191	gram. calc spar	1·4	acid gave	43·934	CO <sub>2</sub>	per cent.
0·3268	„	1·2	„	43·924	„	„
0·3225	„	„	„	43·904	„	„
0·3524	„	„	„	43·974	„	„
0·3291	„	„	„	43·886	„	„

There are obviously at least two sources of error in experiments such as these just described; one is the solubility of the carbonic acid in the acid liquid, and the other is a slight alteration in the tensions of the gas in the measuring tube, owing to a little of the acid being carried over into it. By using only a small excess of the dilute acid, the first source of error, as shown by the experiments, is capable of being almost entirely avoided. With regard to the alteration of tension, it will be found that when a flask of about 120 c.c. in capacity is used, and the reaction not allowed to take place too violently, the alteration is very small indeed. In some of the experiments a little plug of cotton wool was placed in the neck of the flask.

All oxides which give off carbonic acid when mixed with oxalic and sulphuric acids are capable of being readily estimated by this process. A specimen of peroxide of manganese gave the following results:—

1st experiment	gave	58·156	MnO <sub>2</sub>	per cent.
2nd	„	58·101	„	„

In the following experiments hydrogen was the gas measured. Theoretically, 100 pts. of zinc should give 30·769 of hydrogen,

0·1818	gram. of common zinc foil,	gave	3·052	per cent. hydrogen
0·1901	„	„	3·047	„
0·1946	„	„	3·050	„

In this experiment 2·0 c.c. of water were put in the flask with the zinc, and 0·8 c.c. of sulphuric acid in the small tube.

A specimen of pure zinc, given me by Dr. Matthiessen, gave the following results:—

0·1941	gram. gave	3·079	per cent. hydrogen.	
3·2	c.c. of acid used,	consisting of 3 parts of hydrochloric acid and 1 part water.		
0·1835	gram. zinc,	gave	3·078	per cent. hydrogen.

2·8 c.c. of acid used, consisting of 1 part sulphuric acid and 3 parts water.

0·2202 grm. zinc, gave 3·069 per cent. hydrogen.

2·0 c.c. of water and 0·8 c.c. of sulphuric acid used.

Some magnesium ribbon gave the following results. Theoretically, the amount of hydrogen which 100 parts of magnesium should yield, is 8·333 :—

0·0720 grm.	gave	8·256	per cent. hydrogen
0·0755	„	8·255	„
0·0708	„	8·268	„
0·0786	„	8·282	„

In the last experiment 1·4 c.c. of a mixture of 2 parts of hydrochloric acid and 1 part of water was used.

A specimen of magnesium, which had been distilled, was tried; 0·0702 grm. gave 8·281 per cent. hydrogen. 1·5 c.c. of a mixture of 1 part of sulphuric acid and 3 parts of water used.

The foregoing experiments will give some idea of the degree of accuracy which is very easily attained by this method. If a larger measuring tube were used, and the gas not expanded so much, by using a lower mark on the pressure tube, no doubt still more accurate results would be obtained.

It is believed that a process for collecting and accurately measuring the volume of gas given off in any reaction, will be found useful, and receive many applications. The special advantages of it as a means of analysis are, that accurate results are obtained by a very simple and quick process, and one which requires only small quantities of the substance operated on.

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XXXV.—*Rough Notes on the formation of Nitre, as observed in the North Western Provinces of India.*

By W. J. PALMER, M.D., F.R.C.S.L., Surgeon, Bengal Army, and Additional Chemical Examiner to the Government of India.

A CLASS or caste of men, called *sorawallahs*, from the Hindu word *sora*, meaning nitre, make it the business of their lives to collect the raw material, manufacture, and sell the salt, either

for local use, as a cooling agent in frigorific mixtures, or for exportation.

The *sorawallah* goes about the village, examining the small surface drains which issue from holes in the mud-wall, usually found around native dwellings and their cow-houses; when he detects a faint white veil-like patch of crystalline formation, on or near the dark-coloured borders of these little drains, he knows that a considerable quantity of nitre exists, on or near the surface of all the surrounding earth; he accordingly proceeds to scrape off a very thin layer of the surface soil, which he carries away to his place of manufacture, as soon as his morning's collections are finished. On arriving there, the impregnated earth so collected is thrown into an earthen vessel containing either water, or water which has been poured off from previous supplies of similarly impregnated earth. When the water so used is pretty well saturated, it is poured into shallow pans of unglazed earthenware, in which it is then exposed to the combined influence of hot winds and the solar rays; these cause rapid evaporation, and the formation of crystals of nitrate of potash, which, after one or two more crystallisations, are ready for sale. The mother-liquor, on being further evaporated, yields a proportion of common salt, varying from one to seven or nine per cent. The *sorawallah* makes fresh collections from precisely the same spots of ground, from week to week, year to year, and from generation to generation, after the manner of the eastern world; the production of nitre is constant so long as the place continues to be inhabited; it even continues to appear in large, though gradually decreasing quantities, for years after the village may have been deserted. The intervals at which fresh collections may be made from the same spot, vary in different localities, and in different seasons of the year, from one to seven, ten, or more days. Before suggesting any theory of the mode of formation of this nitre, it will be necessary to direct attention for a few moments to some points in the physical geography of the country, and in the economy of a native village, which differ widely from anything seen in Europe.

Nitre is found in the plains of India, being most abundant in the parts most distant from the mountain ranges. The soil in these parts is composed of a very uniform alluvium, or river-sand; for a depth of more than 200 feet, the uniformity of

this is only broken by occasional thin layers of clay, indicating former river courses, and still more rarely by beds of rough, nodular, friable, stony masses, called *kunkur*,\* each nodule of which is made up of granules of carbonate of lime so agglomerated that they enclose much of the surrounding sand, the proportion of carbonate of lime varying from fifteen to seventy per cent. These beds lie in a horizontal plane, at depths varying from one to twenty feet; they are from six inches to three or four feet thick; from one to three yards wide; and from one to several miles in length, with occasional interruptions. The yield of nitre is abundant only where these beds of *kunkur* exist in the soil, and where at the same time the natural water level is from twenty to forty feet below the surface. In parts where the surface of the well-water is only a few feet below the level, there no nitre is gathered; it is probably carried away and diffused as soon as formed. Where, on the other hand, the water level is more than twenty feet from the surface, all the watery parts of fluids thrown on the sandy surface are drawn to the surface and evaporated by the powerful sun, the solid particles remaining on the surface, to be gathered or washed away when the new rain falls.

*Climate.*—For eight months in the year no rain falls in the nitre-producing parts of India; the soil is exposed to the continuous influence of a dry wind and a burning sun; during the remaining four months it is exposed to alternations of heavy tropical storms of rain with thunder and lightning, and a burning sun. The rain generally falls so rapidly that it rushes off the surface of the earth into neighbouring rivers; some, however, soaks for a varying distance into the soil, where it dissolves any soluble material it may come in contact with, leaving it again on the surface as the water is drawn up and evaporated by the sun's influence. A greater quantity of nitre is collected in the rainy season than in any other, although it is

\* These beds of "*kunkur*" are interesting as being the only stone-like formation seen for hundreds of miles along the left bank of the Ganges; as being the only available source of lime in the plains of India for ages; and also in their formation. In the extreme hot dry season, water, holding bicarbonate of lime in solution, appears to be drawn up from the depths of the earth; as this approaches the surface the whole of the water and part of the carbonic acid being driven-off, granules of carbonate of lime are deposited, which coalescing imperfectly form these rough granular nodules.

evident that much more must at the same time be washed away.

*The Village.*—The nitre-producing parts of India are more densely populated than England; the villages are large, and are made up for the most part of mud-houses surrounded by a mud-wall, which generally encloses the dwellings of a whole family, including uncles and aunts and their families, as well as grand parents and grand children; every family will have at least one pair of plough-oxen. The only drains from these houses are the small surface ones before alluded to, and the only fluids which pass by these drains are urine and the small quantity of refuse water brought to the house for culinary or drinking purposes;\* these drains open on to a small open plot of ground where the drainage diffuses itself, and is rapidly dried in the sun, the only other domestic refuse which finds its way to this spot being the daily contribution of wood-ashes, which results from cooking processes, any refuse food, or leaves used as plates by these people, being rapidly devoured by hungry eastern dogs, crows, or their own cattle. It now appears that we have all the necessary elements for the continuous production of nitre; there is urea in abundance, which, in the presence of carbonate of lime is probably converted into nitric acid and nitrate of lime by the influence of the severe thunder-storms in the rainy season, and possibly also by the active chemical influence of the sun's rays at other seasons. The nitrate of lime so formed is probably again decomposed by solution of carbonate of potash, giving rise to nitrate of potash, the solution of which is drawn to the surface of the earth in the ordinary course of evaporation, where it crystallises and is gathered by the *sorawallah*. The small amount of chloride of sodium associated with the nitre is also probably derived from the urine.

The evidence in favour of this theory is:—

1stly. That no other known source of nitre exists.

\* All things requiring washing in a native house are carried to a neighbouring bank. All coarser refuse, as broken pots, &c., are thrown into a hole made when the earth was dug to build the house. Ordure does not find a place in this plot of ground, as a rule, for it is the custom for all members of an Indian household to retire once daily, in the early dawn, to the "bushes," or to a field, sheltered by a high growing crop, where they at once defecate and manure their land; at all other times in the day, urine is voided in the little open drain or gutter. Cow-dung does not find a place there, it being invariably collected, dried in the sun, and used for cooking purposes.

2ndly. That nitre is found only in and near populous villages ; that it continues to be found on the same spot of ground so long as it is inhabited, and gradually ceases when a village is deserted.

3rdly. That the process is imitated successfully in some of our Indian gaols, where the expense of removing urine to a distance has been avoided by setting apart a plot of ground to receive it ; lime is then added to this, in case it does not exist in the soil naturally, and all the refuse wood-ashes are thrown in the same place. Nitre is formed, collected, and manufactured for sale to cover the cost of production.

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### XXXVI.—*Researches on Vanadium.*

By HENRY E. ROSCOE, B.A., Ph. D., F.R.S.

[From the Philosophical Transactions for 1868, being the Bakerian Lecture delivered before the Royal Society, December 19, 1867.]

#### I. INTRODUCTION.

AMONGST the physical properties which point out the general relationship and classification of chemical substances, none has so deservedly obtained the confidence of chemists as isomorphism. The vanadium compounds have, however, proved a remarkable and unexplained exception to the conclusions which generally follow from well ascertained identity of crystalline form.

Rammelsberg,\* and afterwards, more completely Schabus,† pointed out the fact that the mineral vanadinite from several localities (a compound of lead vanadate and lead chloride) is isomorphous with apatite, pyromorphite, and mimetesite, minerals consisting of calcium phosphato-fluoride, lead phosphato-chloride, and lead arsenato-chloride, having the formulæ  $3(\text{Ca}_3\text{P}_2\text{O}_8) \cdot \text{CaF}_2$ ;  $3(\text{Pb}_3\text{P}_2\text{O}_8) \cdot \text{PbCl}_2$ , and  $3(\text{Pb}_3\text{As}_2\text{O}_8) \cdot \text{PbCl}_2$ . The crystalline form of all these minerals is a hexagonal prism terminated by six-sided pyramids. The angle P : P (terminal) found by

\* Pogg. Ann. Bd., xviii, p. 249 (1856).

† Ibid. Bd., c, p. 297



Rammelsberg for vanadinite, and by different observers for the other minerals, is as follows :—

- |                   |            |                   |            |
|-------------------|------------|-------------------|------------|
| (1) Vanadinite .. | 142° 30' ; | (3) Pyromorphite  | 142° 15' ; |
| (2) Apatite ....  | 142° 20' ; | (4) Mimetesite .. | 142° 7' ;  |

and the relation of the axes

- |                 |                 |
|-----------------|-----------------|
| (1) 1 : 0.727 ; | (3) 1 : 0.736 ; |
| (2) 1 : 0.732 ; | (4) 1 : 0.739 . |

So far, indeed, has the isomorphism of these compounds been traced, that in many specimens these minerals have been found to crystallise together in all proportions; and Heddle\* describes a crystal in his possession the upper half of which consists of vanadinite, and the lower half of pyromorphite.

We are indebted to the researches of Berzelius for almost all we know concerning the chemical relations of vanadium and the composition of its compounds. From his celebrated investigation on Vanadium† (1831), the results of which have since been more or less completely confirmed by Schafarik‡ and Czudnowicz,§ it appears that the formula of vanadic acid is  $\text{VO}_3$ . Hence it is evident that we have here to do with either a case of dissimilarly constituted substances acting as isomorphous bodies and crystallising together, or else the conclusions of Berzelius are erroneous, and the true formula of vanadic acid is  $\text{V}_2\text{O}_5$ , corresponding to the pentoxides of phosphorus and arsenic. The first of these alternatives has been properly accepted by most chemists as the only present solution of the difficulty, inasmuch as the definite experimental data given by Berzelius render the assumption of any other formula but  $\text{VO}_3$  for vanadic acid perfectly gratuitous in the absence of experiments proving these data to be erroneous.

Berzelius based his conclusions on the following experiments, viz. (1) the constant loss of weight which vanadic acid undergoes on reduction in hydrogen at a red heat; (2) the action of chlorine on this reduced oxide, when a volatile chloride is formed and a residue of vanadic acid remains, which is found to be exactly one-third of the quantity originally taken for

\* Greg and Lettsom's British Mineralogy, pp. 409-410 (1858)

† Pogg. Ann. Bd. xxii, p. 1 (1831).

‡ Ann. Ch. Pharm. cix, p. 84 (1859).

§ Pogg. Ann. Bd. cxx, p. 38 (1863).

reduction in hydrogen. Hence Berzelius concludes that the number of atoms of oxygen in the oxide is to that in the acid in the proportion of 1 to 3; so that (assuming the lowest oxide to contain one atom of oxygen) the acid contains three atoms, a result which Berzelius finds borne out by its capacity of saturation. The question whether the acid contains one or two atoms of metal, Berzelius decides in favour of the former view, by finding that no compound corresponding to the alums is formed when vanadic acid is brought together with sulphuric acid and potash. The analyses of the volatile chloride made both by Berzelius and Schafarik confirm this conclusion, and place beyond all doubt the fact that, if the atomic weight of vanadium be taken to be 68.5 and  $O = 8$ , the formula of vanadic acid is  $VO_3$ , that of the oxide prepared by reduction  $VO$ , and that of the chloride  $VCl_3$ .

In the present communication I shall show that, whilst confirming these fundamental results in every particular, I still arrive at a totally different conclusion from Berzelius respecting the constitution of vanadic acid, and all the other vanadium compounds; for I shall prove that the true formula of vanadic acid is  $V_2O_5$  (when  $O = 16$ ), and the true atomic weight of vanadium 51.3, inasmuch as the substance supposed by Berzelius to be vanadium is not the metal, but an oxide with an atomic weight of 67.3, nearly that of Berzelius's metal, whilst the supposed terchloride is an oxychloride.

The following are the grounds upon which I base my conclusions: the experimental proofs are contained in the sequel:—

(1.) An oxide of vanadium exists which unites with three atoms of oxygen to form vanadic acid. Hence this latter substance must contain more than three atoms of oxygen.

(2.) The following vanadium oxides have been obtained both in the dry and wet way, and their compositions determined:—

* (1.) $V_2O_2$ , vanadium dioxide, or divanadyl ..	=	134.6
(2.) $V_2O_3$ , vanadium trioxide (Berzelius's) suboxide ..	=	150.6
(3.) $V_2O_4$ , vanadium tetroxide .. .. .	=	166.6
(4.) $V_2O_5$ , vanadium pentoxide (vanadic acid) ..	=	182.6

\* I had originally intended to call the first and third oxides of vanadium monoxide and dioxide respectively, giving to these substances the simplest empirical formulæ  $VO = 67.3$  and  $VO_2 = 83.3$ , as it is as yet uncertain whether the molecular

(3.) The so-called trichloride of vanadium  $VCl_3$ , ( $V = 67.3$ ) contains oxygen; it is an oxychloride having the formula  $VOCl_3$ , ( $V = 51.3$ ); it may be called vanadyl trichloride, or vanadium oxytrichloride, and corresponds to  $POCl_3$ , phosphorus oxychloride.

(4.) Three other solid oxychlorides exist, having the compositions:

(1.)  $VOCl_2$ , vanadyl dichloride, or vanadium oxydichloride.

(2.)  $VOCl$ , vanadyl monochloride, or vanadium oxymonochloride.

(3.)  $V_2O_2Cl$ , divanadyl monochloride.

(5.) All the native vanadates are tribasic:—

(a.) Vanadinite from Zimapan, analyzed by Berzelius (Pogg. Ann. xxii., 63), contains nearly three equivalents of lead oxide to one of vanadium pentoxide.

(b.) Eusynchnite, analyzed by Czudnowicz (Pogg. Ann. cxx., 27), contains three equivalents of a mixture of lead and zinc oxides to one of vanadium pentoxide.

(c.) Arœoxene, analyzed by V. Kobell (J. pr. Chem. l., 496), was found to have a similar composition to eusynchnite.

(d.) An American vanadinite, analyzed by Smith (J. pr. Chem. lxvi., 433), is a tribasic compound.

(e.) Dechenite from the Pfalz is, according to Brush (Sill. Am. Journ. [2], xxxiv., 116), identical with arœoxene, and therefore a tribasic compound.

(f.) Volborthite, according to Credner's analysis (Pogg. Ann. lxxiv., 546), also contains one of vanadic acid to three of basic oxide.

(6.) Vanadic acid fused with sodium carbonate displaces three molecules of carbon dioxide, showing that normal sodium vanadate, or sodium orthovanadate, is tribasic, the formula of this salt being  $Na_3VO_4$ .

(7.) The so-called monovanadates are salts corresponding to the monobasic phosphates, and may be termed metavanadates; thus,  $NaVO_3$ ,  $NH_4VO_3$ ,  $Ba_2VO_3$ . The so-called bivanadates

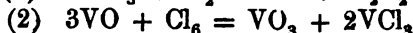
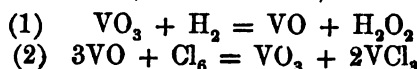
weights of these oxides, in accordance with the law of even atomicities, are multiples of the above, or whether, as in the only similar case, that of the nitrogen oxides, they are represented by the above numbers themselves. Acquiescing in the opinion expressed by several chemists that the former alternative is the most probable, I have now adopted the names as they stand in the text.—Jan. 20, 1868.]

are anhydro-salts, similar in constitution to the anhydro-salts of chromic and boric acids.

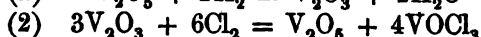
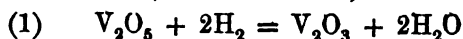
(8.) Vanadium nitride has been prepared, which, on analysis, was shown to contain 51·3 parts by weight of vanadium to fourteen parts of nitrogen.

All the reactions according to which vanadic acid was supposed (Berzelius, Rammelsberg, Schafarik, &c.) to contain three atoms of oxygen with an atomic weight  $V = 67\cdot3$  can equally well be explained when  $V_2O_5$  ( $V = 51\cdot3$ ) is taken to represent the composition of this substance. That this is the case is seen from the following:—

Berzelius's formulæ.  
( $V = 68\cdot5$ .  $O = 8$ .)



New formulæ.  
( $V = 51\cdot3$ .  $O = 16$ .)



## II. OCCURRENCE AND PREPARATION OF THE VANADIUM COMPOUNDS.

1. The sources of vanadium, although numerous, have up to the present time yielded the compounds of this metal in such extremely small quantities, that vanadium salts may still be counted amongst the greatest of chemical rarities; and consequently the satisfactory investigation of their properties has proved so difficult that contradictory statements, concerning even fundamental points, are made by recent experimenters. My attention was directed some time ago to the occurrence of vanadium in some of the copper-bearing beds of the Lower Keuper Sandstone of the Trias, worked at Alderley Edge and Mottram St. Andrews, in Cheshire; and I was fortunate enough to secure a plentiful supply of this rare metal by the purchase of a lime precipitate containing vanadium, which had been obtained as a residue in the extraction of cobalt from the cobalt-bed sandstone at Mottram, by the Alderley Edge Copper Mining Company. The geological features of the remarkable deposit of metallic salts, which occurs in this Keuper Sand-

stone have been well described by Mr. Hull.\* The horizontal beds of sandstone contain copper as blue and green carbonates, lead both as carbonate and as galena, cobalt as black cobalt-ochre, and iron oxides, all in workable quantities, together with arsenic, silver, manganese as dioxide, and barium as heavy spar. The sandstone is of a soft and uniform texture, and is metalliferous to a depth of at least 60 feet; it is coloured variously from green and brown to black, according to the nature of the covering of metallic ore which surrounds the grains of sand. The following arrangement of the beds is given by Mr. Hull:—

	ft. in.
1. Yellowish sandstone.....	4 0
2. Shaly clay with a band of copper-sand at the bottom	2 6
3. Ferruginous sandstone, with large nodules contain- ing carbonate of lead .....	6 0
4. Cobalt bed, laminated sandstone containing earthy cobalt .....	4 6
5. White compact sandstone, with carbonate of lead ..	5 0
6. Iron-stained sandstone, with cobalt, manganese, and iron .....	12 0

The copper is disseminated throughout the sand in quantities on an average of not more than from 0.5 to 2.5 per cent.; it is dissolved out by hydrochloric acid, and the metal precipitated from the solution by scrap iron. The lead is contained in small crystals throughout the mass, and is separated from the sand by maceration and washing; some of the rock contains as much as from 30 to 40 per cent. of the ore.

The sandstone from which the vanadium precipitate was prepared possesses a light colour, and contains from 0.1 to 0.3 per cent. of the oxides of cobalt, nickel, and copper disseminated as small black, green, and red specks throughout the mass. After crushing, the metals were dissolved out by hydrochloric acid; bleaching liquor and milk of lime were then added to alkaline reaction; a portion of the copper, together with the whole of the nickel and cobalt, then remained in solution, whilst the lead, iron, arsenic (partly derived from the acid used), a little copper, and the vanadium were precipitated. As the Mottram mine is now closed, I have been unable to obtain a sample of

\* Geological Magazine, vol. 1, p. 65 (1864).

the above-mentioned sandstone for examination, and therefore I cannot state positively whether the vanadium occurs as vanadinite, although for other reasons I am inclined to think that it does.

The above-mentioned lime precipitate was believed by the manager of the mines to contain about 10 per cent. of copper; but when it was dissolved in acid and the copper thrown down by zinc, the solution still retained a bright blue colour, which I soon recognised as being due to vanadium. A rough analysis of the crude lime precipitate shows that it contains about 2 per cent. of vanadium, together with lead, arsenic, iron, lime, and sulphuric and phosphoric acids.

In order to prepare pure vanadium compounds in quantity from this material, I was glad to avail myself of the kindness of my friends Messrs. Roberts, Dale, and Co., who were good enough to place their works at my disposal for this purpose. Three cwt. of the crude material was dried, and then finely ground with four times its weight of coal, and the mixture well furnaced with closed doors for several days, until the greatest part of the arsenic had been driven off. The coal having been thus burnt off, the mass was then ground up with one quarter of its weight of soda-ash, and well roasted in a reverberatory furnace with open doors for two days, to oxidize the vanadium to a soluble vanadate; the mass was then lixiviated, and the solution drawn off from insoluble matters: the liquid was acidified with hydrochloric acid, and sulphurous acid was then passed into the solution to reduce the arsenates, when the remaining arsenic was precipitated by sulphuretted hydrogen.

The deep-blue solution thus obtained was carefully neutralised by ammonia (an excess causes much of the vanadium to pass into solution), the precipitated vanadium oxide washed on cloth filters, oxidized by nitric acid, and evaporated to dryness. The well-dried crude vanadic acid was then boiled out with a saturated solution of ammonium carbonate, which left iron oxide and calcium sulphate, alumina, &c., insoluble, and the filtrate was evaporated until the insoluble ammonium vanadate separated out. This crude vanadate was then washed with sal-ammoniac solution, to free it from soda-salt, and recrystallised. In order to prepare from this salt pure vanadic acid, it was roasted in the air, and the powdery acid obtained was suspended in water, into which ammonia gas was passed; the dissolved ammonium vana-

date was separated by filtration from a residue containing silica, phosphates, &c., and was crystallised by evaporation in platinum; the pentoxide obtained from this salt was free from phosphorus. Another mode, which was adopted in order to obtain perfectly pure vanadium pentoxide, was to prepare the pure oxychloride, which, on being decomposed by water, yielded the acid as a fine orange-coloured powder. In order to free this powder from any trace of obstinately adhering silica, it was moistened with sulphuric acid, and exposed in a platinum vessel for some days to hydrofluoric acid gas; after expelling the sulphuric acid and on fusion, a mass of large transparent crystals of chemically pure vanadic acid was obtained.

The vanadium minerals appear invariably to contain more or less phosphorus, and this fact in itself serves to establish the close relationship which exists between these two elements. The complete separation of this substance from vanadium is attended with great difficulty: if much phosphorus is associated with the vanadium, the method which has proved most effectual for its removal is to deflagrate the finely divided impure acid with its own weight of sodium in a well-covered wrought-iron crucible, and wash the resulting mixture of vanadium oxides by decantation, until the wash-water ceases to give an alkaline reaction; frequently this operation had to be repeated three times before the molybdenum test ceased to indicate phosphorus. In other preparations, in which the phosphorus had been more completely removed by previous operations, the process described above of repeated crystallisation of the ammonium salt, was found capable of furnishing a product in which no trace of yellow precipitate was produced by molybdenum.

The action of even traces of phosphoric acid on vanadic acid is most remarkable; if present in quantities exceeding 1 per cent. of the weight of the vanadium, phosphoric acid altogether prevents the crystallisation of the vanadic acid, and the fused mass possesses a glassy fracture, and a black vitreous lustre; this effect is not produced by the presence of either silica, arsenic, or the lower oxides of vanadium. Still more singular is the protective influence which even traces of phosphoric acid exert upon the reducing action of hydrogen on vanadic acid at a red heat. Thus a mixture of pure vanadic acid with 1 per cent. of phosphorus pentoxide weighing 1.5888 grm., on ignition

in a current of hydrogen, lost only 0·0007 grm. ; if no phosphorus had been present, it must have lost 0·2784 grm.

### III. ATOMIC WEIGHT DETERMINATION OF VANADIUM BY REDUCTION OF VANADIUM PENTOXIDE IN HYDROGEN.

The method originally adopted by Berzelius for the determination of the atomic weight of vanadium, viz., the reduction of vanadic acid in a current of hydrogen, is perfectly trustworthy, inasmuch as the reduced trioxide (the suboxide of Berzelius) does not undergo any further change when the temperature is raised to a bright red heat, and the reduction of the pentoxide to trioxide at temperatures much below this is perfectly definite. The number obtained by Berzelius according to this method was  $V = 68\cdot5$ ; the exact number which the following experiments yield, when calculated on Berzelius's hypothesis, is 67·3.

In the following determinations of atomic weights, the quantity of powdered pentoxide employed was always more than 5 grms.\* It was placed either in a bent tube of hard glass, which when heated in a magnesia bath, was found not to lose more than 0·0001 grm. after repeated ignition and cooling, or in a platinum boat enclosed in a glass tube.

Before reduction the powdered vanadium pentoxide was gently heated in a current of dry air, until the weighings, after two successive operations, were found to be constant. After the reduction, the tube was allowed to cool completely in a current of hydrogen, and this gas was then displaced by a stream of dry air. If the reduced oxide be even slightly warm when it is exposed to the air, it absorbs oxygen, suddenly glows, and is superficially converted into a blue oxide; if, however, the oxide be cold, it may be exposed to dry air for some time without change of weight, an experiment in which nitrogen was substituted for air giving results identical with those in which air was used,

In the experiments in which the oxide was contained in the

\* In order to ensure accuracy, it is absolutely necessary to employ a larger quantity of material than was taken by Berzelius. The largest amount which he used was 2·2585 grms. vanadic acid, and the smallest 0·6499 grm. An error of one milligramme on the first weight will produce a variation of  $\pm 0\cdot2$  in the atomic weight, whilst a similar error on the smaller quantity would throw out the result by  $\pm 0\cdot7$ . If 5 grms. of substance are operated upon the variation arising from milligramme error is  $\pm 0\cdot086$ .



glass tube, the latter was carefully stoppered, and allowed to remain for half an hour in the balance-case before weighing; when the platinum boat was used, it was carefully withdrawn, with the reduced oxide, from the combustion-tube, and placed in a stoppered test-tube for weighing. These precautions are absolutely necessary in order to ensure accuracy, owing to the hygroscopic nature of the trioxide.

The hydrogen employed was most carefully purified and dried; all joints and stoppers in the apparatus were well secured by copper wire and paraffin. The gas passed through solutions of silver nitrate, sodium pyrogallate, caustic soda, and sulphuric acid, and a tube filled with metallic copper kept red-hot during the experiment was placed before the final drying-tube, to ensure absence of oxygen. In order to ascertain whether atmospheric oxygen diffused into the apparatus, a weighed tube containing phosphorus pentoxide was attached to the further end of the combustion-tube during an experiment, and allowed to remain for four hours whilst hydrogen was passing through the heated tube; at the end of the operation the drying tube had gained only 0.0002 grm., proving the absence of diffused oxygen. For the purpose of drying the hydrogen, boiled sulphuric acid alone can be used. In many of the preliminary experiments phosphorus pentoxide was used in the last drying-tube, and in all these cases the reducing action of the hydrogen was not complete, the numbers thus obtained for the atomic weight being all too high. After much labour this was found to be entirely caused by small traces of the light particles of the phosphorus pentoxide, which were invariably carried over, in spite of stoppers of cotton-wool, with the air and hydrogen into the vanadic acid, the presence of the smallest quantity of phosphorus pentoxide rendering, as has been shown, the complete reduction of the vanadic acid impossible.

1. The vanadic acid used in the following determinations was prepared from ammonium vanadate by roasting; the acid thus obtained was found to contain traces of phosphorus and silica. To free it from these substances it was treated as follows: the powdered acid was first deflagrated with its own weight of metallic sodium in an iron crucible, the reduced oxide completely washed by decantation, treated with hydrochloric acid to free it from iron, and oxidized with nitric acid. This vanadic acid was then reduced in a current of hydrogen, and converted into

the oxychloride by heating in a current of chlorine; after rectification the chloride was decomposed by water, and the resulting powdery acid dried and afterwards moistened with pure sulphuric acid and exposed in a platinum vessel for ten days to the action of hydrofluoric acid gas. On fusing and cooling this purified acid, dark red transparent crystals, five to six centimetres in length, were obtained, stretching across the bottom of the basin.

The formula of vanadic acid being  $V_2O_5$ , and that of the oxide obtained by reduction  $V_2O_3$ , the atomic weight of vanadium is found from the equation

$$x = \frac{8(5b - 3a)}{a - b},$$

where  $a$  = the weight of vanadic acid taken, and  $b$  = the weight of reduced oxide obtained.

Four experiments gave the following results:—

I.	$a = 7.7397$ ;	$b = 6.3827$ ;	therefore	$V = 51.257$
II.	$a = 6.5819$ ;	$b = 5.4296$ ;	„	$V = 51.391$
III.	$a = 5.1895$ ;	$b = 4.2819$ ;	„	$V = 51.485$
IV.	$a = 5.0450$ ;	$b = 4.1614$ ;	„	$V = 51.358$

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Mean . . . . . 51.371

Hence we may assume the atomic weight of vanadium, as obtained from the reduction of pentoxide to trioxide, to be 51.4 and probably true to within  $\pm 0.07$ .

Berzelius's mean number, calculated for  $V_2O_5$ , is found to be 52.55 with a mean error of 0.12, whilst the subsequent estimations of Czudnowicz serve only as an approximate control of Berzelius's number, giving a mean of 55.35 with a mean error of 2.33.

The fact that these older determinations all give a higher number than the above experiments, shows either that the acid was not fully oxidised, or more probably, that the oxide was not completely reduced. It has already been stated (1) that the presence of the slightest trace of phosphorus prevents the complete reduction of the pentoxide to trioxide in hydrogen; (2) that all the naturally occurring vanadium ores contain phosphorus, which can only be detected, when present in small traces, by molybdic acid, a test unknown in Berzelius's time; and (3) that the complete separation of phosphorus from vanadium is attended with great difficulty. Hence we may fairly conclude

that the difference of 1.15 in the atomic weight between the above experiments and those of Berzelius is due to the presence of small traces of phosphorus in the vanadic acid used by the great Swede.\*

#### IV. THE VANADIUM OXIDES.

The oxides of vanadium, of which Berzelius determined<sup>d</sup> the composition were three in number:—

1. The suboxide, or lowest oxide, obtained by reducing vanadic acid in hydrogen. This oxide Berzelius supposed to contain one atom of oxygen, and gave to it the formula  $VO = 76.5$ .

2. Vanadic oxide, to which Berzelius gave the formula  $VO_2 = 84.5$ , founding his view upon the analysis of a hydrated sulphate, as well as on that of the precipitated oxide dried *in vacuo*.

3. Vanadic acid,  $VO_3 = 92.5$ , was shown to contain three times as much oxygen as the suboxide.

Berzelius describes several other intermediate oxides, but he did not isolate or analyse any of them.

All these three oxides exist, and possess in the main the properties which Berzelius assigns to them; they all, however, contain, for every one atom of Berzelius's vanadium (68.5), one additional atom of oxygen ( $O = 16$ ), with the existence of which he was unacquainted. Besides these oxides, a still lower one has been found containing one atom less oxygen than Berzelius's suboxide, and therefore having the atomic weight of Berzelius's metal; this oxide acts as a radical; it may be termed vanadyl,  $VO$ , and may be supposed to exist in the higher oxides.

Thus we have ( $V = 51.3$ ):—

1. Vanadium dioxide, or vanadyl,  $V_2O_2$ .
2. Vanadium trioxide (Berzelius's suboxide),  $V_2O_3$ , or  $V_2O_2 + O$ .
3. Vanadium tetroxide (Berzelius's vanadic oxide),  $V_2O_4$ , or  $V_2O_2 + O_2$ .
4. Vanadium pentoxide (vanadic acid),  $V_2O_5$ , or  $V_2O_2 + O_3$ .

\* Since the above was written I have been fortunate enough, through the kindness of Dr. Frankland, to be able to examine a specimen of ammonium vanadate, sent by Berzelius to Faraday in 1831, and I find that this contains very considerable quantities of phosphorus.—H. K. R., July 1862.

1. *Vanadium Dioxide (or Vanadyl)*,  $V_2O_2 = 134.6$ .—In its power of uniting with oxygen, vanadium surpasses even uranium, as observed by Peligot.\* Like uranium, the metal vanadium is so extremely difficult to separate from its last atom of oxygen, and the lowest oxide is found to enter as a radical into so many compounds, that to this oxide the name vanadyl (VO) may appropriately be given.

Vanadium dioxide can be obtained in the dry state, as a grey powder possessing a metallic lustre, by passing the vapour of vanadyl trichloride ( $VOCl_3$ ), mixed with excess of hydrogen, through a combustion-tube containing red-hot carbon. Lower solid oxychlorides (see page 347) are found to be deposited in the further portions of the tube, whilst vanadium dioxide remains as a bright grey metallic powder mixed with the charcoal. On strongly igniting this mixture in a current of hydrogen, every trace of chlorine is removed, and a pure mixture of charcoal and dioxide remains.

Vanadium dioxide possesses a grey metallic lustre, dissolves in acids without evolution of hydrogen, and yields a lavender-coloured solution which bleaches strongly. Vanadium dioxide is insoluble in water.

*Vanadium Dioxide in solution.*—If the dark-red solution obtained by dissolving finely powdered vanadium pentoxide in strong boiling sulphuric acid be diluted with fifty times its bulk of water and then digested with metallic zinc, the liquid rapidly changes colour under the influence of the nascent hydrogen, passing through all shades of blue and green, until, after lapse of some time, it assumes a permanent lavender or violet tint. The vanadium is then contained in solution in the lowest degree of oxidation ( $V_2O_2 = 134.6$ ) as sulphate, and this compound absorbs oxygen with such avidity as to bleach indigo and other vegetable colouring-matters as quickly as chlorine itself, and acts far more powerfully than any other known reducing agent. In order to estimate the degree of oxidation of the dissolved vanadium, a standard solution of potassium permanganate was added to the reduced liquid until a permanent pink colour was produced, experiments with vanadium trioxide of known composition having proved that this point is that of maximum

\* Ann. Ch. Phys., 3 sér., tomes v and xii.

oxidation ( $V_2O_5$ ), and that it can be accurately reached provided an excess of sulphuric acid be present.\*

The calculated loss of oxygen on 100 vanadium pentoxide, when reduced to the dioxide  $V_2O_3$ , is 26.3; the mean experimental number obtained was 26.53.

*Reduction with Cadmium and Sodium Amalgam.*—If solutions of vanadium pentoxide in sulphuric acid be reduced by cadmium (platinum scraps being added to facilitate the evolution of hydrogen), or by an amalgam of sodium, the ultimate result is the formation of the lavender-coloured solution of the dioxide.

The mean of these six determinations thus made gave 26.3 as the loss on 100 parts of vanadium pentoxide, exactly corresponding to the calculated numbers.

The salt formed by the reducing action of hydrogen in presence of the above metals and sulphuric acid is doubtless a vanadium sulphate, that is, sulphuric acid in which the equivalent quantity of hydrogen is replaced by the metal. I have yet to determine the composition of these salts. When ammonia or caustic potash is added to the lavender solution, a brown-coloured precipitate, probably of vanadium hydroxide is formed, and this instantaneously absorbs oxygen.

On allowing the neutralized lavender solution to stand exposed to air for a few seconds, the colour changes to a deep chocolate-brown; so rapid, indeed, is this change of colour, when nearly the whole of the free acid is neutralized by zinc, that such a lavender solution may serve as a reagent for the detection of free oxygen, not inferior in delicacy to an alkaline pyrogallate. When a current of air is passed through the lavender solution of sulphate in presence of excess of acid, oxygen is absorbed, the colour of the liquid gradually changes to a bright and permanent blue, and the vanadium is contained in solution as tetroxide, two atoms of oxygen having been taken up (see tetroxide, page 338). If the free acid contained in the lavender solution of vanadium sulphate be completely neutralized by zinc, and air passed through, the liquid assumes a permanent brown colour, which on addition of acids turns

\* This method of estimation was proposed and used by Czudnowicz (Pogg. Ann. Bd. cxx, p. 37); the results described by him differ, however, altogether from my own. He did not obtain the lavender-coloured solution by the action of zinc, and it is clear that in his experiments the reducing action of the hydrogen was not complete.

green, and the vanadium is contained in solution as trioxide (see trioxide, page 336). The point of the reduction at which the bleaching action commences is easily ascertained by testing the liquid from time to time with litmus paper. The changes in colour which the sulphuric acid solution of vanadium pentoxide undergoes when treated with zinc may be divided into seven stages.

Stage.	Colour.	Reaction.	State of oxidation of the metal.
1	Green.....	Acid .....	Vanadium pentoxide to tetroxide.
2	Bluish green.....	Acid .....	Vanadium pentoxide to tetroxide.
3	Blue .....	Acid .....	Vanadium tetroxide.
4	Greenish blue ....	Acid .....	Vanadium tetroxide to trioxide.
5	Green.....	Bleaches slightly	Vanadium trioxide to dioxide.
6	Bluish violet.....	Bleaches strongly	Vanadium trioxide to dioxide.
7	Lavender or violet.	Bleaches strongly	Vanadium dioxide.

This shows that the bleaching action commences in stage 5 with the formation of the dioxide. A quantitative experiment made in the same way showed that the bleaching action of the reduced solution ceased when to 100 parts of the dioxide 9.5 parts of oxygen had been added; in order to pass completely into trioxide, 11.9 parts of oxygen would have been needed.

The reduction of vanadium to dioxide by means of nascent hydrogen in presence of zinc, serves as an easy and accurate method of estimating vanadium when mixed with certain other metals.

2. *Vanadium Trioxide* (the suboxide of Berzelius),  $V_2O_3 = 150.6$ .—The anhydrous trioxide is obtained, as is well known, by reducing vanadium pentoxide in a current of hydrogen at a red heat. It is perfectly stable up to temperatures approaching a white heat; and even when heated in a current of hydrogen to this temperature, the trioxide does not lose weight. 0.411 gm. vanadium pentoxide, when reduced in hydrogen and heated for two hours to whiteness in a wind furnace, yielded 0.366 gm. of black trioxide, the theoretical quantity being 0.368 gm.

In addition to the complete description of the properties of the oxide given by Berzelius, I have only to add that it undergoes oxidation, not only glowing rapidly when exposed whilst warm to the air, but likewise slowly when exposed to the air at ordinary temperatures. Black amorphous trioxide, when allowed to stand exposed to the air for some months, undergoes a remarkable change; it takes up an atom of oxygen,

and is transformed to small dark indigo-coloured crystals of tetroxide (see page 338).

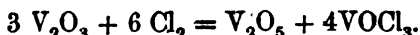
*Vanadium Trioxide in solution.*—The trioxide is insoluble in acids, but it may be obtained in solution as follows:—If solutions of vanadium pentoxide in sulphuric acid are diluted and treated with excess of metallic magnesium, the changes of colour which are observed when zinc, cadmium, or sodium amalgam are used do not continue beyond the green, and the liquid contains vanadium trioxide in solution. Thus the observed loss of oxygen on 100  $V_2O_5$  was 17.6, whilst the calculated loss is 17.5.

Solutions of vanadium trioxide can also be obtained by partial oxidation of the lavender-coloured solution of dioxide. If a current of air be passed through a reduced solution in which the free acid has been neutralized by excess of zinc, and the remaining metallic zinc removed, the liquid attains a permanent brown colour, which, on addition of a few drops of acid, turns to green. Both the brown and green liquids contain trioxide in solution, the dioxide having taken up one atom of oxygen.

In this way 100 parts of vanadium dioxide were found to have absorbed (1) 13.05 and (2) 12.96 parts of oxygen; to pass to trioxide, 11.9 parts are required.

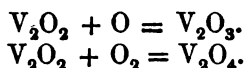
If a few drops of acid are added to the brown solution, which does not undergo change even when air is passed through for several days, it immediately turns green, but does not undergo any alteration as regards its oxygen. Thus a brown solution was divided into two equal parts; the one which was oxidized whilst neutral and brown required 12.13 per cent. of oxygen; the other, to which a few drops of hydrochloric acid were added, became at once green, and required 10.82 per cent. of oxygen to raise it to  $V_2O_5$ .

*Action of Chlorine upon Vanadium Trioxide.*—The action of chlorine upon this oxide led Berzelius to give to it the formula VO, ( $V = 68.5$ ); but, as stated, the fact that one-third of the vanadium remains in combination with oxygen in the residual vanadic acid, follows equally from the formula  $V_2O_3$ , when  $V = 51.3$ . Thus:—



The composition and constitution of the salts forming the green solution still remain to be ascertained.

3. *Vanadium Tetroxide*,  $V_2O_4 = 166.6$  (the vanadic oxide of Berzelius).—The anhydrous tetroxide was obtained by Berzelius\* by precipitating the hydrated oxide from a sulphate with sodium carbonate, washing, and igniting in a vacuum to free it from water. On reducing in hydrogen, Berzelius found that 0.762 grm. yielded 0.691 grm., or 90.67 per cent. of his "suboxide" ( $V_2O_3$ ,  $V = 51.2$ ); and hence he legitimately concludes that vanadic oxide has lost as much oxygen as the suboxide contains,—that is, as much as he thought it contained, for  $V_2O_4$  yields 30.36 per cent. of  $V_2O_3$ :—



The anhydrous tetroxide can also be prepared by the slow oxidation of the black trioxide at the ordinary atmospheric temperature. It possesses an indigo-blue colour, and under the microscope is seen to consist of brilliant blue shining crystals. This remarkable change occurs when the black trioxide is exposed for several weeks to the air, and it has been repeatedly observed. 1.1686 grm. of the blue crystals thus obtained, having been dried completely under the air-pump, yielded 1.2688 grm. vanadium pentoxide, corresponding to a percentage increase of 8.57: 100 parts of the tetroxide require 9.59 parts of oxygen for conversion into the pentoxide. These blue crystals are anhydrous. A weighed portion of trioxide was exposed to the air and from time to time dried *in vacuo* and weighed. On November 13th, 1866, the weight of the black trioxide was 0.7507; on February 4th, 1867, the colour had changed to a bluish black, and the weight was 0.8112; on March 25th, the colour had become blue, and the weight of the oxide was 0.8267, showing a percentage increase of 10.13, or an absorption of nearly one atom of oxygen, as 100 of trioxide require 11.87 of oxygen for conversion into the pentoxide. On further exposure the blue oxide increases in weight, again changes colour to a dark olive-green, and a hydrated oxide is formed.

*Vanadium Tetroxide in Solution.*—Solutions of the salts of vanadium tetroxide are bright blue, as described by Berzelius. They may be obtained (1) by the action of moderate reducing

\* Pogg. Ann. Bd. xxii, p. 19.



agents, such as sulphur dioxide and sulphuretted hydrogen (probably also oxalic acid, sugar, alcohol, &c.) upon solutions of vanadium pentoxide in sulphuric acid; (2) by the action of a current of air upon the acid solution of vanadium sulphate.

(1.) If sulphur dioxide or sulphuretted hydrogen be passed into the yellow solution of vanadium pentoxide in dilute sulphuric acid, the liquid becomes permanently blue, no green or violet colour being obtained by the continued action of these reducing agents. In order to determine the state of oxidation of the metal, these blue solutions were boiled in an atmosphere of carbonic acid until every trace of the reducing agent was expelled, and on cooling standard permanganate was added until the pink tint was noticed.

The experiments gave a mean loss of 9.03, whereas theory requires a loss of 8.75.

(2.) When a current of air is passed through acid solutions of the dioxide, a permanent blue colour is attained, two atoms of oxygen have been absorbed, and the solution contains tetroxide. 100 parts of vanadium dioxide were found to have absorbed (1) 20.9, and (2) 23.4 parts of oxygen; to pass from the dioxide to the tetroxide, 23.78 per cent. is needed. The sulphate obtained by evaporating the blue solution containing this oxide was analysed by Berzelius, and it may be regarded as a vanadyl sulphate, or sulphuric acid in which hydrogen is replaced by vanadyl.

4. *Vanadium Pentoxide* (vanadic acid,  $V_2O_5$ , molec. weight 182.6).—The properties of vanadic acid have been fully described by Berzelius; the only important addition to our knowledge of this oxide made since his time is the determination of the crystalline form (rhombic prisms) made by Nordenskjöld.\* In the present communication I propose to discuss the properties and composition of vanadic acid and the vanadates, only so far as is necessary for the purpose of elucidating the true atomic weight of the metal.

*Constitution of the so-called Monovanadates.*—The analyses made by Berzelius of the ammonium and barium vanadates† suffice to point out the true character of these salts. The formulæ which he there gives, assuming the atomic weight of the metal to be 68.5, show that these compounds must be con-

\* Pogg. Ann. Bd. cxii, p. 160.

† Ibid. Bd. xxii, p. 49.

sidered as metavanadates when the atomic weight of the metal is taken to be 51.3.

Berzelius's formulæ.  $V = 68.5, O = 8.$

Vanadate of ammonia,  $NH_3VO_3 + HO.$

Vanadate of baryta,  $BaOVO_3.$

New formulæ.  $V = 51.3, O = 16.$

$NH_4VO_3$ , ammonium metavanadate, or  $\left. \begin{matrix} NH_4 \\ VO \end{matrix} \right\} O_2.$

$BaV_2O_6$ , barium metavanadate, or  $\left. \begin{matrix} Ba \\ 2VO \end{matrix} \right\} O_4.$

*Constitution of the so-called Bivanadates.*—The bivanadates obtained by the cautious addition of acetic acid to the monovanadates, according to Berzelius's directions, have been analyzed by Von Hauer.\* The ammonium and sodium bivanadates were found to correspond with the formulæ  $NH_4O.2VO_3$  and  $NaO.2VO_3$ , where  $V = 68.5$  and  $O = 8$ . If we assume  $V = 51.3$  and  $O = 16$ , these salts will be expressed by the formulæ  $(NH_4)_2V_4O_{11}$  and  $Na_2V_4O_{11}$ ; or they may be represented as *anhydro-salts*, either  $2NH_4VO_3 + V_2O_5$  and  $2NaVO_3 + V_2O_5$ , or else as  $Na_4V_2O_7 + 3V_2O_5$  as an anhydro-salt of sodium pyro-vanadate.

*Constitution of the Normal Vanadates.*—That vanadic acid in its normal state is tribasic is shown by the fact first pointed out by Czudnowicz†, that when vanadium pentoxide is fused with an excess of sodium carbonate, three molecules of carbon dioxide ( $3CO_2$ ) are displaced for every molecule of vanadium pentoxide ( $V_2O_5$ ) entering into combination. In an experiment carefully conducted, in which sodium carbonate was heated to redness with 0.4323 grm. of vanadium pentoxide until no further loss of weight occurred, the pentoxide was found to expel 0.3078 grm. carbon dioxide ( $CO_2$ ); this corresponds to a ratio of 2.957 molecules of carbon dioxide to 1 of  $V_2O_5$ , or nearly in the proportion of 3 to 1. Normal sodium vanadate or sodium orthovanadate, is  $Na_3VO_4$ , or  $\left. \begin{matrix} Na_3 \\ VO \end{matrix} \right\} O_3$ . Hence there is no doubt that vanadic acid in its normal state acts as a tribasic acid.

\* Journ. prak. Chem. Bd. lxi, p. 383 (1856).

† Pogg. Ann. Bd. cxx, p. 33.

It is my intention to investigate fully the constitution and properties of the vanadates at a future time.

## V. VANADIUM OXYCHLORIDES.

1. *Vanadium Oxytrichloride*, or *Vanadyl Trichloride*,  $\text{VOCl}_3$ , molec. weight 173.67 (terchloride of vanadium of Berzelius).—The fact that the lemon-yellow liquid chloride of vanadium prepared by the action of chlorine upon the trioxide does contain oxygen, contrary to the distinct statements of previous experimenters, was ascertained in various ways:—

(1.) A few grammes of the lemon-coloured liquid chloride were placed in a bulb attached to a long combustion-tube, half filled with pure sugar-charcoal and half with metallic copper. A current of dry hydrogen, purified from oxygen according to the method previously described, was then passed over the bulb and cold tube until every trace of air was expelled; the carbon and copper were then heated to redness, and as soon as the escaping gases had ceased for fifteen minutes to render baryta-water turbid, Liebig's bulbs containing clear baryta-water were attached. The bulb containing the oxychloride, which up to this point had been kept cool, was now warmed, and the chloride distilled into the heated carbon in the tube; as soon as the vapour of the chloride was carried forward by the hydrogen, a dense precipitate of barium carbonate, which effervesced on the addition of hydrochloric acid, was thrown down in the Liebig's bulbs, proving that the liquid contains oxygen, and undergoes partial decomposition when mixed with hydrogen and brought in contact with red-hot charcoal.

This experiment was repeated twice with identical results. It is not possible in this manner to estimate the quantity of oxygen which the oxychloride contains, as only a small portion of the oxygen combines with the carbon, by far the greater portion remaining in combination with the metal to form dioxide, or the lower solid oxychlorides yet to be described.

(2.) The vapour of the lemon-yellow chloride was passed over metallic magnesium heated in a current of pure hydrogen; the action was violent, and the metal took fire. On cooling the tube, the excess of magnesium was carefully removed, and the boat was found to contain a dark-coloured powder, which, on extraction with water, contained both magnesium and

chlorine; after repeated boiling with water, hydrochloric acid extracted from this powder large quantities of magnesia, the oxygen of which could only be derived from the vanadyl trichloride.

(3.) The foregoing experiment, made with sodium instead of magnesium, showed that a thick crust of caustic soda was formed on the tube close to the boat in which the metal was placed.

(4.) The vapour of the liquid oxychloride mixed with pure hydrogen was passed through a red-hot tube. The chloride was decomposed; black, shining crystals of vanadium trioxide were deposited in the first portions of the tube; a mixture of lower solid oxychlorides filled up the further portions; and small quantities of a dark-red liquid were formed. The black crystals were found on analysis to be free from chlorine; 0.0860 grm. of these crystals gave on oxidation 0.1051 grm. vanadium pentoxide, or the substance contained 99.2 per cent. of vanadium trioxide.

(5.) When vanadyl trichloride is rapidly distilled over heated carbon, or when it is prepared by treating a mixture of trioxide and carbon with chlorine, a dark reddish-brown liquid is formed consisting of a mixture of the oxychloride and another chloride. The analysis of this dark liquid yielded results which, when calculated for chlorine and vanadyl ( $VO = 67.3$ ), always added up to from 103 to 105 per cent. on the quantity taken, showing the presence in this liquid of a vanadium chloride containing no oxygen.

(i.) *Preparation of Vanadyl Trichloride.*—Finely divided vanadium pentoxide is intimately mixed with pure sugar-charcoal, and the mixture heated to redness in a current of hydrogen. After cooling in hydrogen, the mixture of trioxide and carbon is removed to a hard glass retort heated by a large Bunsen's lamp, and a current of dry chlorine gas passed in. The crude oxychloride comes off as a reddish-yellow\* liquid, of which 180 grms. were collected in one operation. In order to purify this liquid, it is distilled upwards in a current of carbonic acid for several hours, and afterwards rectified several times over clean sodium in a current of carbonic acid, when the sodium

\* The dark colour of the chloride thus prepared is not due to the presence of vanadic acid, as Schafarik supposes, as the acid is insoluble in the chloride, but rather to some dark-coloured vanadium chlorides containing no oxygen.

becomes coated with a dark substance due to the decomposition of some other chlorides. The liquid gradually assumes a light amber-colour, and on continued distillation it attains a permanent lemon-yellow tint; it began to boil at 126° C., and all came over before 130°. When perfectly pure the boiling-point was accurately determined with 100 grms. of substance; the temperature corrected for freezing-point of the thermometer and mean temperature of the column was found to be 126·7° under 767·0 millims. of mercury.

(ii.) Vanadyl trichloride is obtained at once of a bright lemon-yellow colour, and free from the compounds which accompany its formation in the preceding reaction, by passing dry chlorine over the trioxide gently heated. The reaction is as follows, viz:—



The liquid thus obtained requires only to be distilled upwards for a short time in a current of carbonic acid, to remove excess of chlorine and hydrochloric acid, and then rectified once over sodium to obtain the substance chemically pure.

The general properties of vanadyl trichloride have been already described by Berzelius.

The specific gravity of this liquid was carefully determined at three temperatures, and found to be—

at 14°·5	..	..	..	1·841.
17°·5	..	..	..	1·836.
24°·0	..	..	..	1·828.

The trichloride remains liquid at temperatures above — 15° C. As the co-efficient of expansion of this liquid has not been yet determined above 24°, it is not possible to calculate the atomic volume of this liquid, or to compare it with that of phosphorus oxychloride (POCl<sub>3</sub>).

The vapour-density of vanadyl trichloride was determined according to Dumas's method with the following results:—

Weight of bulb and air at 11° C., and under	
776·5 millims.	6·5172 grms.
Weight of bulb and vapour at 18°·6 C., and	
780 millims..	7·0003 grms.

Residual air = 0·0 cub. centim. Capacity of bulb, 135·13 cub. centims.

Hence the vapour-density is found to be 88·20 ( $H = 1$ ), or 6·108 (air = 1); the calculated density is 86·8 ( $H = 1$ ), or 6·000 (air = 1).

*Analysis of Vanadyl Trichloride. Determination of the atomic weight of Vanadium. Method 2.*—The difficulty attending determinations of the atomic weight of the metals from analysis of their volatile chlorides has already been pointed out by Pierre\* in the case of titanium. The errors here referred to, arising from absorption of moisture by these hygroscopic chlorides, may, however, be avoided by sealing up several portions of the chloride for analysis at once from a large mass of liquid.

The following seventeen determinations were most carefully made, and the numbers obtained, closely coinciding as they do with the results of the reduction experiments already given, serve as a most important verification of the original method.

*Volumetric Determination of the Chlorine.*—Before employing Gay-Lussac's method to this determination, it was ascertained that when the chloride is decomposed by water in presence of nitric acid and silver solution added, no trace of vanadium goes down with the silver.

Pure silver was prepared with all the precautions detailed by Stas† in his first memoir, and the analyses were conducted in the manner described by him.‡ The nitric acid was prepared by distilling a large quantity of pure acid until three-fourths had come over; the remainder was then distilled and collected, and on careful testing with silver showed not the slightest indication of chlorine. The distilled water used had been carefully redistilled, and likewise gave no indication of chlorine. The weight of silver to be taken was calculated from a careful gravimetric analysis, and several volumetric determinations were made at one time. The weighed quantity of silver was placed with ten times its weight of pure nitric acid, sp. gr. 1·2, in well-stoppered 300 cubic centimetre bottles, and heated to about 40° C. until all the silver had dissolved. After cooling, the bulb containing the weighed quantity of vanadyl trichloride was brought into the bottle, the bottle closed, and the bulb

\* Ann. de Ch. et de Phys. 3 sér. t. xx, p. 257.

† Recherches sur les Rapports réciproques des Poids atomiques. Bruxelles, 1860, p. 25.

‡ Idem, p. 62.

broken by shaking; distilled water was then added, so that the weight of the whole liquid amounted to from forty to fifty times that of the silver employed. The lower oxides of nitrogen present in solution in the acid reduced the vanadium to a bright blue solution, in which the slightest turbidity of silver chloride could be well seen.

In the volumetric determination of chlorine, it has already been noticed, both by Gay-Lussac and Stas, that when one or two milligrammes of silver per litre still remain in solution, a turbidity is produced by the addition of both silver and chloride solution. This fact was also observed in the volumetric analysis of vanadyl trichloride; and in order to render the results comparable, the course proposed by Stas was invariably adopted, viz., that of adding the decimal chloride solution until all turbidity ceased. The error thus introduced is, however, extremely small (less than 0.0005), and is counterbalanced by the error arising from a trace of impurity contained in the silver.

In several cases the vanadium in the filtrate was estimated by precipitating the excess of silver, expelling the acid by evaporation, again filtering from the trace of silver chloride which separates out, and evaporating the filtrate to dryness in porcelain, transferring to platinum, oxidizing by nitric acid, and weighing the fused acid.

The following table contains the results of nine chlorine determinations made, according to the above method, with trichlorides of various preparations. Nos. 1, 2, 3, and 4 were made with substances of one preparation, Nos. 5 and 6 of a second preparation, Nos. 7 and 8 of a third preparation.

No. of experiment.	Weight of tri-chloride taken.	Weight of silver required for complete precipitation.	Percentage of chlorine.*	
1.	2.4322	4.5525	61.49	Analyst A.
2.	4.6840	8.7505	61.37	"
3.	4.2188	7.8807	61.37	"
4.	3.9490	7.3799	61.39	"
5.	0.9243	1.7267	61.37	"
6.	1.4330	2.6769	61.37	"
7.	2.8530	5.2853	60.86	Analyst B.
8.	2.1252	3.9535	61.11	"
9.	1.4248	2.6642	61.43	"

Mean result . . . . 61.306

\* Stas's numbers are here used, viz., O = 16, Ag = 107.93, Cl = 35.457.

*Gravimetric Determination of the Chlorine.*—As a check on the volumetric analysis, weight estimations were made in the usual way, it having been proved that no trace of vanadium is carried down with the silver in nitric acid solution.

The trichloride used in these experiments was taken from four different preparations; analyses Nos. 4, 5, and 7 were made from the same sample by two different experimenters.

No. of experiment.	Weight of trichloride taken.	Weight of silver chloride obtained.	Percentage of chlorine.	
1.	1·8521	4·5932	61·33	Analyst B.
2.	0·7013	1·7303	61·01	„
3.	0·7486	1·8467	61·00	„
4.	1·4408	3·5719	61·30	„
5.	0·9453	2·3399	61·21	„
6.	1·6183	4·0282	61·55	„
7.	2·1936	5·4309	61·22	Analyst A.
8.	2·5054	6·2118	61·31	„
Mean result....			61·241	

The atomic weight of vanadium calculated from the mean (61·276) of the above seventeen determinations is—

$$\frac{(106\cdot371 \times 100) - (122\cdot371 \times 61\cdot276)}{61\cdot276} = 51\cdot29.$$

Taking the mean of the numbers found (1) by the reduction of vanadium pentoxide in hydrogen, viz. 51·37, and (2) by the determination of chlorine in vanadyl trichloride, viz. 51·29, we have the number 51·33 as the mean atomic weight of vanadium.

*Determinations of Vanadium.*—The vanadium in vanadyl trichloride was directly estimated in some instances (Nos. 1 and 4) in separate portions of the trichloride, whilst in other cases (Nos. 2 and 3) it was estimated in the filtrate from the chlorine determinations.

Nos.	Weight of trichloride taken.	Weight of vanadium pentoxide found.	Percentage of vanadium.
1.	1·4188	0·7368	29·20
2.	0·7013	0·3679	29·47
3.	0·7486	0·3959	29·71
4.	1·1731	0·6252	29·94
Mean.....			29·58



These results give as the composition of vanadyl trichloride:—

	Calculated.	Found.
V = 51·3	29·54	29·58
Cl <sub>3</sub> = 106·37	61·25	61·27
O = 16·00	9·21	—
173·67	100·00	

2. *Vanadium Oxydichloride*, or *Vanadyl Dichloride*,  $\text{VOCl}_2 = 138\cdot21$ .—This substance is formed, together with other lower solid oxychlorides, when the vapour of vanadyl trichloride mixed with hydrogen is passed through a red-hot tube. It is easily obtained, however, in the pure state by the action of metallic zinc on the oxytrichloride in sealed tubes at  $400^\circ$ . For this purpose strips of zinc and slight excess of the liquid chloride are heated in a strong tube placed in an inclined position in an air-bath for three or four days in a temperature considerably above the boiling-point of mercury; the oxytrichloride is decomposed, a black oxide of vanadium is formed, together with zinc chloride, and a sublimate of splendid grass-green tabular crystals of the oxydichloride collects in the upper part of the tube. On opening the tube, the portion containing the crystals was quickly pushed inside a wider tube heated to  $130^\circ$  in a paraffin bath through which a current of dry carbonic acid was passed; the excess of liquid oxychloride was thus easily expelled, and the green crystals obtained of a constant weight. The black oxide formed, together with the green crystals, consists of the lowest oxide,  $\text{V}_2\text{O}_3$ , as on treatment with dilute acid it bleaches strongly.

Vanadium oxydichloride is a grass-green body crystallising in thin plates, and possessing an unctuous feel. It is slowly decomposed by water, and on exposure to moist air it deliquesces; it easily dissolves in dilute nitric acid. Its specific gravity at  $13^\circ \text{C}$ . is 2·88.

The composition of the oxydichloride is readily determined by precipitating the chlorine in nitric-acid solution, and estimating the vanadium in the filtrate.

	Calculated.	Found.
V = 51·3	37·12	37·58
Cl <sub>2</sub> = 70·91	51·39	50·73
O = 16·0	11·59	—
138·21	100·00	

3. *Vanadium Oxymonochloride*, or *Vanadyl Monochloride*,  $\text{VOCl} = 102.76$ .—Vanadyl monochloride is a brown, light, powdery solid, formed by the action of hydrogen upon vanadyl trichloride. It is obtained by passing the vapour of the trichloride, together with hydrogen, through a red-hot tube, and is deposited at the end nearest to the point where the trichloride enters the tube. It is insoluble in water, but easily soluble in nitric acid. It may readily be distinguished and separated from the preceding and following oxychlorides by its appearance and light flocculent nature. The analysis was made in the manner already described, the substance being dried at  $130^\circ$  in a stream of carbon dioxide till its weight was constant.

	Calculated.	Found.
V = 51.3	49.92	50.21
Cl = 35.46	34.51	34.53
O = 16.0	15.57	—
102.76	100.00	

4. *Divanadyl Monochloride*,  $\text{V}_2\text{O}_2\text{Cl} = 170.06$ .—This substance is likewise formed in a similar manner to the foregoing oxychlorides. It has a bright, shining, metallic lustre and a brownish-yellow colour, closely resembling the tin disulphide, known as "mosaic gold." This substance is always deposited in the portion of the heated tube furthest from the trichloride, and it adheres firmly to the glass. From its heavy coherent nature it can easily be separated from the preceding compound. Under the microscope it is seen to consist of brilliant-yellow, metallic crystals, and it has been mistaken for metallic vanadium by Schafarik.

It is insoluble in water, but dissolves, like the other solid oxychlorides, easily in nitric acid. The brown shining crystals were heated in carbon dioxide at  $140^\circ$ , until their weight was constant, and then they were analysed, as above described.

Hence we have—

	Calculated.	Found.
$\text{V}_2 = 102.60$	60.33	61.69
Cl = 35.46	20.84	18.93
$\text{O}_2 = 32.00$	18.83	—
170.06	100.00	

VI. VANADIUM NITRIDES.

1. *Vanadium Monotride*,  $VN = 65.3$ .—The process described by Berzelius for preparing metallic vanadium by heating the ammonio-oxychloride in an atmosphere of ammonia, does not yield the metal, but a nitride.

The monotride is obtained by passing dry ammonia gas over vanadyl trichloride contained in a bulb-tube, and igniting the ammonio-oxychloride formed until the ammonium chloride has volatilised. The black powder thus produced (vanadium dini- tride?) is then placed in a platinum-boat, which is exposed for some hours to the white heat of a wind-furnace in a porcelain tube, through which dry ammonia (or rather a mixture of its constituent gases) passed. The substance thus obtained is a greyish-brown powder, which does not undergo change on exposure to air at ordinary temperatures, and remains unaltered, when it is again strongly heated in ammonia. When roasted in the air it slowly oxidises, glows, and forms a blue oxide; on further heating it melts, and ultimately forms pure vanadium pentoxide. Heated with soda-lime in a glass tube, the mono- nitride readily evolves ammonia.

Its composition is as follows:—

	Calculated.		Found.		
Vanadium.....	51.3	78.6	77.8	—	—
Nitrogen .....	14.0	21.4	—	20.3	20.0
	65.3				

2. *Vanadium Dinitride*,  $VN_2 = 79.3$ .—This substance is obtained as a black powder by passing dry ammonia over vanadyl tri- chloride heated in a glass tube to expel sal-ammoniac, washing with ammonia-water, and drying *in vacuo* over sulphuric acid.

This nitride was obtained in 1858 by Uhrlaub,\* but this chemist made no direct determination of the nitrogen, by which alone the true nature of these compounds can be dis- covered; and he, adopting, as a matter of course, the atomic weight 68.5, showed that the body obtained as above described cannot be represented by any simple formula. If, however, Uhrlaub's experimental results be calculated with the true atomic weight 51.3, it is seen that, according to the mean of

\* Pogg. Ann. Bd. ciii, p. 184.

three determinations, the substance contains 64·1 per cent. of vanadium, the formula  $VN_2$  requiring 64·6 per cent.

The existence of vanadium mononitride,  $VN$ , not only demonstrates with absolute certainty the true atomic weight of the metal, but it also serves as the starting point from which to commence the study of the metal, as well as of an entirely new class of bodies, viz., the compounds of the metal vanadium with chlorine and the other halogens, which I have in vain endeavoured to obtain from vanadyl compounds. In the next communication I hope to describe these interesting substances.

*XXXVII.—On the Solubility and Crystallisation of Plumbic Chloride in Water, and in water containing various percentages of Hydrochloric Acid, specific gravity 1·162.*

By J. CARTER BELL, F.C.S., Associate of the Royal School of Mines.

ALL the manuals I have consulted give the solubility of plumbic chloride,  $PbCl_2$ , as one part dissolved in 135 parts of water; according to my results, which were conducted with the greatest care, I find it still more soluble than the above states it to be. I used pure crystals of plumbic chloride, which had been recrystallised five or six times from a watery solution, and distilled water which was redistilled specially for this result; the water was allowed (with an occasional shake of the solution) to act upon the crystals for about ten days at a temperature of  $15^{\circ}5$  C. ( $60^{\circ}$  F.); some days perhaps it would rise a little more, other days fall, but as near as possible it was kept at the temperature named; it was then taken exactly at  $15^{\circ}5$  C., filtered through Swedish filtering paper (the first portion being rejected) into small beakers; the solution was weighed most accurately to the thousandth of the grain in the covered vessel; it was then carefully evaporated in a steam-bath; and the crystals heated to  $110^{\circ}$  C. ( $230^{\circ}$  F.) cooled down in a desiccator, and then weighed. The four results were:—

No. 1	..	..	·8207
2	..	..	·8256
3	..	..	·8264
4	..	..	·8259

giving a mean of .8246, and showing that one part of plumbic chloride dissolves in 121 parts of water at  $15^{\circ}5$  C. ( $60^{\circ}$  F.).

Another fact I have observed in the behaviour of plumbic chloride with water, is, that the salt is partially decomposed, and the solution gives a slight acid reaction to litmus paper, even in the cold, on taking perfectly pure crystals and distilled water, which singly have no acid reaction, but immediately they are brought in contact the acidity is developed, which I can only attribute to the decomposition of the salt; but this acid reaction is much more marked on heating the solution to  $100^{\circ}$  C. and keeping it at that temperature for several hours; it also has a very striking effect upon the solubility of the salt. 100 parts of distilled water at  $17^{\circ}7$  C. ( $64^{\circ}$  F.) dissolve .947 of the pure crystals of plumbic chloride. Another portion of the crystals was boiled in water for three minutes, and the solution was allowed to cool down to  $17^{\circ}7$  C.; it then contained, according to two results, .927 per cent. of plumbic chloride. To show what a marked effect boiling the solution of plumbic chloride had upon the solubility, I prepared some crystals of plumbic chloride from an acid solution; they were well washed and dried so as not to leave the slightest trace of acid upon them; then acted upon at the common temperature by 20 ounces of pure water for several days. At the end of that time the water was found to contain .942 per cent. of plumbic chloride at  $17^{\circ}7$  C. The twenty ounces were boiled down to six, and the solution cooled to  $17^{\circ}7$  C.: it then contained .823 per cent. of plumbic chloride. A second solution of plumbic chloride was boiled for about two hours, and cooled as before; according to the mean of two experiments, it contained .741 per cent. of the salt. From these experiments I think I am justified in saying that plumbic chloride is decomposed by water, with production of free hydrochloric acid: and it is this acid up to a certain point, as we shall see further on, which diminishes the solubility of plumbic chloride. This salt, as regards its solubility in water, behaves in a very peculiar manner. One would have supposed that water at  $100^{\circ}$  C., poured upon pure crystals, then well shaken, and poured off when clear into a beaker, would have formed a saturated solution at  $17^{\circ}7$  C. I have found this not to be the case; when boiling redistilled water was poured upon pure crystals, shaken, poured off into a beaker, and allowed to cool to  $17^{\circ}7$  C., it was found from the mean of two experiments to con-

tain only .7668. A second experiment was tried in the same manner, and from the clear solution a very few detached crystals were formed; the mother liquor at  $17^{\circ}7$  C. contained .8984  $\text{PbCl}_2$ . A second quantity of boiling water was poured upon the original crystals, and treated as before; the liquor contained .8373. A third quantity of water was poured upon the crystals, and this solution only contained .6854 per cent. of  $\text{PbCl}_2$ , at  $17^{\circ}7$  C. In these experiments only the small crystals were dissolved, thus forming an almost saturated solution; but the second and third portions of water had only the large crystals to act upon, and could not dissolve a sufficient quantity in the time allotted to them to form a saturated solution. Powdered plumbic chloride was taken, water at the ordinary temperature poured upon it, and allowed to stand for some time; the solution contained at  $17^{\circ}7$  C., according to two results, .946 per cent. of  $\text{PbCl}_2$ .

*Solubility of Plumbic Chloride in dilute Hydrochloric Acid of various strengths.*—The solubility of the salt decreases as the quantity of hydrochloric acid increases up to a certain point, but beyond this the solvent power increases step by step as the hydrochloric acid increases. Starting with pure water, which we have already seen dissolves .946 per cent. of  $\text{PbCl}_2$  at  $17^{\circ}7$  C., then if one-tenth per cent. of hydrochloric acid sp. gr. 1.162 be put into the water, the solubility at once sinks to .838; with two-tenths per cent. of hydrochloric acid, .716, and goes on decreasing till the acid reaches 15 per cent., when the minimum percentage of plumbic chloride is attained; but whether fifteen is the turning point it is difficult to say, because from the tenth to the sixteenth, the difference only varies by the thousandth and ten thousandths per cent., which may be looked upon as errors of experiment; the greatest difference between ten and sixteen is .004; therefore I think I may safely call those numbers the line of no variation. After the sixteenth the percentage steadily ascends, with here and there a break to mar the uniformity, till they culminate in 100 per cent. Theoretically speaking, one would suppose that the differences between the percentages ought to fall and rise with perfect equality; but experiment does not seem to verify this hypothesis, but rather to point to an unequal oscillating movement, for I have found that the differences are great at the two extremes and smaller towards the middle; for instance between 0.1 and 0.9 they vary between tenths and hundredths, and the same again

between 80 and 100; from 10 to 60 the differences are small, ranging only between hundredths and thousandths; from 60 to 80 they ascend considerably, and the differences vary from seven to nine hundredths.

The mode of conducting the experiments was the following:—pure crystals of plumbic chloride, and pure hydrochloric acid of sp. gr. 1.162 were used; the water and acid were weighed out most carefully into stoppered bottles; plumbic chloride was then put in, and the solutions allowed to stand from ten to fourteen days at a range of temperature from 14° to 18° C. (the solutions receiving an occasional shake); they were then taken at 17°·7 C., filtered through Swedish filtering paper (the first portion being rejected) into small weighed beakers, which were then covered with a watch-glass and again weighed with the contents; the beakers were then covered with filtering paper to prevent any dust falling into them, put into a steam-bath, and the solutions were gently evaporated to dryness; the crystals were heated to 110° C., cooled over sulphuric acid in a desiccator, and weighed; the results were then calculated.

*Crystallisation of Plumbic Chloride.*—The works which I have consulted inform me that this compound crystallises in fine brilliant needles. This statement must be taken with some little reserve, as it is only under certain conditions that needle-shaped crystals can be procured. When boiling distilled water is poured upon plumbic chloride in the powdered state, and the clear solution poured off into a beaker and allowed to cool down slowly, white brilliant crystals are not obtained, but cream-coloured cuneiform or arrow-shaped crystals are formed; these crystals cover the bottom and line the sides of the vessels in a peculiar tuft-like manner; when dry, they are very compact and heavy, and under a low power of the microscope appear massive like quartz, but with a distinct pearly lustre; but if the saturated solution is boiled for a few minutes the appearance of the crystals is at once altered; they are now very small needle-shaped crystals. The addition of hydrochloric acid changes the size considerably, and crystals of great beauty may be sometimes obtained; but as the addition of hydrochloric acid increases, the appearance of the crystals also changes, and they pass from needles into hexagonal plates, but it is better seen when the various solutions are evaporated at a gentle heat; for this purpose not more than twenty or thirty grammes should be used. Thus, when the solu-

tion of plumbic chloride, which has been prepared without heat, is evaporated to dryness in the water-bath, beautiful feathery crystals are obtained, not at all like needles, but more like a quill pen with the feathers only on one side; they are not attached to the vessel in which they have been crystallised, as in some cases they are; when the crystals were boiled in water for a short time, the solution allowed to cool down, and then evaporated in the water-bath, a mass of small feathery crystals is obtained, interlaced one with another, so that the vessel can be inverted without detaching the crystals which adhere to the bottom. When the saturated solution is boiled for two or three hours, then cooled, and a portion of the liquor evaporated, no distinct crystals are formed, but a magma of very fine crystalline particles is obtained; when one per cent. of hydrochloric acid is added the solution heated to  $100^{\circ}$  C., and then cooled, white feathery crystals are formed, and on evaporating the liquid the crystals which form are like feathers compressed, very similar to the crystalline form of antimony; they also adhere tenaciously to the beaker; as the percentage of hydrochloric acid increases, the crystals also undergo a change. On evaporating the solution containing 51 per cent. of hydrochloric acid, the crystals obtained were like fern leaves; on performing the same experiment with 60 per cent. of hydrochloric acid, the crystals appeared to be in a state of transition, passing from the plumose to the lamellar state; with 80 per cent. of hydrochloric acid, the transition was complete, no longer presenting a feathery appearance, the crystals being flat hexagonal plates similar to the drawing; they also glistened like mica; with 100 per cent. the same appearance was presented as with 80. Here again we have a singular phenomenon regarding plumbic chloride; beginning with water, we have cream-coloured arrow-shaped crystals (or perhaps some would call them feathery, as they are wide at the top and pointed at the bottom), then they pass into fern crystals, thence into the transitional state, and lastly become hexagonal plates.



In concluding this paper I am sensible of many defects which perhaps might be removed by repeating the whole of the experiments; I did not think it necessary to do so, as I thought it was possible for all to see that there must be a descending and ascending scale; I therefore preferred leaving the results as I found them.



*Table of the Solubility of Plumbic Chloride in Water, and in Water containing various percentages of Hydrochloric Acid (sp. gr. 1.162) at a temperature of 17.7 C.*

Pure water dissolves	0.946 p. c.	46 p. c. HCl	0.316 p. c.
Do. containing 0.1 p. c. HCl	0.838 "	47 "	0.327 "
0.2 p. c. HCl	0.716 "	48 "	0.328 "
0.3 "	0.652 "	49 "	0.336 "
0.4 "	0.605 "	50 "	0.356 "
0.5 "	0.502 "	51 "	0.371 "
0.6 "	0.499 "	52 "	0.374 "
0.7 "	0.441 "	53 "	0.395 "
0.8 "	0.426 "	54 "	0.406 "
0.9 "	0.385 "	55 "	0.433 "
1 "	0.347 "	56 "	0.462 "
2 "	0.201 "	57 "	0.469 "
3 "	0.165 "	58 "	0.518 "
4 "	0.145 "	59 "	0.542 "
5 "	0.131 "	60 "	0.559 "
6 "	0.107 "	61 "	0.550 "
7 "	0.100 "	62 "	0.575 "
8 "	0.099 "	63 "	0.600 "
9 "	0.096 "	64 "	0.630 "
10 "	0.098 "	65 "	0.666 "
11 "	0.093 "	66 "	0.721 "
12 "	0.093 "	67 "	0.739 "
13 "	0.098 "	68 "	0.828 "
14 "	0.090 "	69 "	0.854 "
15 "	0.090 "	70 "	0.933 "
16 "	0.094 "	71 "	0.971 "
17 "	0.101 "	72 "	1.040 "
18 "	0.100 "	73 "	1.118 "
19 "	0.100 "	74 "	1.137 "
20 "	0.111 "	75 "	1.208 "
21 "	0.118 "	76 "	1.305 "
22 "	0.112 "	77 "	1.398 "
23 "	0.114 "	78 "	1.347 "
24 "	0.118 "	79 "	1.413 "
25 "	0.129 "	80 "	1.498 "
26 "	0.131 "	81 "	1.475 "
27 "	0.131 "	82 "	1.503 "
28 "	0.134 "	83 "	1.636 "
29 "	0.150 "	84 "	1.677 "
30 "	0.151 "	85 "	1.819 "
31 "	0.157 "	86 "	1.809 "
32 "	0.151 "	87 "	1.898 "
33 "	0.161 "	88 "	1.968 "
34 "	0.165 "	89 "	2.089 "
35 "	0.170 "	90 "	2.117 "
36 "	0.170 "	91 "	2.244 "
37 "	0.181 "	92 "	2.297 "
38 "	0.194 "	93 "	2.407 "
39 "	0.201 "	94 "	2.470 "
40 "	0.216 "	95 "	2.577 "
41 "	0.237 "	96 "	2.611 "
42 "	0.249 "	97 "	2.745 "
43 "	0.258 "	98 "	2.829 "
44 "	0.264 "	99 "	2.851 "
45 "	0.279 "	100 "	2.900 "

XXXVIII.—*On the Reducing Action of Peroxide of Hydrogen and Carbohc Acid.*

By JOHN PARNELL.

1. WHEN peroxide of hydrogen is mixed with ferrous sulphate, the ferrous salt becomes, as is well known, converted into a ferric salt, and the addition of carbohc acid then causes the usual violet colour. But if the carbohc acid be added before the peroxide of hydrogen, the last named substance will produce a permanent green coloration. If the solutions are sufficiently concentrated a dark green deposit takes place, which bears a strong resemblance to iron reduced by electrolysis from a ferrous salt.

2. These three substances, ferrous sulphate, carbohc acid, and peroxide of hydrogen, thus exhibit the oxidising and reducing actions of the peroxide, according to the order in which they are mixed together.

3. The green reaction above mentioned is a very delicate test for peroxide of hydrogen: for if that substance, as prepared by Messrs. Garden and Robbins be diluted with thirty times its bulk of distilled water, one-tenth of a cubic centimetre of such diluted solution will produce a distinct result.

4. Alcohol, ether, or any free acid interferes with the reaction.

5. If the green solution be heated, the iron is thrown down as ferric oxide.

6. The action of the peroxide of hydrogen upon a solution of bichromate of potassium is, as every one knows, very transient; but if carbohc acid has been previously added, the solution becomes turbid, but very slowly, and a brown precipitate is deposited after some hours of rest.

7. An ammoniacal solution of cupric oxide has its oxide reduced to sub-oxide by carbohc acid and peroxide of hydrogen.

8. Carbohc acid retards the reducing action of the peroxide on plumbic iodide, and the oxidization of the blue tungstate of tungsten.

9. The results previously described take place with cold solu-

tions. The effects of heating certain other solutions with carbolic acid and the peroxide are as follows:—

a. Tungstic acid or tungstate of sodium: a dark brown solution with brown deposit.

b. Molybdate of ammonium: a dark brown solution with a black deposit.

c. Ammonia: a pale green solution.

d. Ferricyanide of potassium: a deposit of Prussian blue, hydrocyanic acid being evolved.

e. Ferrocyanide of potassium: dark red solution and turbid.

f. The addition of carbolic acid to a solution of chloride of aluminium produces a pink colour; on adding the peroxide and heating, the solution becomes first red and then green, with a dark green deposit.

There appears to be some analogy between this reaction and that previously described in connexion with ferrous sulphate.

10. The carbolic acid employed in these experiments was a saturated solution in water of the acid prepared by Messrs. Calvert and Co., of Manchester.

11. There are some metallic salts which are partially reduced by being heated with carbolic acid, such as the auric and platonic chlorides, and the nitrates of nickel and cadmium; and the addition of peroxide of hydrogen in most cases appears to increase the effect, but the results are not sufficiently marked to deserve special notice.

12. Among the numerous substances unaffected by the operations here described, I may mention mercuric iodide.

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XXXIX.—*Researches into the Chemical Constitution of Narcotine, and of its Products of Decomposition.*—Part II.

By A. MATTHIESSEN, F.R.S., Lecturer on Chemistry in St. Mary's Hospital Medical School, and G. C. FOSTER, B.A., Professor of Physics in University College, London.

Received May 23,—Read June 20, 1867.

It was shown in a previous paper\* that narcotine and its principal derivatives, opianic acid, meconin, hemipinic acid, and

\* Philosophical Transactions, 1868, p. 345; for abstracts see Proc. Roy. Soc. vol. xi, p. 55, and vol. xii, p. 501; Jour. Chem. Soc. [2], i, 342.

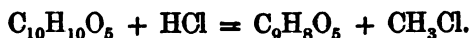
cotarnine, are decomposed when heated with hydrochloric acid or hydriodic acid, into iodide or chloride of methyl and one or more other products. With the exception, however, of those obtained from hemipinic acid and cotarnine, these second products had not been examined: the present memoir relates principally to the further study of these reactions.

### 1. Action of Hydrochloric and Hydriodic Acids on Opianic Acid.

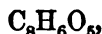
When opianic acid is heated to 100° or 110° with three or four times its weight of strong hydrochloric acid, either in a sealed tube or in an open flask, under a layer of paraffin\* for about twenty hours, or with about twice its weight of fuming hydriodic acid, and evaporated to dryness on a water-bath, chloride or iodide of methyl is produced, and at the same time a crystalline acid containing



The reaction may be represented by the equation



For reasons explained in the Journal of the Chemical Society†, we regard opianic acid as the dimethylized derivative of a hitherto unknown normal opianic acid,



between which and opianic acid itself the product above mentioned is exactly intermediate:

Opianic acid . . . . .	$C_{10}H_{10}O_5$
New compound . . . . .	$C_9H_8O_5$
Normal opianic acid . . . .	$C_8H_6O_5$

For want of a better name we therefore propose to call the compound  $C_9H_8O_5$  *monomethyl-normal opianic acid*, or if the contraction is admissible, *methyl-noropianic acid*.

\* When preparing a large quantity of this or any other substance by the action of hydrochloric acid, this method is very advantageous, as there is no danger of loss by bursting as often happens with sealed tubes. In preparing a new base from narcotine, where we employed 200 grms. at each operation, the saving of time and expense by using this method was very great.

† Second series, vol. i, p. 342.

This substance crystallises with  $2\frac{1}{2}$  molecules of water, which it gives up at  $100^{\circ}$  C.

The crystallised acid, when heated, first melts in its water of crystallisation, and then, as the water evaporates, solidifies to a white crystalline mass. Hence it appears that the acid dissolves in less than a quarter of its weight of hot water; in cold water, however, it is only sparingly soluble. It is easily soluble in alcohol, but almost insoluble in ether.

Like hypogallic acid, it strikes a dark blue with perchloride of iron, but, on addition of ammonia in excess, a light-red solution is produced, whereas the hypogallic-acid blue becomes blood-red with ammonia.

To determine the basicity of the acid, the ammonium salt was precipitated by nitrate of silver, which forms a gelatinous precipitate, becoming crystalline on standing. It is soluble in hot water, from which it crystallises on cooling.

This salt, dried at  $100^{\circ}$  and heated to redness, gave results agreeing with the formula

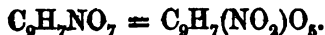


It therefore appears that methyl-noropianic acid is monobasic. The fact that opianic acid, when heated with excess of strong caustic potash splits up into meconin and hemipinic acid, led us to hope that methyl-noropianic acid would with the same reagent undergo a similar decomposition. It was, however, found that the acid remains unaltered; for after treating it with strong caustic potash, a silver-salt was made, which yielded on ignition, 35.5 per cent. silver, methyl-noropianate of silver requiring 35.64 per cent.

The reduction of opianic acid to meconin by the action of sodium-amalgam caused us to try this reagent on the new acid, but here again we could not produce the corresponding reduction.

When methyl-noropianic acid is dissolved in cold water, and about a sixth of its volume of strong nitric acid added, an action is immediately set up, and the solution becomes dark from nitric oxide, and afterwards again light, when a nitro-acid crystallises out. To prevent the action going on too far, the solution must be kept cold.

This new nitro-acid contains

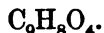


We have called this acid nitromethyl-noropianic acid.

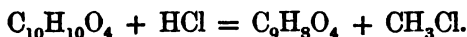
Nitromethyl-noropianic acid crystallises with one molecule of water, which it loses at 100° C.

### 2. Action of Hydrochloric and Hydriodic Acids on Meconin.

When meconin is treated with hydrochloric or hydriodic acid, as above described in the case of opianic acid, it is resolved into chloride or iodide of methyl and a new compound containing



The reaction which takes place is—



This substance may be regarded as a monomethylized derivative of a hypothetical normal meconin,



and we therefore propose to name it *monomethyl-normal meconin*, or shorter, *methyl-normeconin*.

Methyl-normeconin crystallises without any water of crystallisation; it is soluble in cold, but much more so in hot water; it is easily soluble in alcohol, and slightly so in ether.

With perchloride of iron it behaves exactly in the same manner as methyl-noropianic acid. It reduces salts of silver in the cold, so that to determine its basicity we employed its barium-salt, from the analysis of which it appears that this new acid is monobasic, the barium-salt containing  $(C_9H_7O_4)_2Ba$ .

### 3. Action of Hydrochloric and Hydriodic Acids on Hemipinic Acid.

In our former paper we have described the action of hydriodic acid on hemipinic acid. We there stated that when hemipinic acid is treated with hydriodic acid the following reaction takes place:—



The acid  $C_7H_6O_4$  we called hypogallic acid.

We also mentioned that when hemipinic acid is heated with strong hydrochloric acid, the reaction is—



The further investigation and analyses confirm the formula,



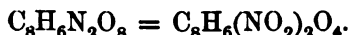
for this acid; and as it contains one molecule of methyl more than hypogallic acid, and may be converted into that body by the prolonged action of hydrochloric acid, it may be called *methyl-hypogallic acid*.

One of the simplest modes of preparing this acid is to digest the hemipinic acid with strong hydrochloric acid on a water-bath at 100° C. under a layer of paraffin for about three days. The purification of the acid is very simple, owing to its being almost insoluble in cold and sparingly soluble in hot water, whence it crystallises out on cooling in long transparent prisms. The crystals contain no water of crystallisation.

The silver salt contains  $\text{C}_8\text{H}_7\text{AgO}_4$ .

The properties of this acid are given in our former communication.

When methyl-hypogallic acid is treated with dilute nitric acid (1 part acid to three parts water) and gently heated till the acid is dissolved, it is converted into a nitro-acid which separates out on cooling. Its composition was found to be



This acid may be called dinitromethyl-hypogallic acid, as it contains  $(\text{NO}_2)_2$  in place of  $\text{H}_2$ .

It crystallises with one molecule of water.

#### 4. On the different Crystalline Forms of Hemipinic Acid.

Whilst experimenting with hemipinic acid, we found that this acid may crystallise in different forms. The crystals were found to contain different amounts of water; thus (I.) when crystallised from a dilute solution by spontaneous evaporation, the crystals contain half a molecule of water; (II.) when from a supersaturated solution, they contain one molecule; and lastly, (III.) when crystallised in the ordinary way by cooling a hot solution, they contain two molecules.

- I. 11·281 grms. acid lost at 100° C. 0·448 grm. water.
- II. 3·130 grms. acid lost at 100° C. 0·230 grm. water.
- III. 7·646 grms. acid lost at 100° C. 1·0576 grm. water.

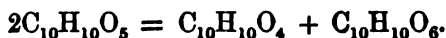
	Calculated. Water per cent.	Found. Water per cent.
I. $C_{10}H_{10}O_6, HO_4$ . . . .	3.83	3.97
II. $C_{10}H_{10}O_6, H_2O$ . . . .	7.33	7.35
III. $C_{10}H_{10}O_6, 2H_2O$ . . . .	13.74	13.83

In the following Table the acids, &c., are tabulated which have been and probably may be prepared from opianic acid.

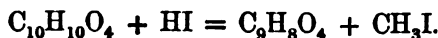
$C_{10}H_{10}O_4$ 1. Dimethyl-normeconin (ordinary meconin).	$C_{10}H_{10}O_5$ 2. Dimethyl-noropianic acid (ordinary opianic acid).	$C_{10}H_{10}O_6$ 3. Dimethyl-norhemipinic acid (ordinary hemipinic acid).
$C_9H_8O_4$ 4. Methyl-normeconin.	$C_9H_8O_5$ 5. Methyl-noropianic acid.	$C_9H_8O_6$ Methyl-norhemipinic acid.
$C_8H_6O_4$ Normeconin.	$C_8H_6O_5$ Noropianic acid.	$C_8H_6O_6$ Norhemipinic acid.
		$C_8H_8O_4$ 6. Methyl-hypogallic acid.
		$C_7H_6O_4$ 7. Hypogallic acid.

Of the above, the following have been made, namely:—

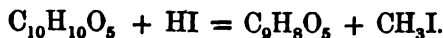
1 and 3.  $C_{10}H_{10}O_4$  and  $C_{10}H_{10}O_6$  by the action of potash on opianic acid; thus,



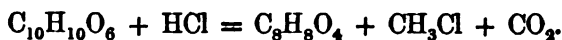
4.  $C_9H_8O_4$  by the action of hydrochloric and hydriodic acids on meconin; thus,



5.  $C_9H_8O_5$  by the action of hydrochloric and hydriodic acids on opianic acid; thus,



6.  $C_8H_6O_4$  by the action of hydrochloric on hemipinic acid; thus,



7.  $C_7H_6O_4$  by the action of hydriodic acid on hemipinic acid; thus,



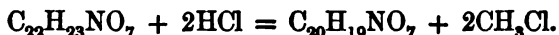


### 5. Action of Hydrochloric and Hydriodic Acids on Narcotine.

When narcotine is treated with strong hydrochloric acid for some time on a water-bath, in a flask under a layer of paraffin, a thick oily mass gradually separates out on cooling, which on examination was found to be the chloride of a new base. The best method of preparing this base is as follows:—

200 grms. of narcotine are put into a large flask with 1000 cub. centims. of strong hydrochloric acid (the pure commercial acid), and are digested together on a water-bath under a layer of paraffin at 100° C. Much chloride of methyl is given off, and a thick oily mass separates out on cooling, and when no further quantity is formed, the reaction may be considered finished.\*

The reaction which takes place may be written thus—



To purify the chloride, and to obtain the base from it, advantage is taken of the fact that it is comparatively insoluble in dilute hydrochloric acid, whereas in strong hydrochloric acid as well as in pure water, it dissolves readily. After the reaction is finished the contents of the flask are allowed to cool. The liquid portion (strongly acid) is poured into a large beaker, and the oily mass dissolved in hot water, allowed to cool, and then poured into the strongly acid solution. This causes a precipitate, and water or hydrochloric acid is added in case either produces a further precipitate. The precipitated chloride is collected on a filter and washed with dilute hydrochloric acid (1 part acid, 9 parts water); after washing, the precipitate is dissolved in water, and carbonate of sodium added in excess, in which the new base is soluble, but narcotine insoluble; after filtering off any undecomposed narcotine, the solution is carefully neutralized with hydrochloric acid to precipitate the base, which becomes curdy on heating and may be filtered and washed with ease. After being well washed, it is redissolved in hydrochloric acid, and fractionally precipitated with carbonate of

\* From two to six days are required for the completion of the reaction; it appears that the larger the quantities employed the shorter the time necessary for conversion. In an experiment made with the above quantities, the whole of the narcotine was converted into the new base in three days (i.e. in about twenty-four hours), whereas in another experiment made with 50 grms. narcotine and 250 cub. centims. hydrochloric acid the time required was six days.

sodium. The first portion precipitated contained most of the colouring matter; the second portion was used for analysis. Dried at 100° C. in a Liebig's drying tube, it gave results agreeing with the formula  $C_{20}H_{19}NO_7$ ,  $\frac{1}{2}$  aq.

For reasons which will be clear from what follows, we have called the base methyl-nornarcotine. When freshly precipitated it forms an almost white amorphous powder, insoluble in water and ether, slightly soluble in alcohol, and easily soluble in carbonate of sodium, by which means it may be separated from narcotine.

None of its salts form crystalline compounds (the chloride, sulphate, and nitrate have been tried).

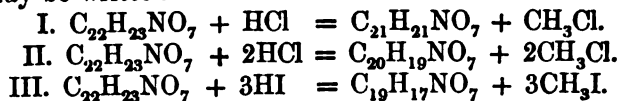
On determining the amount of chlorine and sulphuric acid in the chloride and sulphate, results were obtained which agree with the formulæ  $C_{20}H_{19}NO_7, HCl$  and  $(C_{20}H_{19}NO_7)_2, SO_4$  respectively.

The chloride was prepared as follows: the base was dissolved in strong hydrochloric acid and fractionally precipitated by water, the middle portion collected, washed with dilute hydrochloric acid, and dried over sulphuric acid and lime, before drying it in the water-bath.

The chloride must not be washed with pure water, as that liquid converts it immediately into a sticky mass.

The sulphate was precipitated by dissolving the base in sulphuric acid (one part acid, three parts water) and pouring the solution into water, collecting the precipitated sulphate, and washing with water, redissolving the precipitate in hot water, and collecting the sulphate as it separates out in different portions. Like the chloride, it must be first dried over sulphuric acid, and then in a water-bath.

It may be as well to mention that in the further prosecution of this research, one of us has already obtained two more bases from narcotine: the one by digesting it for a short time with hydrochloric acid, and the other as indicated in our former paper (p. 359), by the action of hydriodic acid on it. The reactions may be written—



The preparations and properties of two of these bases (I., III.) will form the subject of a future communication.

6. *On the Crystalline Forms of some of the above-mentioned substance.*

By Professor VICTOR V. LANG.

(a) Acid derived from meconin,  $C_9H_8O_4$ .

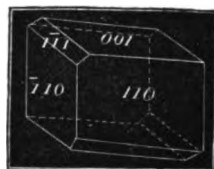
System monoclinic:—

$$a : b = 2.7864 : 1,$$

$$ac = 127^\circ 56'.$$

Observed forms:—

(110), (001).



$$110, 110 = 49^\circ 56' \text{ observed.}$$

$$110, 001 = 78^\circ 20' \text{ ,,}$$

The observed forms do not completely determine the crystallographic elements. The crystals are perfectly cleavable, parallel to the plane (001).

(b). Acid derived by the action of nitric acid on the hypogallic acid,  $C_8H_6N_2O_8.H_2O$ .

System monoclinic:—

$$a : b : c = 1.0122 : 1 : 0.7156,$$

$$ac = 104^\circ 0'.$$

Observed forms:—

(001), (110), ( $\bar{1}11$ ).



	Calculated.	Observed.
110, $\bar{1}10$	= $88^\circ 58'$	o /
110, $\bar{1}10$	= $91^\circ 2'$	*91 2
110, 001	= $80^\circ 4'$	*80 4
$\bar{1}11$ , 001	= $49^\circ 40'$	49 38
$\bar{1}11$ , $\bar{1}11$	= $65^\circ 40'$	*65 40

Cleavage very perfect, parallel to the planes (110).

(c) Hemipinic acid,  $C_{10}H_{10}O_6, HO$ .

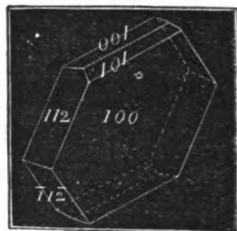
System monoclinic:—

$$a : b : c = 2.5210 : 1 : 2.9597,$$

$$ac = 92^\circ 40'.$$

Observed forms:—

(100), (001), (101), (112).



	Calculated.	Found.
100, 001	= $\overset{\circ}{87} \overset{\prime}{20}$	$\overset{\circ}{87} \overset{\prime}{30}$
101, 100	= 39 18	
101, 001	= 48 2	48 2
112, 100	= 71 10	
112, $\bar{1}\bar{1}\bar{2}$	= 79 20	79 20
112, 001	= 56 20	56 20
112, 101	= 52 42	52 42

Cleavage perfect, parallel (001).

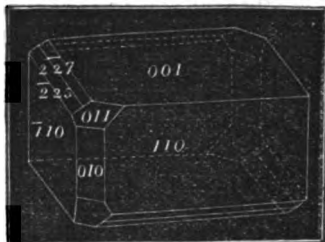
(d) Hemipinic acid,  $C_{10}H_{10}O_6, H_2O$ .

System monoclinic:—

$$a : b : c = 0.5407 : 1 : 1.2620,$$

$$ac = 97^\circ 42'.$$

Observed forms:—

(001), (110), (011), ( $\bar{2}\bar{2}5$ ), ( $\bar{2}\bar{2}7$ ).

	Calculated.	Observed.
110, 010	= $\overset{\circ}{61} \overset{\prime}{49}$	* $\overset{\circ}{61} \overset{\prime}{49}$
110, $\bar{1}\bar{1}0$	= 56 22	
011, 010	= 38 40	*38 40
011, 001	= 51 20	
110, 001	= 83 13	
110, 011	= 63 44	63 28
$\bar{2}\bar{2}5$ , 010	= 68 33	
$\bar{2}\bar{2}5$ , 001	= 50 14	
$\bar{2}\bar{2}5$ , $\bar{1}\bar{1}0$	= 46 28	46 24
$\bar{2}\bar{2}7$ , 010	= 72 23	
$\bar{2}\bar{2}7$ , 001	= 39 30	
$\bar{2}\bar{2}7$ , $\bar{1}\bar{1}0$	= 58 12	58 40
$\bar{1}\bar{1}0$ , 001	= 96 47	*96 47

**XL.—The Calculus of Chemical Operations ; being a Method for the Investigation, by means of Symbols, of the Laws of the Distribution of Weight in Chemical Change.—Part I. On the Construction of Chemical Symbols.**

By Sir B. C. BRODIE, Bart., F.R.S., Professor of Chemistry in the University of Oxford.

(From the Philosophical Transactions, Part II, 1866.)\*

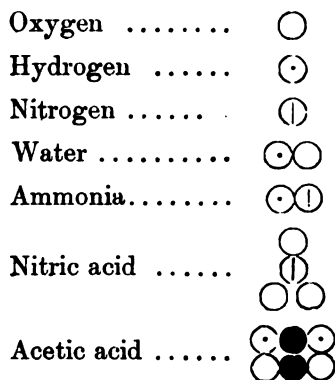
*“ Les formules chimiques, comme nous l'avons dit, ne sont pas destinées à représenter l'arrangement des atomes, mais elles ont pour but de rendre évidentes, de la manière la plus simple et la plus exacte, les relations qui rattachent les corps entre eux sous le rapport des transformations.”*—Gerhardt.

**EVEN** in the earliest times the attention of chemists seems to have been directed to the symbolic expression of the facts of their science, a method which had its origin in the mystic spirit of alchemy, and the subject has never ceased to occupy a prominent position in chemical philosophy. However, the development of our symbolic system has by no means kept pace with the general progress of the science. Indeed no essential improvement in the method has been effected since its first invention by Berzelius; and though this notation has doubtless afforded much aid to memory, and through memory incidentally to reasoning, yet it is difficult to point to even one discovery in the science, for which we are indebted to symbolic operations. In this respect chemical symbols present a marked contrast to other symbolic systems. The application of symbols to geometry and mechanics immediately led to the discovery of important truths, which were followed by the most original and unexpected development of the symbolic method itself. A very slight examination, however, of our present system is sufficient to render evident, that not only are the symbols of the chemist wanting in precision, but that they are of a totally different order from those symbols, the employment of which has been attended with such great results.

The question of chemical symbols cannot well be separated

\* It has been necessary, for convenience of printing, to transfer in this reprint the table of contents to the end of the paper.

from the consideration of the hypothesis which is expressed in them. The actual theory of chemistry is based upon the atomic theory of Dalton, and in the "New System of Chemical Philosophy" may be found the germ whence our notation has been developed. According to the views of this eminent philosopher, the ponderable matter of any portion of the elemental bodies is assumed to consist of a vast yet finite number of minute, indivisible, and homogeneous particles or atoms, by the varied combinations of which all other substances may be produced. With the object of elucidating his theory, Dalton gave (in the plates at the end of his work) a kind of pictorial representation of the nature of matter from the point of view of his hypothesis. He represented the atoms of the elements by single circles with a characteristic mark, and the molecules of compound substances by systems of circles placed side by side in the figure, as the atoms were supposed to be placed in nature. Such pictures, for instance, are the following,\* by which he figured oxygen, hydrogen, nitrogen, water, ammonia, nitric and acetic acids.



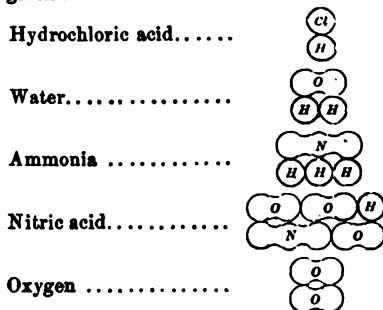
In our present system these signs have been replaced by letters marking the weights of the atoms, and the circles have been removed. But no fundamental change has been made in his conception, and in the arrangement of letters  $H_2$ ,  $O_2$ ,  $H_2O$  and the like, we still retain the image of Dalton under another form. Indeed where special clearness is required, we not unfrequently find the circles restored to the picture; and the most recent representation of the nature of matter consists in a modification of this concrete symbol to meet the necessities

\* See "New System of Chemical Philosophy," part 1, p. 219.

of modern ideas.\* On this view that arrangement of letters in the symbol which we call a formula is to be regarded as a figure by which the arrangement of atoms in the substance is represented; the symbolic system being a sort of orrery,† in which is imperfectly imitated the structure and movements of that unseen molecular world, on the mechanism of which chemical transformations are assumed to depend. A still more exact comparison would perhaps be to a diagram of Euclid, which bears a certain, though a confessedly inexact, resemblance to the object signified, and serves by this likeness to bring it vividly before the imagination.‡

This molecular interpretation is, it must be admitted, rather a matter of tacit convention than of express statement, and the above remarks, without qualification, would be too general. For it is a striking feature in our science that no system of chemical notation has yet been devised of such a nature as to receive universal and unqualified assent, or even a uniform interpretation. Berzelius,§ who is generally regarded as the originator of our present method, considered that the letters

\* See Kekulé, "Lehrbuch der organischen Chemie," 1861, p. 160, where the following diagrams are given:—



† "But formulæ may be used in an entirely different and yet perfectly definite manner, and the use of the two distinct points of view will perhaps not be unserviceable. They may be used as an actual image of what we rationally suppose to be the arrangement of the constituent atoms in a compound, as an orrery is an image of what we conclude to be the arrangement of our planetary system."—"On the Constitution of Salts," by A. W. Williamson, *Journal of the Chemical Society*, vol. iv, p. 351.

‡ An interesting account of the development of our present system of notation, and its relation to the atomic theory, is given in the article "Notation" in *Watts's Dictionary of Chemistry*, by Professor G. C. Foster.

§ Berzelius, "Traité de Chimie," 1845, vol. i, p. 119; and "Jahresbericht," vol. xv, p. 201.

which he employed simply represented certain weights of matter, and that in the symbol of a chemical substance the sign + was to be understood as connecting every letter in the symbol, and was suppressed only from motives of brevity and convenience. So that  $H_2O$  was an abbreviated expression for  $H + H + O$ ;  $H$  and  $O$  being numbers by which the relative weights of the combining proportions of hydrogen and oxygen were expressed. Sir John Herschel, in a paper contained in the Edinburgh Philosophical Journal for 1819,\* and more recently in his introductory address to the Chemical Section of the British Association at Leeds, in the year 1858, objected to this system of chemical notation as opposed to algebraic convention, and suggested the replacement of the symbol  $H_2O$ , for example, by the expression  $2\overline{H} + \overline{O}$ , arguing that the apposition of letters, being the algebraic sign of multiplication, cannot, consistently with the conventional principles of algebra, be employed to express the sum of two weights. Gerhardt, while he admitted the general principles of the atomic mode of representation, ridiculed all attempts to express the grouping and arrangement of atoms. Such, indeed, is the prevailing uncertainty, that even in express treatises on chemistry, all details on the subject are frequently evaded, and symbols are introduced and employed without any precise meaning being assigned to them. Such latitude is obviously inconsistent with the methods of science, and it has been proposed by more than one chemist, to whose more exact turn of mind it was eminently distasteful, that we should return to the simpler system of Berzelius. We are not, however, justified in concluding, as some have done, that because these symbols are wanting in precision, therefore they are utterly without reason or utility, mere idle arrangements of letters to which no serious meaning can be attached.† On the contrary, a more candid

\* See Edinburgh Philosophical Journal, vol. i, pp. 8, 18, 28.

† See Berthelot, "Chimie organique, fondée sur la synthèse," 1860, Introduction, p. cxxii, and p. 189. If the principles laid down by M. Berthelot are to be regarded as literally correct, the questions raised in the present memoir are unworthy of any serious consideration whatever.

"Ce serait méconnaître étrangement la philosophie des sciences naturelles et expérimentales, que d'attribuer à de semblables mécanismes une portée fondamentale. En effet, dans l'étude des sciences, tout réside dans la découverte des faits généraux, et dans celles des lois qui les rattachent les uns aux autres. Peu importe le langage par lequel on les exprime; c'est une affaire d'exposition, plutôt que



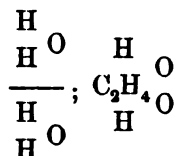
appreciation cannot fail to recognize that, notwithstanding many imperfections, they have rendered a most important service, by affording an external and visible image of the world of chemistry on which the attention may advantageously be concentrated. Ordinary language is too vague and too diffuse for the purposes of science, and in chemistry especially the facts are so numerous and so complicated, that it is only when embodied in a concrete form that they can be stored in the memory, and become the object of reflection. Hence even an imperfect and material picture may, in a certain epoch of the development of the science, be found of indispensable utility.

The actual theory of chemistry may be regarded as an expansion of the hypothesis of Dalton. In science, as in other spheres of thought, hypotheses often pass without question which come to us recommended by early use, and by even a short tradition; and when embodied in symbolic language, and thus intimately blended with our conceptions, they are readily mistaken for facts. No statement, perhaps, would receive more universal or unqualified assent from chemists than that the molecule of ammonia contains three atoms of hydrogen, that ethylamine is derived from ammonia by the substitution of an atom of ethyl for an atom of hydrogen, and that the reason why there are three, and only three, such derivatives of ammonia is, that each derivative is formed by a repetition of the same process, and that, the molecule of ammonia containing only three atoms of hydrogen, this process can only be repeated three times. These conclusions are regarded as so certain as to be almost removed from discussion. But nevertheless they cannot

*d'invention véritable: les signes n'ont de valeur que par les faits dont ils sont l'image. Mais les conséquences logiques d'une idée ne changent point, quelle que soit la langue dans laquelle on la traduit."*

It is a fundamental principle of symbolic reasoning, to whatever science it may be applied, that we cannot by the aid of symbols arrive at any conclusion which is not implicitly contained in them. And it might with equal justice be asserted that it was a matter of very little consequence whether we employed for the purposes of calculation Arabic or Roman numerals, the number expressed being in either case precisely the same, and "the language by which it is expressed being of little moment." Or again, that the discovery of the method of denoting the position of points in space by means of the symbols of algebraic geometry was a very unimportant matter. Our conception of a circle is the same as that of the ancient geometers, and "the logical consequences of an idea do not change into whatever language we translate it." Nevertheless our power of following out and appreciating those consequences may be very materially affected by such a method, as experience has amply proved.

but partake of the hypothetical nature of the theory in which they originated. It is only because our primary hypothesis has led us to take this peculiar view of the atomic constitution of ammonia, and to express it by the symbol  $\text{NH}_3$ , that chemists have adopted these further hypotheses as to the nature of the process by which ethylamine is formed, and as to the cause of the limitation which exists in regard to the number of these derivatives. Again, the theory of atomicity has a similar origin. Glycol is supposed to be derived from two molecules of water by the substitution of an atom of the diatomic hydrocarbon ethylene for two atoms of hydrogen; the diatomic radical, in the forcible language of the distinguished discoverer of this substance, "welding" and "riveting" together the residues of the two molecules of water.\* What is this doctrine? It is simply the expression in language of the relation of the symbols



And if the course of the science had been, as might have been the case, such as to have led us to a different view of the atomic constitution of these substances, we should have a different order of chemical ideas, and the theory, in its actual form, would never have existed.

It is frequently asserted that our present hypothesis affords a clear and simple explanation of chemical phenomena, which is the evidence of its truth. Now it may be considered that such an explanation was perhaps afforded of the incomplete system of facts known to Dalton, but with our present knowledge this account can no longer be regarded as satisfactory. The most important feature in our modern system is the identification of the weight of the chemical molecule with the weight of the unit of gaseous volume, to which we are brought by physical as well as chemical considerations. This great simplification was

\* "Toutes ces molécules sont cimentées, en quelque sorte, par des éléments polyatomiques, qui possèdent la propriété de se souder les uns aux autres."

"Il est bien entendu que dans l'éthyle lui-même les atomes sont rivés ensemble par le carbone tétratomique."—Wurtz, "Leçons de Philosophie Chimique," 1864, pp. 138-140.

practically introduced by Laurent and Gerhardt, and it is generally allowed that this assumption affords the surest basis of chemical theory. Now the atomic theory of Dalton accounts for the fact that the weight of the chemical molecule may be regarded as consisting of an integral number of the atomic weights of those elemental bodies into which it can finally be decomposed. But this is not the only limitation with which we are acquainted. The chemists before mentioned discovered the existence of a peculiar numerical relation between the atomic weights of certain elemental bodies, when combined in the chemical molecule, to which they gave the name of "the law of even numbers." This law may be thus stated:—"The sum of the volumes of the hydrogen, chlorine, bromine, iodine, nitrogen, and generally of that class of elements which goes under the name of the dyad elements, which are formed by the decomposition of two gaseous volumes of any chemical substance, is an even number."\* This statement rests upon evidence quite as satisfactory as that by which the atomic doctrine is supported. A formula containing an uneven number of these elements jointly is rendered as improbable, from our experience, as a formula containing fractions of atoms. But the atomic theory in its present form takes no account of this relation, and so little has this great discovery been appreciated that such formulæ are often met with, even in the works of accomplished chemists; and indeed they are truly admissible, so far as the limitations imposed by our actual theory are concerned. It need not certainly be a matter for surprise or reproach, that the speculations of Dalton should not apply to a class of facts with which he was unacquainted; nor even can this be regarded as conclusive evidence against the truth of his system. But nevertheless this omission indicates some profound defect in chemical theory, and if it should be found that another view of the constitution of matter should cover the whole ground, and account by one and the same hypothesis for both numerical relations, there can be but little room for doubt as to which should be preferred.

Another, although a less important, defect in our method is the singular unit of volume which chemists have been compelled to adopt, for which selection no reason can be assigned except

\* See Laurent, "Méthode de Chimie," Ed. 1854, p. 57, "Sur les nombres pairs d'atomes;" "Chemical Method," English translation, 1855, p. 46.

the necessities of the atomic hypothesis. In the so-called "two-volume" and "four-volume" notations the weight of the chemical unit or molecule is assumed as twice or four times the weight of the unit adopted for the purposes of physical measurement, the numbers which express the weight of the chemical molecule being proportional to, but not identical with, the numbers which express its density. An attempt has been made to remedy this imperfection, retaining the general features of our present method, but the changes proposed have never been adopted, such alterations being always attended with some inconvenience, and the question at issue being one neither of theory nor of fact.\*

The following pages contain the outline of a new method for the expression, by means of symbols, of the exact facts of chemistry, and for reasoning upon these facts by their aid. This method is quite independent of any atomic hypothesis as to the nature of the material world, and in it the symbol is placed in immediate relation with the fact, being indeed its symbolic equivalent or expression. It does not, however, preclude or deny such an hypothesis; the question is not raised. This method may be regarded as a special application of the science of algebra, and in its construction I have been guided by the similar applications of that science to geometry, to probabilities, and to logic, to which it presents many curious and interesting analogies. In these branches of science the symbol is not a figure of the object, nor is any resemblance attempted between the symbol and the thing signified by it. The symbols which I shall have occasion to employ are of the same abstract character; they pretend to no resemblance to any object in nature, and are simply to be regarded as arrangements of marks which it is convenient to employ for the purposes of thought. The conditions to be satisfied by such a method are few and simple. It is only necessary that every symbol should be accurately defined; that every arrangement of symbols should be limited by fixed rules of construction, the propriety of which

\* See Laurent, "Méthode de Chimie," p. 88, English translation, p. 67. Also Mr. J. J. Waterston, "On Chemical Notation in conformity with the Dynamical Theory of Heat," *Phil. Mag.* vol. xxvi, pp. 248 and 515, and vol. xxvii, p. 273. Also "Remarks on Chemical Notation," by W. Odling, *ib.* vol. xxvi, p. 380, and vol. xxvii, p. 380. The proposition of Mr. Waterston is the same as that of Laurent, and amounts to the obvious expedient of cutting the molecules and atoms in half.

can be demonstrated; and that the symbolic processes employed should lead to results which admit of interpretation.

The object of this method may be considered to be the investigation of the laws of the distribution of weight in chemical changes, and the symbols here employed represent "weights" in the same sense as the symbols of geometry represent lines or surfaces. Now the symbol  $a$  in geometry, in its primary sense, may be regarded as the symbol of the operation performed upon the unit of length, by which a line is generated, that is, of which the result is a line. In like manner the symbol  $a$ , as a chemical symbol, is to be regarded as the symbol of the operation performed upon a unit of space, by which a weight is generated, that is, of which the result is a weight. Symbols of operation have not hitherto been adopted in chemistry, and their introduction forms a distinctive feature of the present method, which I have hence termed "the Calculus of Chemical Operations."

It is my intention to divide the subject into three parts. The first part, which alone is here given, relates to the construction of chemical symbols. In the second part I purpose to treat of the theory of chemical equations, which is intimately connected with the general processes of chemical reasoning, and especially with the consideration of the nature of that event which is termed a chemical change, of which I shall give a new analysis founded on its symbolic expression. In the third part it is intended to consider the principles of symbolic classification and the light thrown by this method upon the origin and nature of the numerical laws which limit the distribution of weight in chemical change: I shall then have occasion to contrast the view of the science which is here given with that afforded by our existing system.

It is now some years since the conception of such a work first arose in my mind, and these pages are a very imperfect record of the time and consideration bestowed upon it, which yet can hardly be regarded as excessive in relation to the end I have had in view, which has been no other than to free the science of chemistry from the trammels imposed upon it by accumulated hypotheses, and to endow it with the most necessary of all the instruments of progressive thought, an exact and rational language. "Toute langue est une méthode analytique, et toute méthode analytique est une langue."—Condillac. The views here advocated may appear novel, but nevertheless

I strongly feel that one claim, at least, which they have on the consideration of chemists is that they are in truth the rational and simple consequence of opinions at which the most reflecting minds have already arrived, and offer a more complete expression of current ideas than has hitherto been given. Indeed on such subjects novelty is almost inconsistent with truth. For the conceptions through which sciences pass necessarily have their origin in the views which preceded them, of which they are but the natural fruit. The method here developed will be seen, if carefully considered, to be but another step in the direction of the chemical movement of the last twenty years, which some imagine to have found its final consummation in the doctrines of "modern chemistry." Such could never have been the conclusion of the great chemists from whom this impulse emanated, who definitely refused to recognize the atomic doctrine as the adequate exponent of their ideas, and who implanted in the science the germ of a more abstract philosophy, which it has ever since retained.

The object of the following method has been defined as the investigation by means of symbols of the laws of the distribution of weight in chemical change, a problem evidently of the widest range, and embracing many distinct questions. To the consideration of one, and certainly not the least important, of these the first part of this work will be more especially devoted, namely, to the discovery of a system of symbolic expressions by which the composition of the units of weight of chemical substances may be accurately represented, and which may hereafter be employed for the purposes of chemical reasoning. The value of our conclusions must depend upon the degree of precision and certainty with which this point is determined. It will be shown that the problem is of a perfectly real nature, admitting, where the experimental data are adequately supplied, of only one solution. The discussion of this question involves the consideration of the fundamental principles of symbolic expression in chemistry.

#### SECTION I.—DEFINITIONS.

It is essential for the purposes of exact reasoning that the terms employed should be accurately defined. This can only be effected either by the invention of new words or by the selec-

tion from the many shades of meaning which may be attached to existing words of some one definite and appropriate signification, in which it shall be agreed to employ them. I shall adopt the latter and more obvious course.

1. The term "ponderable matter," in its chemical application, is a term by which that class of objects is denoted, the transformations of which form the special study of the chemist. Not that the property of weight can exist apart from those other properties of form, colour, and the like, with which, so far as our experience extends, it is invariably associated, but that in the actual phase of the science this property is chiefly considered, it being the only property of matter in regard to the chemical changes of which we possess any exact knowledge. No further explanation of this term can advantageously be offered, except by exhibiting or enumerating the objects (such as water, silica, oxygen) which are comprehended in the class.

2. A "chemical substance" is a portion of ponderable matter, of which every part has the same properties.

It is often difficult to decide whether this condition be satisfied or not, but the propriety of the above definition will be manifest from the line of argument which is applicable to such cases. Take, for example, the case of atmospheric air. To a superficial observation, every part, however minute, of any given portion of the atmosphere has the same properties. But a more exact scrutiny leads us to infer that this is really not the case, but that it consists of parts, which diffuse with different velocities, and are unequally soluble in water. On these principles it has been established that the gas procured from the decomposition of acetic acid is truly, in the sense of the above definition, one chemical substance, marsh-gas, and not two chemical substances, hydrogen and methyl.

3. "A weight" is a portion of ponderable matter of any specified kind considered as regards weight.

This application of the term *a weight* is only a slight extension of its ordinary use. A gramme of platinum which serves for the purposes of weighing is termed *a weight*, this being the only property of that portion of matter of which it is necessary to take cognisance.\* Now the weight of matter, from a different

\* The term *weight* is, in ordinary language, used with two distinct meanings.

(1) In what may be termed its abstract signification, as denoting a certain measurable property of matter, as when we inquire, "What is the weight of that loaf?"

and far wider point of view, in the laws of its composition and resolution, is the special subject of this investigation; and the aspect in which every chemical substance, every portion of ponderable matter, will be here regarded is exclusively as a *weight*. In speaking of such *weights* we habitually employ, by a tacit convention, the terms by which the chemical substances, of which the weight alone is referred to, are usually designated. But this is not a strictly accurate use of language; and it is necessary to observe that in the following pages, where chemical substances, such as chlorine or alcohol or water, are mentioned, or the term "a portion of matter" is employed, the objects referred to are certain weights of the substances under consideration, to the exclusion of all other properties.

4. A "single weight" is a portion of ponderable matter of any specified kind considered as regards weight and as one object, as for example a portion of oxygen, or a portion of ponderable matter consisting of oxygen and hydrochloric acid considered as one object, or two portions of oxygen similarly considered.

5. A "group of weights" is some number of single weights, such as a portion of oxygen and a portion of hydrochloric acid considered as two objects, or two portions of oxygen similarly considered. The single weights of which a group consists are termed the "constituents" of the group, which is said to be "constituted" of them.

6. Two portions of ponderable matter which consist of the same "weights" are said to be identical as regards weight.

It follows from this definition that what may be termed the absolute weight, or weight in grammes, of "identical weights" is equal.

Our knowledge as to the identical relations of ponderable matter is derived exclusively from the science of chemistry. Were we unacquainted with the peculiar phenomena of chemical transmutation, or were we ignorant of the circumstance that in chemical change the total weight of matter is unaltered, the existence of such relations would be unknown to us. It is so important to have a clear perception of that distinction, which

(2) In its concrete sense, as denoting certain objects, which we discriminate from others by naming them from their most essential property, as when we say "Bring me that box of weights." It is in an extension of this concrete meaning that the word is here employed. It is not, of course, intended to assert that the transformation of *weights* is the only subject of chemical science, but simply to fix the attention upon that subject as the only topic which is here discussed.



is here made, I believe for the first time, between equality and identity of weight, that a few words in somewhat fuller explanation of the grounds on which this distinction rests may not be deemed out of place.

If we were to take any portion, say a gramme, of water, and observe its properties on two successive days, the conditions under which the water was placed being assumed as fixed, it would be found that the properties of the water were precisely the same at the second as at the first observation. In this case the identity of properties would be absolute, and as we know that at whatever time the observation had been made, under the same conditions, the same result would have been obtained, we should hence arrive at the conception of the continuous existence of one and the same object, which we should denote with perfect precision by one and the same name, a gramme of water. Now let it be assumed that some condition varies, that the temperature, for example, rises from  $60^{\circ}$  to  $90^{\circ}$ , and let another observation be made of the properties of the water. It would be found that these properties were no longer identical with those previously observed; that the bulk of the water had increased, and that some properties had varied while others had remained constant. If the expansion of water were the point under consideration, those properties which had varied would be of fundamental importance; but as for most purposes these variations may be disregarded, the object is still assumed to be the same, and called by the same name, a gramme of water. Let the temperature rise to  $100^{\circ}$ , and let a new observation be made. The liquid has become a gas, and the change of properties is so great that a new name is assigned to the portion of matter, and it is said that the gramme of water has been converted into a gramme of steam. Nevertheless many of the properties of the steam are identical with those of the water, and these being the properties with which the chemist is mainly concerned, he asserts the identity of the two objects for the purposes of his science, and says, notwithstanding this transformation, that steam is simply the gaseous form of water. Now let the conditions be again varied. At a further elevation of temperature it will be found that a more profound change has occurred. In the place of one continuous portion of matter, in every part of which the same properties may be recognised, we have two distinct chemical substances, each characterised by a

special set of properties. The volume has permanently altered ; many chemical as well as physical properties of the water have entirely disappeared. The chemist marks this change by assigning a new name to the portion of matter, and says that the water has been *converted* into oxygen and hydrogen. It has, however, been found that even in this profound change one property has not been affected, namely, weight. This property is constant ; and we assert in the most absolute sense that the weight of a gramme of water is identical with the weight of the gramme of oxygen and hydrogen into which it is transformed, for this property, throughout this series of changes, has never varied nor ceased to have a continuous existence. Now a gramme of water will produce the same effect on a balance as a gramme of lead, and it is this relation which is here termed equality of weight. This relation also subsists between the weight of a gramme of water and the weight of the gramme of oxygen and hydrogen into which it is transformed ; but these weights are also connected by another relation, which I have termed identity, which does not exist between the gramme of water and the gramme of lead.

It is thus that we are led by experience to the inference comprised in the following statement.

If a portion of matter A be chemically converted into a portion of matter  $A_1$ , then the weights (or portions of matter considered as regards weight) of which A consists are identical with the weights (or portions of matter considered as regards weight) of which  $A_1$  consists.

It will be found, on analysing the process of reasoning by which we conclude the continuous existence of the same weight in a chemical change, that the evidence by which it is supported is precisely of the same order as that by which we are enabled to assert the continuous existence of any external object whatever. This evidence is brought spontaneously and without effort before the mind, and is so perfectly conclusive, however difficult it may be to submit it to analysis, that an eminent writer has actually imagined the doctrine of the permanence of weight in chemical changes to be a truth which the mind recognises at once when stated, by some special intuition, as "flowing from the idea of substance."\* As to the nature of this process

\* See Whewell's "Philosophy of the Inductive Sciences," vol. i, chap. iv, p. 412, ed. 1847, "On the Application of the Idea of Substance in Chemistry."

we are left in the dark. However, such assumptions are happily as unnecessary as they are unmeaning, and it is sufficient for all the objects of science if we admit this axiom to be the undoubted acquisition of those combined processes of reasoning and observation, which are the only sources of exact knowledge.

7. A "compound weight" is a single weight of which the whole is identical with two or more weights. Such weights are termed the components of the compound weight, which is said to be composed of them.

It follows from this definition that every part, individually or separately considered, of a compound weight is proportionally identical with the same weights of which the totality is composed; that is to say, if the whole of a compound weight be identical with the weights A and B,  $\frac{1}{n}$ th part of that compound weight, in whatever way the division into parts be effected, is identical with  $\frac{1}{n}$ th part of the weight A and  $\frac{1}{n}$ th part of the weight B, and is similarly composed of those parts; and also it is to be inferred that if every  $\frac{1}{n}$ th part of a single weight be identical with  $\frac{1}{n}$ th part of a weight A and  $\frac{1}{n}$ th part of a weight B, the whole of that single weight is composed of the weights A and B.

A group of two or more weights may, in the sense of this definition, be regarded as a compound weight, if only every constituent of the group have a common component. Thus, for example, a group consisting of two portions of matter, of which the one is composed of A and B, and the other of A and C, may be regarded as a single weight (Sec. I., Def. 4) of which the totality is composed of A and  $\overline{B}$  or  $\overline{C}$ ; for if, regarding the group as one object, we agree not to effect the separation of its constituents, every  $\frac{1}{n}$ th part of that weight satisfies proportionally the same condition.

Some difficulty may perhaps be felt in assenting to the above reasoning, from a certain ambiguity in language in the use of the conjunctions "and" and "or." That these conjunctions have the same meaning, so far as the purposes of enumeration are concerned, is apparent on enumerating the constituents of a

group with each conjunction. The language of symbols is free from this ambiguity, the two conjunctions being represented by one mark, as will hereafter be explained.

8. A "simple weight" is a weight which is not compound. It may also be defined as a weight which has only one component. Two weights are said to be simple in regard to one another which have no common component.

9. An "integral compound weight" is a weight which is composed of an integral number of simple weights.

10. It is necessary to select a "unit of ponderable matter" which may serve as the common measure of those chemical properties which it is our desire to investigate. Such a standard, for example, would be supplied to us were we to select as the common term of comparison that portion of ponderable matter of which the absolute weight is one gramme. This plan would have the great advantage of proceeding upon accurate and certain data, but, on the other hand, the conclusions to which it leads would be of comparatively little interest. The present method aims at effecting a comparison of the chemical properties of those portions of ponderable matter which, in the condition of perfect gases, and compared at the same temperature and pressure, occupy equal volumes.

In the numbers which express the specific gravity of gases a similar comparison is made of the absolute and relative weights of the same portions of matter; and it will be found convenient to refer physical and chemical properties to the same standard. I shall therefore define the "chemical unit of ponderable matter" as that portion of ponderable matter which occupies the volume of 1,000 cub. centims. at  $0^{\circ}$  C., and a pressure of 760 millims. of mercury. The weights of the chemical unit of ponderable matter may be expressed in two ways according to the object in view; as the absolute weight in grammes, and as the relative weight in reference to the weight of some one unit assumed as the standard of comparison. For this purpose the weight of the unit of hydrogen will be selected.

11. The volume of 1,000 cub. centims. is here termed "the unit of space."

The system of chemical measurement which has grown up around the atomic theory is of a singular and artificial character. The chemist is accustomed to assume as his standard of comparison, not some real and existing object, but a "molecule," an

imaginary arrangement of imaginary atoms, of which no precise definition, by which it can be recognised, has ever been given. It should at least be shown that a system thus constructed offers special faculties for thought. But in truth it has been found so perplexing in practice, that the most skilled teachers\* have been forced to admit that the student requires to be initiated into this world of hypothesis by means of more concrete and exact ideas.

12. The term "distribution of weight" may be defined as that operation by which a compound weight is resolved into its component weights, or by which it is made up from those weights, regard being had to some special system of such events which is the subject of consideration.

A "distributed weight" is a weight which, in such a system of events, is resolved into two or more weights, or made up from such weights.

An "undistributed weight" is a weight which, in the same system of events, is not so resolved, or so made up. An undistributed weight may also be defined as a weight which is resolved into one weight, or made up from one weight alone.

This division of weights into distributed and undistributed weights is coextensive with the previous division of the same into compound and simple weights. A distributed weight is necessarily a compound weight, for we can always assert its identity as a whole with the parts into which it is distributed; and a weight which is not distributed, can only be regarded as a simple weight, for, by hypothesis, no information is supplied to us from the system of events under consideration, which enables us to assert its identity with any other weights, such an assertion in every case being purely relative to the facts before us, and open to modification by the acquisition of further knowledge.

\* Two eminent chemists have recently given independent testimony to the value of a more real standard than is afforded by this imaginary "molecule." Dr. Hofmann, in his "Modern Chemistry," has adopted the term "crith" to denote such a real unit,—a crith being the weight of 1000 cub. centims. of hydrogen at standard temperature and pressure. Professor Williamson has, from similar motives of utility, adopted an "absolute volume" of 11.2 litres, which is the bulk of a gramme of hydrogen, also at standard temperature and pressure. I now propose to advance another step in the same direction, and to substitute the real for the fictitious unit, not for a special object alone, or to pave the way for more important theories, but for all the purposes of chemistry.

See "Modern Chemistry," by A. W. Hofmann, 1865, pp. 121 and 130; and "Chemistry for Students," by A. W. Williamson, p. 4.

It is essential to remark that the previous definitions are definitions of abstract conceptions, which have immediate reference to the symbolic method developed in the following section, for the construction of which they afford an adequate basis, and which is necessarily more comprehensive than those special subjects of physical investigation to which it is hereafter to be applied.

## SECTION II.—ON THE SYMBOLS OF CHEMICAL OPERATIONS.

Having explained the nature of those objects and relations which fall under the consideration of the chemist as the investigator of the laws of the distribution of weight, I proceed to consider their symbolic expression.

(1.) Let a chemical operation be defined as an operation performed upon the unit of space, of which the result is "*a weight*" (Sec. I., Def. 3), and let  $x, x_1, x_2$  be the symbols of such operations, of which the weights  $A, A_1, A_2$  are the results. Then the symbols of operations,  $x, x_1, x_2$  are termed (for brevity and convenience) the symbols of the weights,  $A, A_1, A_2$ .

Any symbolic expression into which the symbols of chemical operation enter is termed a chemical function.

(2.) Two chemical operations are said to be identical of which the results are identical as regards weight (Sec. I., Def. 6). Now let the symbol  $=$  be the symbol of identity. Hence if the weight  $A$  be identical with the weight  $A_1, x = x_1$ .

(3.) Further, let the symbol  $+$  be the symbol of that operation by which a weight is added to a weight so as to constitute with it one group (Sec. I., Def. 5); and let the symbol  $-$  be the symbol of that operation by which a weight is removed from a group of weights. These operations are expressed in language by the words "and" and "without."

From these definitions  $x + x_1$  is to be regarded as the symbol of a group constituted of the two weights  $A$  and  $A_1$ , and  $x + x$ , that is,  $2x$ , is the symbol of two weights  $A$ , and  $x - x_1$  is to be regarded as the symbol of the weight  $A$  without the weight  $A_1$ . For this latter operation to be performed, it is necessary that the weight  $A_1$  should be part of the weight  $A$ .

Now since a group which is constituted of the weights  $A$  and  $A_1$  is identical with (Sec. I., Def. 6) a group which is constituted of  $A_1$  and  $A, x + x_1 = x_1 + x$ .

Also, since it is immaterial in what order the operation is performed which results in the exclusion of a weight from a group  $x - x_1 = -x_1 + x$ .

If, in the expression  $x - x_1$ ,  $x_1 = x$  the expression becomes the symbol of a group in which no weight appears; for it is the symbol of that weight which is the result of removing the weight A from the weight A, in other words,  $x - x$  is the symbol of the weight A without the weight A, but the result of the successive performance of these operations is *no* ponderable matter. By analogy of interpretation to that of the symbol 0, regarded as a numerical symbol, let 0 be the symbol of a group in which no weight appears, and which has had its origin in the several performance of the operations  $x$  and  $-x$ ; so that  $x - x = 0$ .

The chemical symbol 0 has the property of the numerical symbol 0 given in the identity  $0 + x = x$ ; for the ponderable matter which results from adding the weight A to a group in which no weight appears is identical with the ponderable matter A.

Also, since a group is not affected by removing from it no weight, the symbol of a group is not affected by removing from it the symbol of no weight, and  $0 + x = +x = x$ .

The interpretation which is here assigned to the symbols  $+$  and  $-$  is strictly analogous to that which has been given to them in the arithmetical and logical systems.\* They are the symbols of those operations by which we form a group from its constituents, or remove the constituents from a group. These operations, which may be termed the operations of "aggregation" and "segregation," are found in every department of thought. No uniform meaning has hitherto been attached to the symbols  $+$  and  $-$  in chemistry, notwithstanding their constant use. The prevalent opinion seems to be in favour of the use of the symbol  $+$  as the symbol of "mechanical mixture."† It is difficult to say what may be the exact signification of this

\* Boole, "Laws of Thought," p. 32.

† See Odling's "Manual of Chemistry," vol. i, p. 4. "The sign  $+$  signifies addition to, or rather mixture with." Also, Williamson's "Chemistry for Students," p. 37. "The sign  $+$  interposed between symbols denotes addition or mixture of the atoms or molecules which the symbols represent. Thus  $H + O$  denotes a mixture of 1 part by weight of hydrogen with 16 parts by weight of oxygen."

term. In the present method, at any rate, no such interpretation is to be attached to the symbol, it being quite immaterial for the end in view whether the objects referred to be what is termed "mixed" or not. A similar uncertainty prevails in the use of the symbol of identity.\* The symbol = is sometimes employed in chemistry as the symbol of numerical equality, at other times as the symbol of chemical transmutation. So far as I am aware it has never yet been employed with the signification which I have assigned to it, nor has the relation which it here expresses been recognized in the conceptions of the science, among which it occupies so fundamental a position.

(4.) Further, let  $\overline{x + x_1}$  or  $(x + x_1)$  be the symbol of the two weights A and  $A_1$  collectively considered as constituting a single weight. Then  $\overline{x + x_1 + y + y_1}$  will be the symbol of a group of which two such weights are the constituents, and  $\overline{(x + x_1) + (y + y_1)}$  will be the symbol of two such weights collectively considered, and as constituting a single weight.

Now, since the result is the same whether we add or remove a group of weights collectively, or add or remove the constituents of the group severally,

$$\begin{aligned}\overline{x + y + y_1} &= x + y + y_1, \\ \overline{x - y + y_1} &= x - y - y_1, \\ \overline{x + y - y_1} &= x + y - y_1, \\ \overline{x - y - y_1} &= x - y + y_1.\end{aligned}$$

From this we may infer that the chemical symbols + and - have the properties of the numerical symbols + and -, so that

$$\begin{aligned}+ + x &= + x, \\ - + x &= - x, \\ + - x &= - x, \\ - - x &= + x.\end{aligned}$$

(5.) Now, let W be a compound weight, of which certain

\* Odling's "Chemistry," vol. i, p. 4. "The sign = signifies equivalency with, or rather conversion into." Williamson says, p. 37, "The sign = is used in describing chemical changes. It only denotes equality in weight between the sum of the atoms of each kind on one side of it, and the sum of the atoms of the same kind on the other side of it. . . .  $H^2 + O = H_2O$  means that 2 parts by weight of hydrogen added to 16 parts by weight of oxygen, can be made to combine to form 18 parts by weight of water."



portions of matter named A and B are the components (Sec. I., Def. 7). Let  $\phi$  be the symbol of the weight W, and  $x$  and  $y$  the symbols of the weights A and B respectively. Further, let  $xy$  be selected as the symbol of the weight W, so that

$$\phi = xy;$$

$xy$  is termed a composite symbol, of which  $x$  and  $y$  are the factors. The symbol  $xy$  is also termed a combination of  $x$  and  $y$ , which are said to be combined in it.

If  $y = x$ , then  $\phi = xx$ , which may also be written  $x^2$ ; and generally if  $\phi$  be the symbol of a compound weight of which the component weights are  $n$  weights named A,  $n_1$  weights named  $A_1$ ,  $n_2$  weights named  $A_2$  . . . . ., of which  $x, x_1, x_2, \dots$  are the symbols, then

$$\phi = x^n x_1^{n_1} x_2^{n_2} \dots$$

If in this expression  $x = x_1 = x_2 \dots$ ,

$$\phi = x^{n + n_1 + n_2 + \dots}$$

Now, recurring to the symbol  $xy$ , since a portion of ponderable matter composed of A and B is identical with a portion of ponderable matter composed of B and A,

$$xy = yx,$$

that is to say, the order in which apposed symbols of chemical operations are written is indifferent. Symbols possessing this property are termed "commutative."

A consequence of this commutative property is that

$$(xy)^n = x^n y^n;$$

for

$$\begin{aligned} (xy)^2 &= xyxy \\ &= xxyy \\ &= x^2 y^2. \end{aligned}$$

Further, let there be a compound weight V, of which  $\theta$  is the symbol, of such a nature that it is identical with the component weight A without the component weight B, and let  $\frac{x}{y}$  be selected as the symbol of the weight V. Then

$$\theta = \frac{x}{y},$$

whence, on similar principles, if  $\theta$  be the symbol of a compound weight V identical with  $n$  component weights A,  $n_1$  component weights  $A_1$ ,  $n_2$  component weights  $A_2, \dots$  without  $m$  component weights B,  $m_1$  component weights  $B_1$ ,  $m_2$  component weights,  $B_2, \dots$ ,

$$\theta = \frac{x^n x_1^{n_1} x_2^{n_2} \dots}{y^m y_1^{m_1} y_2^{m_2} \dots},$$

where  $x, x_1, x_2, \dots, y, y_1, y_2, \dots$  are the symbols of the weights A,  $A_1, A_2, \dots, B, B_1, B_2, \dots$  respectively.

We may also reason thus:  $xy$  is the symbol of a weight which results from the successive performance upon the unit of space of the operations  $y$  and  $x$ ,  $yx$  is the symbol of a weight which results from the performance of these operations in an inverted order, and  $(xy)$  is the symbol of a weight which results from their joint performance. Now, since the result is the same in whatever order the operations be performed, and since it is immaterial whether the operations be performed jointly or successively, we infer that

$$xy = yx = (xy).$$

(6.) If in the composite symbol  $\phi$  one of the factors be the symbol of a group, so that

$$\phi = x(y + y_1),$$

$\phi$  is to be interpreted as the symbol of the weight which results from the combination of the weight A with the group of weights B and  $B_1$ , the group being collectively considered and as constituting a single weight (Sec. I. Def., 4, 5, and Sec. II. (4)),—not, however, be it observed, a single weight *compounded* of the weights B and  $B_1$ , which would be symbolized by  $yy_1$ , but a single weight *constituted* of B and  $B_1$ , which is symbolized by  $(y + y_1)$ . (Sec. I. Def. 4, 5, and 7). Now the weight A will be combined with the group of weights *collectively* considered, if it be combined with the constituents of the group *severally*, but the symbol of the weight A combined with the two constituents of the group *severally* is  $xy + xy_1$ . We hence arrive at two symbols for the same weight, which express indeed two different aspects of the same object, but which are identical as regards the object signified; whence

$$x(y + y_1) = xy + xy_1.$$

Also by a strictly analogous interpretation to that assigned to the symbol  $xy$  as a symbol of operation, the symbol  $x(y + y_1)$  is to be interpreted as the symbol of a weight which results from the successive performance upon the unit of space of the single operations  $(y + y_1)$  and  $x$ . Now the result of performing the *single* operation  $(y + y_1)$  is the same as that of performing *severally* the two operations  $y$  and  $y_1$ ; and as regards the result, it is immaterial whether we first perform *severally* the two operations  $y + y_1$ , and then perform upon these *two* operations the operation indicated by  $x$ , as expressed in the symbol  $xy + xy_1$ , or whether we perform the *single* operation  $(y + y_1)$  and then perform  $x$  upon that, as expressed in the symbol  $x(y + y_1)$ . From whichever point of view we regard the symbols, whether as symbols of operation or as symbols of the results of operations, we are brought to the same conclusion, that

$$x(y + y_1) = xy + xy_1.$$

In like manner it may be shown that

$$(x + x_1)(y + y_1) = xy + xy_1 + x_1y + x_1y_1,$$

$(x + x_1)(y + y_1)$  being the symbol of a single compound weight, of which the groups  $A$  or  $A_1$  and  $B$  or  $B_1$  are the components. Symbols which possess this property are termed distributive symbols.

(7.) Although the selection of a symbol is in a certain sense arbitrary, it is by no means a matter of indifference; and the symbol  $xy$  which is here assigned to a continuous compound weight, so far from being (as might be thought from a superficial consideration) contrary to symbolic analogy, is the only symbol by which the desired end could be attained, consistently with usage. The symbol  $xy$  in its abstract interpretation is the symbol of the operations  $x$  and  $y$  operating *successively* upon the unit or subject of operations;  $(xy)$  is the symbol of the same operations but operating *jointly*;  $x + y$  is the symbol of the same operations operating upon the same subject but operating *severally*, and  $(x + y)$  the symbol of the same operations, but operating *collectively*. This fundamental distinction in operations as *successively*, *jointly*, *severally*, or *collectively* performed, appears in various forms in the different sciences, and is found in every branch of knowledge which admits of symbolic treat-

ment. In chemistry it expresses the various ways in which we may conceive of the existence of the same ponderable matter. The language of symbols supplies the means of simply and adequately expressing these conceptions, isolated from every other consideration, which are not only very imperfectly expressed by the usual molecular representation, but are there complicated by many considerations which are totally irrelevant to the real point at issue.

### SECTION III.—ON THE CHEMICAL SYMBOL 1.

(1.) The preceding considerations suggest the inquiry as to the symbol of a compound weight, of which the weight A and no weight are the components. Now, since any portion of ponderable matter is not altered by the combination with it of no ponderable matter, a weight of which the weight A and no weight are the components is the same as the weight A. Hence if  $x$  be the symbol of the weight A, and  $y$  the symbol of no weight,

$$xy = x.$$

Now the symbol 1 regarded as a numerical symbol, possesses the property given in the equation

$$x1 = x.$$

From this correspondence of symbolic properties, and guided by the same considerations of analogy as those on which the symbol 0 was selected as the symbol of no weight, regarded as the constituent of a group, I shall select the symbol 1 as the chemical symbol of no weight regarded as a component of a compound weight.

Since any portion of matter whatever may be considered as a compound weight of which that matter itself and no weight are the components, if  $\phi$  be the symbol of any weight,

$$\phi = \phi 1.$$

The symbol 1, therefore, is implicitly contained as a common factor in every chemical symbol, being either expressed or understood as the symbol of the common subject of all chemical operations. Now this subject of chemical operations has been defined as the "unit of space" (Sec. I., Def. 11), a term already

appropriated to it in language, for it is in space that we conceive of the existence of ponderable matter. This interpretation of the symbol 1, as the symbol of the unit of space is identical with the meaning before assigned to it as the symbol of "no weight;" the only property of matter under consideration being weight, by the absence of which the unit of space is defined.

(2.) The correctness of the above reasoning is further evident from the identity of the other algebraic forms of the chemical symbol 1 with the algebraic forms of the same numerical symbol, notwithstanding the difference in interpretation.

We have seen that  $x^n$  is the symbol of a compound weight, of which  $n$  weights A are the components. Hence the symbol of a compound weight, of which 0 (or no) weights A are the components, is  $x^0$ . But a weight of this kind is the same as "no weight;" whence

$$x^0 = 1.$$

The symbols 1 and  $x^0$  correspond to the different ways in which "no weight" may have originated, the result being the same whether the operation performed do not cause weight, or whether an operation causing weight be not performed; the former view being expressed by the symbol 1, the latter by  $x^0$ .

Again, if in the expression  $\frac{x}{y}$  (Sec. II. (5)),  $y = x$ , this expression becomes the symbol of a compound weight composed of the weight A without the weight A, that is to say, which is composed of no weight; whence also

$$\frac{x}{x} = 1.$$

This third form of the symbol 1 corresponds to a third origin of the absence of weight, which we may also regard as effected by the simultaneous performance of inverse operations upon the unit of space, the result of one of which is to cause "a weight," and of the other to remove the same. A correct system will take cognisance, not of one only, but of every way in which a given result can be attained.

There is considerable difficulty in the use of language for the expression of such abstract ideas, and these points would hardly

become clearer by fuller explanation. Let it be sufficient, in conclusion, to state that the chemical symbol 1, while it is a necessary constituent of the system of chemical symbols, and may be and indeed must be employed to give effect to the purposes of the chemical calculus, is not to be interpreted in weight.

(3.) An inquiry not without theoretical interest is immediately suggested by the previous considerations. We have arrived at the symbol of no ponderable matter, regarded as a component of a compound weight; what is the symbol of all ponderable matter, similarly regarded? Now all ponderable matter is characterized by the property that the addition to it of any finite weight does not alter our conception of it. Hence a compound weight, of which all ponderable matter and a finite weight are the components, is the same as a compound weight of which all ponderable matter is the single component. Hence, if  $y$  be the symbol of all ponderable matter thus regarded,

$$yx = y.$$

Now the numerical symbols 0 and  $\infty$  satisfy this condition, since  $0x = 0$ , and  $\infty x = \infty$ ; and either symbol, so far as this equation is concerned, may be with equal propriety selected as the symbol of all ponderable matter. This is by no means contrary to analogy. As the numerical symbols 0 and  $\infty$  are symbols of which all numbers are factors, so the chemical symbols 0 and  $\infty$  are symbols of which all other chemical symbols are components,

$$\begin{aligned}\infty &= xx_1x_2\dots\infty, \\ 0 &= xx_1x_2\dots 0.\end{aligned}$$

In the same sense as the symbol 1 is to be interpreted as the symbol of space, so it will appear, on consideration, that the symbol  $\infty$  is to be interpreted as the symbol of the ponderable universe regarded as a whole. Neither object can be presented to the imagination, but, nevertheless, they are to be treated as realities in the order of ideas, and appear in the chemical system as the necessary limits of our conceptions.

(4.) Similar ideas occur in every symbolic method. In symbolic chemistry 1, as the symbol of the unit of space, the subject of chemical operations, occupies the place held in the geometric calculus by 1, the symbol of the unit of length con-

sidered as the subject of the operations of geometry. Again, the chemical symbol  $\infty$  holds a position analogous to that occupied by the symbol 1 in the calculus of probabilities, as denoting the total subject matter of the science, and the chemical symbols 1 and  $\infty$ , the symbols of space and of the ponderable universe, represent in the calculus of chemistry the limits between which the values of all other symbols are comprised, precisely as in arithmetical algebra the corresponding limits are represented by the symbols 0 and  $\infty$ , and in the calculus of logic by the symbols 0 and 1.\*

#### SECTION IV.—ON THE FUNDAMENTAL CHEMICAL EQUATIONS.

(1.)  $xy$  is the symbol of a single weight which is composed of the same weights as those of which that group of weights is constituted of which  $x + y$  is the symbol. Now according to the definition which I have given of chemical identity, two weights are said to be identical which consist of the same weights (Sec. I., Def. 6). Hence the weight of which  $xy$  is the symbol is identical with the weight of which  $x + y$  is the symbol; and

$$xy = x + y.$$

In like manner, since  $\frac{x}{y}$  is the symbol of a single weight composed of the same weights as that of which the group of weights  $x - y$  is constituted,

$$\frac{x}{y} = x - y.$$

These equations may justly be termed the fundamental equations of the Chemical Calculus, for from them chemical symbols derive their distinctive character, and, through the limitations thus imposed upon them, are discriminated from numerical symbols, which in many respects they resemble.†

\* Boole, "Laws of Thought," p. 47.

† This equation occupies a somewhat similar place in the chemical calculus to that held in the logical system by the equation  $x^2 = x$  (Boole, "Laws of Thought," p. 81), as being expressive of a characteristic property by which the symbols are distinguished. The possibility of the existence of a class of symbols, other than the symbols of the logarithms of numbers, which should satisfy the condition

$$f(x) + f(y) = f(xy),$$

was indicated by D. F. Gregory in his paper "On the Real Nature of Symbolical Algebra" (Edin. Phil. Trans. vol. xiv, p. 208). This anticipation is here realized.

(2.) If, in the equation  $xy = x + y$ ,  $y = 1$ ,  $x1 = x + 1$ ; whence since  $x = x1$  and  $x - x = 0$ , we infer that

$$0 = 1.$$

This equation informs us of the identity of the ponderable matter of which 0 and 1 are the symbols, which has already been shown.

The same point may be proved in a similar manner as regards the other forms of the symbol 1. For since

$$\begin{aligned} x - x &= x - 1x, \\ x - x &= xx^{-1}, \end{aligned}$$

and

$$0 = x^0.$$

Or, since

$$\begin{aligned} mx &= x^m, \\ 0 &= x^0. \end{aligned}$$

And again, since

$$\frac{x}{y} = x - y,$$

if  $y = x$ ,

$$\frac{x}{x} = x - x,$$

and

$$\frac{x}{x} = 0.$$

We thus arrive from the general properties of chemical symbols at the same result as regards the forms of the symbol 1, and the interpretation of that symbol, as was inferred from the special interpretations of each form of that symbol.

(3.) If, in the equation  $xy = x + y$ ,  $x = 1$  and  $y = 1$ ,

$$1^2 = 1 + 1$$

and

$$1 = 2.$$

From this and the previous equation,  $0 = 1$ , it is to be inferred that

$$0 = 1 = 2 = 3 = \dots n.$$

It hence follows that any number of numerical symbols of this class may be added to a chemical function without affecting its



interpretation; a property which will hereafter be shown to admit of important applications. The reason of this is that in every independent symbol of number which enters into a chemical function the chemical symbol 1 is understood as the subject of operation, so that  $2 = 2 \times 1$ , and that this symbol has no interpretation in weight. We have a parallel to this property of chemical symbols in the property conferred upon numerical symbols by the factor 0, where

$$0 = 1 \times 0 = 2 \times 0 = 3 \times 0 = \dots n \times 0.$$

The chemical equation  $0 = 1$  may at the first glance appear paradoxical. But this apparent paradox arises merely from the associations connected with the interpretation of these symbols in those symbolic systems with which we are most familiar. In these systems there is a profound antithesis between the symbols, which reaches its climax in the logical system, where 0 is the symbol of nothing and 1 the symbol of the universe of thought.\* It need not, however, be a matter of surprise that in the chemical system we should have two symbols for "no weight," since in that system the same ponderable matter may be denoted by  $xy$  and  $x + y$ . Indeed it might even be expected from analogy that as a real weight may have several symbols, so the absence of weight should be expressed in more than one way. Nor is it, in truth, more singular or paradoxical that in chemistry 0 and 1 should be symbols denoting the same object, than that in geometry  $x^0$  and 1 should have the same interpretation.

Now it would appear that the symbols 0 and 1 may occur in a chemical function with two distinct interpretations, as chemical symbols and as arithmetical symbols, and that to prevent ambiguity, it might be desirable to make evident by some special notation the meaning to be assigned to them. But this is not necessary. The chemical symbol 1, although implicitly contained as the subject of operations in every chemical function, yet conformably to the principles of algebraic notation may be invariably suppressed, and every numerical symbol which appears in this calculus may be interpreted with its usual arithmetical signification, regard being had to those special properties which are derived from the subject on which it operates. If, for

\* Boole, "Laws of Thoughts," p. 48.

a moment, we discriminate between the chemical and arithmetical symbols 0 and 1, marking the former as 0' and 1', and the latter as (0) and (1), it is at once evident that  $(1) = (1)1' = 1'$ , and that  $(0) = (0)x = 0'$ . Hence we may in every case replace the chemical symbols 0' and 1' by the arithmetical symbols (0) and (1), which are, so far as the purposes of this calculus are concerned, identical with them both in interpretation and in properties. These symbols 0 and 1 may be termed the zero-symbols of the chemical system, being marks by which we denote the absence of ponderable matter. That such symbols may serve most important ends is evident from the use which has been made in arithmetic of the zero-symbol 0, which is the very key-stone of the arithmetical system; and yet it is not too much to assert that the system of chemical symbols without the zero-symbol 1 is as incomplete and as little adapted to the purpose which it is destined to fulfil as the arithmetical system would be deprived of the symbol 0.

(4.) No other known system of symbols is characterized by the same property as that by which chemical symbols are defined, but the equation  $x + y = xy$  is similar in form to the equation connecting the logarithms of numbers; and the relation which subsists between the absolute weight (or weight in grammes) of the ponderable matter of which  $x$  and  $y$  are the symbols is the same as the logarithmic relation. For, writing  $w(x)$  and  $w(y)$  as the absolute weights of the ponderable matter symbolized by  $x$  and  $y$ ,

$$\begin{aligned}w(x) + w(y) &= w(xy), \\w(1) + w(y) &= w(y), \\w(1) &= 0,\end{aligned}$$

similar in form with the logarithmic equations

$$\begin{aligned}l(x) + l(y) &= l(xy), \\l(1) + l(y) &= l(y), \\l(1) &= 0.\end{aligned}$$

The property of chemical symbols given in the equation  $x + y = xy$  may from these analogies appropriately be termed the "logarithmic" property of these symbols.

(5.) It is sufficiently obvious that we may operate between chemical equations by means of addition and subtraction as with numerical equations. This is a consequence of the axiom

that if identical weights be added to or removed from identical groups the resulting groups are identical. So that, if  $x = y$ , and  $x_1 = y_1$ ,  $x \pm x_1 = y \pm y_1$ . The operations, however, which correspond to the algebraic operations of multiplication and division can only be performed under certain conditions, which will be considered in a subsequent part of this memoir.

#### SECTION V.—ON THE SYMBOLS OF SIMPLE WEIGHTS.

(1.) A simple weight has been defined as a weight which is not compound, and two weights as simple in regard to one another which have no common component.

It follows from this definition that the symbol of a simple weight cannot be expressed by more than one factor, and also that the symbols of weights simple in regard to one another cannot have a common factor.

The symbol of a simple weight is termed a prime factor, and the symbols of weights simple in regard to one another are said to be prime to one another.

The symbols of simple weights have the following properties:—

(2.) The operations of algebraic subtraction and division cannot be performed between such symbols. For let  $a$  and  $b$  be two symbols of simple weights, and, if possible, let  $a - b = a_1$ . Then  $a = a_1 + b = a_1 b$ , that is,  $a$  is the symbol of a compound weight, which is contrary to the hypothesis.

Or again, if possible, let  $\frac{a}{b} = c$ . Then  $a - b = c$ , and  $a = b + c = bc$ , which is, as before, contrary to the hypothesis.

(3.) If  $a$  and  $b$  be two symbols of weights simple in regard to one another, and if  $aa_1 = bb_1$ , then

$$a_1 = bk, \text{ and } b_1 = ak;$$

for since  $aa_1 = bb_1$ ,  $a + a_1 = b + b_1$ , and  $a_1 = b + b_1 - a$ ; and since by hypothesis  $b$  is the symbol of a weight simple in regard to  $a$ , no part of  $a$  is a constituent of  $b$ , therefore  $a$  must be a constituent of  $b_1$ , so that  $b_1 = a + k$ , and  $a_1 = b + k$ . Whence also  $b_1 = ak$ , and  $a_1 = bk$ .

(4.) Hence also if  $a_1$  be the symbol of a weight simple in regard to the weights  $a$  and  $b$ ,  $a_1$  is the symbol of a weight simple in regard to the weight  $ab$ .

For otherwise, if possible, let  $a_1$  and  $ab$  have a common com-

ponent  $k$ , so that  $a_1 = ck$ , and  $ab = c_1k$ ; then, since by hypothesis  $k$  is a factor of  $a_1$ ,  $k$  is by hypothesis prime to  $a$ . Therefore  $k$  is a factor of  $b$ , which is also contrary to the hypothesis.

We may also argue thus. If possible, let  $k$  be the factor common to  $a_1$  and  $ab$ . Then  $ab = kd$ , and  $d = a + b - k$ . But by hypothesis no part of  $k$  is a constituent of  $a$ ; therefore  $k$  is a constituent of  $b$ , and  $b = k + c = kc$ , which is contrary to the hypothesis.

(5.) Hence if  $a$  is prime to  $b$ ,  $a^p$  is prime to  $b^q$ , and no part of  $qb$  is a constituent of  $pa$ ,  $p$  and  $q$  being positive and integral numbers.

(6.) Also, if  $a, b, c, d, \dots$  be prime to  $a_1, b_1, c_1, d_1, \dots$  then  $a^p b^{p_1} c^{p_2} d^{p_3} \dots$  is prime to  $a_1^{q_1} b_1^{q_2} c_1^{q_3} d_1^{q_4} \dots$  where  $p, p_1, p_2, p_3, \dots, q, q_1, q_2, q_3, \dots$  are positive and integral numbers; and also the operation of subtraction cannot be performed between the weights  $pa + p_1b + p_2c + p_3d + \dots$  and  $qa_1 + q_1b_1 + q_2c_1 + q_3d_1 + \dots$ .

(7.) Whence, if  $a, b, c, d, \dots$  be symbols prime to one another, and if

$$a^p b^{p_1} c^{p_2} d^{p_3} \dots = 1,$$

$$p = 0, p_1 = 0, p_2 = 0, p_3 = 0 \dots;$$

and if

$$pa + p_1b + p_2c + p_3d + \dots = 0,$$

$$p = 0, p_1 = 0, p_2 = 0, p_3 = 0 \dots$$

(8.) Lastly, a composite symbol can only be expressed in one manner by means of prime factors. That is to say, a compound weight can only be assumed to be composed of one set of simple weights. This proposition may be proved in the same manner as the corresponding numerical proposition.

This assertion does not imply that we cannot make more than one hypothesis as to the expression of any given composite symbol by means of prime factors, that is, as to the simple weights of which a given compound weight is composed, but only that two or more such hypotheses cannot simultaneously be true.

There is a close analogy between the symbols of simple weights in chemistry and the symbols of prime numbers in arithmetic, but owing to the condition imposed on chemical symbols, given in the equation  $x + y = xy$ , a chemical symbol which has only one factor is also incapable of partition.

The prime symbols of chemistry may be indifferently defined by either property, the one being a consequence of the other, and constitute a new and peculiar order of symbols. There is, however, one numerical symbol of the class, namely, the symbol 1, which has only one factor and one part, and like the primes of chemistry is incapable of division or partition.

(9.) An integral compound weight has been defined (Sec. I. Def. 9) as a weight which is composed of an integral number of simple weights. If  $\phi$  be the symbol of such a weight,  $a, b, c, \dots$ , as before, the symbols of simple weights, and  $n, n_1, n_2, \dots$  integral numbers,

$$\phi = a^n b^{n_1} c^{n_2} \dots$$

This symbol is termed an integral composite symbol. It is identical in form with the symbol of an integral number expressed by means of its prime factors.

(10.) It remains to consider the method by which we may arrive at the expression of chemical symbols by means of an integral number of prime factors in a given system of equations, if such an expression be possible, and further may select from the various forms of symbols which satisfy this condition that form in which the symbols are expressed by the smallest possible number of such factors. In this form the symbol is said to be expressed in the simplest possible manner by means of prime factors, it being the only symbolic expression which is at once both necessary and sufficient to satisfy the conditions of the problem.

To these conditions it is to be added that the prime factors thus chosen are to be the symbols of real weights, it being possible to find symbolic expressions which satisfy the requirements of the equation, but which do not admit of interpretation, the weights of which they are the symbols being affected with the negative sign. Such expressions will here be rejected.

Now, first let the system of equations in which it is required to express the chemical symbols by means of prime factors consist of one equation, and to render the problem determinate, let the equation contain only two undetermined symbols, and be of the form

$$m\phi + m'\phi_1 + m''\phi_2 = 0,$$

where  $m, m', m''$  are known, being positive or negative numerical

symbols; and let  $\phi_2 = a^n b^{n_1}$ ,  $a$  and  $b$  being the symbols of simple weights, and  $n, n_1$  given positive and integral numbers.

Then putting  $\phi = a^p b^{p_1}$ ,  $\phi_1 = a^q b^{q_1}$ ,

$$ma^p b^{p_1} + m'a^q b^{q_1} + m''a^n b^{n_1} = 0,$$

whence, from the fundamental equation  $x + y = xy$ ,

$$(a^p b^{p_1})^m (a^q b^{q_1})^{m'} (a^n b^{n_1})^{m''} = 1,$$

and from the property of simple weights before given (Sec. V. (7)).

$$\begin{aligned} mp + m'q + m''n &= 0, \\ mp_1 + m'q_1 + m''n_1 &= 0. \end{aligned}$$

The integral and positive solutions of these equations as regards  $p, q, p_1, q_1$ , if such can be found, will give all the possible ways by which the symbols  $\phi$  and  $\phi_1$  can be expressed by means of prime factors in the above equation, the symbol  $\phi_2$  being of the form given; and the minimum solution in whole numbers of these equations, as regards the same indeterminate quantities, will give the simplest expression of the symbols by means of prime factors, subject to the same condition.

The number of admissible forms of these symbols is, however, further limited by the requirement that the factors  $a$  and  $b$  are to be the symbols of real weights.

Putting  $W, W_1, W_2$  as the known absolute weights of the portions of matter of which  $\phi, \phi_1, \phi_2$  are the symbols, and  $w(a), w(b)$  as the unknown absolute weights of the simple weights of which  $a$  and  $b$  are the symbols, we have for the determination of  $w(a)$  and  $w(b)$  the equations

$$\begin{aligned} pw(a) + p_1w(b) &= W, \\ qw(a) + q_1w(b) &= W_1, \\ nw(a) + n_1w(b) &= W_2, \end{aligned}$$

which, subject to the equation of condition

$$mW + m'W_1 + m''W_2 = 0,$$

are equivalent to two independent equations. All values, therefore, of  $p, p_1, q, q_1$  are to be rejected which would give a negative value for  $w(a)$  or  $w(b)$  in the above equations.

If in the original equation the given symbol  $\phi_2$  be expressed by more than two factors, so that  $\phi_2 = a^n b^{n_1} c^{n_2}$ , the problem is

indeterminate unless the absolute weight of one of the simple weights be given; for in this case we should have only two equations to determine the three values  $w(a)$ ,  $w(b)$ ,  $w(c)$ .

Or again, if no symbol were given, so that  $\phi_2 = a^r b^q$ ,  $r$  and  $r_1$ , being indeterminate quantities, the indeterminate equations, whence the value in whole numbers of  $p$ ,  $p_1$ ,  $q$ ,  $q_1$ ,  $r$ ,  $r_1$  are to be ascertained, become

$$\begin{aligned} mp + m'q + m''r &= 0, \\ mp_1 + m'q_1 + m''r_1 &= 0, \end{aligned}$$

the two equations containing three indeterminate quantities.

If in the original equation two symbols were given as determined from other considerations, as that

$$\begin{aligned} \phi_2 &= a^r b^q, \\ \phi_1 &= a^t b^s, \end{aligned}$$

$s$ ,  $s_1$ ,  $t$ ,  $t_1$  being given positive and integral, the indeterminate equations would contain only one unknown quantity, and the problem would be possible in that case alone where the values of  $p$  and  $p_1$  derived from them were positive and integral, and where the conditions before referred to and given in the equations connecting  $w(a)$  and  $w(b)$  were satisfied.

The course to be pursued in other cases is sufficiently obvious from the above instance. It remains only to state the nature of the problem in its most general form.

If there be a system of  $N$  equations connecting the chemical symbols  $\phi$ ,  $\phi_1$ ,  $\phi_2$ ,  $\phi_3$ , . . . . of the form

$$m\phi + m'\phi_1 + m''\phi_2 + m'''\phi_3 + \dots = 0,$$

where  $m$ ,  $m'$ ,  $m''$ , . . . are numerical symbols, negative, positive, or 0, putting as before

$$\begin{aligned} \phi &= a^p b^q c^r \dots, \\ \phi_1 &= a^{p_1} b^{q_1} c^{r_1} \dots, \\ \phi_2 &= a^{p_2} b^{q_2} c^{r_2} \dots, \end{aligned}$$

we shall have  $N$  sets of indeterminate equations connecting  $p$ ,  $q$ ,  $r$ , . . . and  $p_1$ ,  $q_1$ ,  $r_1$ , . . . and  $p_2$ ,  $q_2$ ,  $r_2$ , . . . of the form

$$\begin{aligned} mp + m'q + m''r + \dots &= 0, \\ mp_1 + m'q_1 + m''r_1 + \dots &= 0, \\ mp_2 + m'q_2 + m''r_2 + \dots &= 0, \end{aligned}$$

If a common positive solution in whole numbers of these  $N$  sets of equations for

$$p, q, r, \dots, p_1, q_1, r_1, \dots, p_2, q_2, r_2, \dots$$

can be found, then the symbols  $\phi, \phi_1, \phi_2, \dots$  can be expressed in the given system of equations by means of the prime factors  $a, b, c, \dots$ ; if such a solution does not exist, then the symbols cannot be so expressed; and the simplest expression of the symbols  $\phi, \phi_1, \phi_2$  in that system of equations, by means of the prime factors  $a, b, c, \dots$  is that expression in which the indices  $p, p_1, p_2, \dots, q, q_1, q_2, \dots, r, r_1, r_2, \dots$  have the minimum integral values which satisfy the above  $N$  sets of indeterminate equations.

The admissible values are limited by the conditions

$$\begin{aligned} pw(a) + p_1w(b) + p_2w(c) \dots &= W, \\ qw(a) + q_1w(b) + q_2w(c) \dots &= W_1, \\ rw(a) + r_1w(b) + r_2w(c) \dots &= W_2, \\ \vdots & \\ \vdots & \end{aligned}$$

where  $w(a), w(b), w(c)$  are positive, and  $W, W_1, W_2, \dots$  are connected by  $N$  equations of the form

$$mW + m'W_1 + m''W_2 + m'''W_3 + \dots = 0.$$

SECTION VI.—ON THE CONSTRUCTION OF CHEMICAL EQUATIONS FROM THE DATA AFFORDED BY EXPERIMENT.

Our knowledge as to the identical relations of ponderable matter is derived, as has already been observed, exclusively from the science of chemistry. The next step in this inquiry is to embody in a system of chemical equations the information on this subject which experiment affords to us. The process is very simple by which this may be effected. To take, for example, a single instance. Let it be supposed that we have ascertained by experiment that 3,000 cub. centims. of chlorine and 2,000 cub. centims. of ammonia have been converted into 6,000 cub. centims. of hydrochloric acid, and 1,000 cub. centims. of nitrogen. We hence infer the identity of the ponderable matter of which the two groups respectively consist, and putting

- $\phi$  as the symbol of a unit of chlorine,
- $\phi_1$  as the symbol of a unit of ammonia,
- $\phi_2$  as the symbol of a unit of hydrochloric acid,
- $\phi_3$  as the symbol of a unit of nitrogen,



we assert this identity in the chemical equation

$$3\phi + 2\phi_1 = 6\phi_2 + \phi_3.$$

Proceeding in other cases in a similar manner, we should arrive at a system of equations corresponding in number to the experiments of which the results were thus recorded. It would soon, however, be perceived that we could not in this manner indefinitely add to our knowledge, but that the information thus supplied to us was soon exhausted, the equations not being independent, but capable of being derived from one another by the processes of addition and subtraction; and that, in fact, they could be replaced by a single system of equations connecting every chemical symbol equal in number to the total number of chemical substances, exclusive of the elemental bodies. Such a system is afforded to us by those equations which express the relations of identity which subsist between the ponderable matter of compound substances, and the ponderable matter of the elemental bodies of which they are composed, which we may consider as a solution of the entire system of chemical equations in regard to the symbols of the elements. From this primary system every other chemical equation may be derived, and our total knowledge as to the identical relations of ponderable matter is implicitly comprised in it. Indeed it may readily be shown that, however numerous may be our experiments, we can never arrive at any greater number of independent equations without effecting the decomposition of the elements. For if such an independent equation were discovered, it either would be an equation connecting the symbols of the elements themselves, or if it contained the symbols of other substances, we might eliminate between it and the other equations of the system, and thus derive such an equation. It is possible that the limited range of physical conditions under which we necessarily operate, or other obstacles equally insuperable, may for ever preclude such an addition to our knowledge, but nevertheless we can form a conception of another and a wider chemistry, of which our actual system should be but an imperfect fragment, and in which we should have  $n$  independent equations containing  $n + 1$  symbols admitting of a solution of the form

$$\phi = m\theta,$$

when we should recognize but one primary elemental form of

ponderable matter, and the great problem of analysis would be completely and finally resolved.

Every chemical equation is necessarily the expression of a hypothesis; for even the most accurate experiments are attended with error, and can only be regarded as affording a certain approximation to that true result at which it is our object to arrive. Even the assertion that two gaseous volumes of water consist of the same ponderable matter as two volumes of hydrogen, and one volume of oxygen involves hypothesis as to the gaseous densities of those substances, and the relations of absolute weight before and after chemical change, which go beyond our actual experience. Experiment proves this proposition to be true within certain limits of error, but in the equation

$$2\phi = 2\phi_1 + \phi_2,$$

an assertion is made in which the errors of observation are not included. Regard being had to the total evidence on which it rests, no statement of the kind is perhaps more credible than this; and the above equation may serve to mark the extreme limit to which chemical certainty has attained. Such equations form the true basis of the science.

It is, however, only in comparatively few instances that we are able to ascertain by direct observation the gaseous densities of all the chemical substances which enter into a reaction; and where this cannot be effected, we are compelled to have recourse to indirect methods of a less satisfactory character, to attain the desired end.

There are many admirable examples of such chemical reasoning,\* which, divested of the theoretical considerations with which they are unnecessarily complicated, may be regarded as arguments based upon actual observation of the laws of chemical change, by which certain forms of these equations are established with superior probability, to the exclusion of other forms. The conclusions thus arrived at must obviously have very different values, and while some are in the highest degree probable, others can only be regarded as tentative and conjec-

\* For example, Odling "On the Atomic Weight of Oxygen and Water," *Journal of the Chemical Society*, vol. xi, p. 107. Also the article in *Watts's Dictionary of Chemistry* by the same author "On the Atomic Weights of the Metals;" and Wurtz, "On the Oxide of Ethylene considered as a link between Organic and Inorganic Chemistry," *Journal of the Chemical Society*, vol. xv, p. 387.

tural. But, nevertheless, uncertain as such results may often appear, a profound distinction is to be drawn between this order of hypothesis, and those molecular speculations which can neither be confirmed nor disproved by facts. In the former case experiment is constantly controlling our conclusions, and we have the most positive evidence that the methods pursued by the chemist are in the main correct; since in numerous cases he has been able to anticipate the results of direct observation, and in others even to correct by theory the erroneous results which observation apparently afforded.

It is essential to have clear ideas upon this point, that we may not over-estimate the value of our results, since any uncertainty attached to the data must undoubtedly attend the conclusions which are derived from them; but nevertheless the question does not fall within the scope of a deductive and symbolic method, the province of which commences only where the task of experiment terminates; and in the consideration of chemical equations I have not, in uncertain cases, attempted any full discussion of the evidence on which they rest, but have limited myself to arguments, in regard to which the application of symbolic reasoning afforded some peculiarity or advantage.

#### SECTION VII.—ON THE SYMBOLS OF THE UNITS OF CHEMICAL SUBSTANCES.

Group 1.—*Symbols of Hydrogen, Oxygen, Sulphur, Selenium, Chlorine, Iodine, Bromine, Nitrogen, Phosphorus, Arsenic, and Mercury.*

(1.) *Symbol of Hydrogen.*—I am about to show by the aid of the principles which have been established in the previous pages that the units of chemical substances are composed of an integral number of simple weights; that is to say, according to the definition previously given (Sec. I., Defs. 9 and 10), that these units are “integral compound weights.” The point will be demonstrated, if it be found possible to express the symbols of these units in the actual system of chemical equations by means of an integral number of prime factors, these factors being the symbols of real weights (Sec. V. (9 & 10)). Now it will be found that such an expression is not only pos-

sible, but possible in a great variety of ways; in other words, many assumptions may be made as to the composition of ponderable matter which are consistent with the above fundamental hypothesis. From these possible expressions, that one will in each case be selected, as the correct inference from the facts, in which the symbol is expressed by the smallest possible number of such factors; since any other expression, as has before been indicated, must involve hypotheses which are unnecessary.

The problem is not dissimilar to that of the determination of the density or relative weight of the same units. We are about to estimate the number and the absolute weight of the simple weights of which the units (Sec. I., Defs. 8 & 10) of ponderable matter are composed; and, as in the former case the problem is unmeaning, unless the standard of absolute weight be previously determined, so in the latter case also it is necessary that some one simple weight shall be selected from external considerations as the standard of comparison, before any statement can be made upon the subject. This case, however, differs from the preceding in the circumstance that the selection of a simple weight is not the choice of an arbitrary unit, to be determined by considerations of convenience alone, but involves the assertion of a hypothesis as to the actual composition of the chemical units of ponderable matter, which may be verified and tested by experience.

Now the hypothesis on which the present method is based, and which is the only assumption of the kind which I shall have occasion to make, is that the unit of hydrogen is a simple weight, that is to say, that in chemical transformations this weight is never distributed (Sec. I., Def. 12). The symbol of this "weight" (Sec. I., Def. 3) will be expressed by the letter  $\alpha$ , which may be termed the "modulus" of the symbolic system, it being that symbol by which the form of every other symbol is regulated. The absolute weight of the portion of ponderable matter thus symbolized, that is to say, of 1,000 cub. centims. of hydrogen at 0° C., and 760 millims. pressure, is 0.089 gm.

In considering this question I shall select certain examples which may serve to illustrate the way in which the subject may be treated, and the difference in the result arrived at, according to the degree of information supplied to us by experiment.

The first, and for the present object the most important, group of symbols to be considered are the symbols of those

elements of which the density in the gaseous condition can be experimentally determined, and which also form with one another gaseous combinations. I shall then consider the symbols of carbon and its combinations with the previous group, and subsequently the symbols of certain other elements and their combinations as to which we possess less adequate information.

(2.) *Symbol of Oxygen.*—It is known from experiment that two units of water can be decomposed into two units of hydrogen, and one unit of oxygen. We hence infer the identity of the weights of which these portions of ponderable matter consist, and putting

$\phi$  as the symbol of the unit of water,  
 $\phi_1$  as the symbol of the unit of hydrogen,  
 $\phi_2$  as the symbol of the unit of oxygen,

$$2\phi = 2\phi_1 + \phi_2.$$

Now, if possible, let

$$\begin{aligned}\phi &= \alpha^m \xi^{m_1}, \\ \phi_1 &= \alpha, \\ \phi_2 &= \alpha^n \xi^{n_1},\end{aligned}$$

where  $\alpha$  and  $\xi$  are prime factors, that is to say, the symbols of simple weights, and  $m, m_1, n, n_1$  positive integers. Then

$$2\alpha^m \xi^{m_1} = 2\alpha + \alpha^n \xi^{n_1},$$

and from the fundamental equation which connects chemical symbols,  $x + y = xy$  (Sec. IV. (1)),

$$(\alpha^m \xi^{m_1})^2 = \alpha^3 \alpha^n \xi^{n_1},$$

whence

$$2m = 2 + n \text{ and } 2m_1 = n_1,$$

to which is attached the condition

$$\begin{aligned}w(\alpha) &= 1, \\ m + m_1 w(\xi) &= 9;\end{aligned}$$

1 and 9 being the densities of hydrogen and of water, and  $w(\alpha)$  and  $w(\xi)$  being positive.

The integral and positive solutions of these equations as regards  $m, m_1, n, n_1$ , give all the possible hypotheses which can be made as to the components of oxygen and of water, which

are consistent with the hypothesis, that the unit of each of these substances is composed of an integral number of simple weights, and that the unit of hydrogen is a simple weight, and the minimum solution selects from these that one hypothesis which is both necessary and sufficient to satisfy the condition given in the equation

$$2\phi = 2\phi_1 + \phi_2.$$

This solution is

$$\begin{aligned} n &= 0, & m &= 1, \\ n_1 &= 2, & m_1 &= 1, \end{aligned}$$

whence the symbols of water and oxygen as determined from considering the above equation are

$$\begin{aligned} \text{Symbol of water } &\alpha\xi, \\ \text{Symbol of oxygen } &\xi^2, \end{aligned}$$

and the relative weights corresponding to the prime factors  $\alpha$  and  $\xi$  are

$$\begin{aligned} w(\alpha) &= 1, \\ w(\xi) &= 8, \end{aligned}$$

the equation being thus expressed,

$$2\alpha\xi = 2\alpha + \xi^2.$$

It is not to be assumed without proof that these symbols will satisfy the conditions afforded by other equations. This is a matter for inquiry. But we have arrived at the knowledge that no symbol can be found for these substances composed of a smaller number of prime factors, and also that if these symbols can be so expressed, the indices of these factors will be found among the integral solutions of the above equations, which are given in the forms

$$\begin{aligned} m &= 1 + t, & n &= 2t, \\ m_1 &= 1 + t_1, & n_1 &= 2(1 + t_1). \end{aligned}$$

Hence we arrive at the following general forms for the symbol of oxygen and water,

$$\begin{aligned} \text{Oxygen } &\alpha^t \xi^{2(1+t)}, \\ \text{Water } &\alpha^{1+t} \xi^{1+t}, \end{aligned}$$

which include all the possible forms of symbols which satisfy the above conditions.

From the equation

$$m + m_1 w(\xi) = 9$$

we have, substituting for  $m$  and  $m_1$  the above values,

$$w(\xi)(1 + t_1) = 8 - t,$$

whence  $t$  is not greater than 8. If  $t = 8$ , either  $w(\xi) = 0$  and  $\xi = 1$  (Sec. III. (1)), or  $t_1 = -1$ , when  $n_1 = 0$ , and  $m_1 = 0$ ; in which case  $w(\xi) = \frac{0}{0}$  and may have any value. In either case we have

Symbol of oxygen  $\alpha^{16}$ ,  
 Symbol of water  $\alpha^9$ .

In this case, therefore, owing to the peculiar numerical relation which subsists between the densities, it is possible to express all the symbols by means of the one factor  $\alpha$ . The different forms of symbol are given by assigning to  $t$  and  $t_1$  all possible values; thus, for example,

		Symbol	
		Oxygen.	Water.
$t = 0$	$t_1 = 0$	$\xi^2$	$\alpha\xi$
	$t_1 = 1$	$\xi^4$	$\alpha\xi^2$
	$t_1 = 2$	$\xi^6$	$\alpha\xi^3$
	. . . . .		
$t = 1$	$t_1 = 0$	$\alpha^2\xi^2$	$\alpha^2\xi$
	$t_1 = 1$	$\alpha^2\xi^4$	$\alpha^2\xi^2$
	$t_1 = 2$	$\alpha^2\xi^6$	$\alpha^2\xi^3$
	. . . . .		
$t = 2$	$t_1 = 0$	$\alpha^4\xi^2$	$\alpha^3\xi$
	$t_1 = 1$	$\alpha^4\xi^4$	$\alpha^3\xi^2$
	$t_1 = 2$	$\alpha^4\xi^6$	$\alpha^3\xi^3$
	. . . . .		
$t = 3$	$t_1 = 0$	$\alpha^6\xi^2$	$\alpha^4\xi$
	$t_1 = 1$	$\alpha^6\xi^4$	$\alpha^4\xi^2$
	$t_1 = 2$	$\alpha^6\xi^6$	$\alpha^4\xi^3$
	. . . . .		
. . . . .			
. . . . .			
. . . . .			

		Symbol.	
		Oxygen.	Water.
$t = 7$	$t_1 = 0$	$\alpha^{14}\xi^2$	$\alpha^8\xi$
	$t_1 = 1$	$\alpha^{14}\xi^4$	$\alpha^8\xi^2$
	$t_1 = 2$	$\alpha^{14}\xi^6$	$\alpha^8\xi^3$
. . . . .			
$t = 8$	$t_1 = - 1$	$\alpha^{16}$	$\alpha^9$

The problem before us is the selection from this system of symbols of that symbol for oxygen (if such can be found) which shall satisfy the conditions afforded by the other equations of the system, and in which it shall be expressed by the smallest possible number of prime factors. Our hypothesis must be necessary as well as sufficient. Owing to the peculiar and simple laws which prevail in the actual system of chemical changes, this selection is attended with no difficulty. It will be found by trial that the symbol of oxygen,  $\xi^2$ , that symbol in which it is expressed by the smallest number of prime factors in the above equation, will satisfy all other known conditions.

There is only one other known compound of oxygen and hydrogen, the peroxide of hydrogen. Our knowledge as to this substance is very imperfect, but let us assume that it can be decomposed with the formation of water and oxygen, in the ratio of two units of water to one of oxygen. Then putting  $z$  as the unknown number of the volumes of the peroxide decomposed, and  $y$  as the number of volumes of oxygen formed, and  $\phi_3$ , as the symbol of peroxide of hydrogen,

$$z\phi_3 = 2y\phi + y\phi_2, \dots \dots \dots (1)$$

whence, substituting for  $\phi$  its value  $\phi_1 + \frac{\phi_2}{2}$ ,

$$z\phi_3 = 2y\phi_1 + 2y\phi_2;$$

and putting  $\alpha^p\xi^{p_1}$  as the symbol of the peroxide of hydrogen,  $\alpha$  as the symbol of hydrogen, and  $\xi^2$  of oxygen,

$$z\alpha^p\xi^{p_1} = 2y\alpha + 2y\xi^2 \dots \dots \dots (2)$$

and

$$(\alpha^p\xi^{p_1})^z = \alpha^{2y}(\xi^2)^{2y},$$

whence

$$\begin{aligned} zp &= 2y, \\ zp_1 &= 4y. \end{aligned}$$



Now, if  $p$  and  $p_1$  be positive integers, since  $z$  is prime to  $y$ ,  $z$  must be either 1 or 2.

If

$$z = 1, p = 2y, p_1 = 4y;$$

if

$$z = 2, p = y, p_1 = 2y.$$

In either case the above equation (2) is of the form

$$(\alpha\xi^2)^{p_1} = y_1(\alpha + \xi^2).$$

Now, although it undoubtedly cannot be considered that this equation is established with the same certainty as the equation

$$2\alpha\xi = 2\alpha + \xi^2,$$

yet regarded as a question of probability the evidence in favour of this view is very conclusive. For the only hypotheses involved in it are (1) that in this equation the symbol of the peroxide of hydrogen can be expressed by an integral number of prime factors, and (2) that the symbol of hydrogen can be expressed as  $\alpha$ , and the symbol of oxygen as  $\xi^2$ , in favour of which hypotheses we have (as will hereafter be seen) the evidence of an extensive and uniform experience.

We may proceed by the aid of further hypotheses, and still with great probability, to determine the value of  $y_1$  in this symbol. The most probable hypothesis is that  $y_1 = 1$ , and that the symbol of peroxide of hydrogen is  $\alpha\xi^2$ , in which case the above equation is thus expressed,

$$\alpha\xi^2 = \alpha + \xi^2.$$

The chief arguments by which this view is supported are derived from the observations (1) that it is very rarely that the indices of the prime factors of chemical symbols have a common measure; (2) that on this assumption the symbols of hydrogen, water, and peroxide of hydrogen constitute a series of the form  $\alpha, \alpha\xi, \alpha\xi^2$ ; and that the densities of these substances form an arithmetical progression, being 1, 9, 17; and that such series so frequently occur in the actual system of chemical symbols as to render probable their existence in the future system.

The conclusions at which we thus arrive are not to be regarded as necessarily final. Not only is it possible that further information as to the chemical properties of the peroxide of hydrogen might lead us to the adoption of a more complex

symbol, but we can even specify the very facts, the discovery of which would induce us to modify our opinion. But, nevertheless, the choice of the expression  $\alpha\xi^2$  as the symbol of the unit of this substance is not an arbitrary and conventional selection. It expresses the most probable opinion which, with our actual knowledge, we can form as to the nature of the equation from which it is derived, and which we provisionally embody in the symbol for the purpose of tracing the consequences of our hypothesis.

The weight of that portion of any chemical substance which I have termed the chemical unit of ponderable matter, is (Sec. I., Def. (10)) the weight of that portion of each substance which in the gaseous condition, at  $0^\circ$  C. and 760 millims. pressure, occupies the space of 1,000 cub. centims. This weight may be measured in two ways; either by comparison with the weight of a cubic centimetre of distilled water at  $4^\circ$  C., or by comparing it with the weight of the chemical unit of hydrogen. We shall hence have two series of numbers by which the weights of the portions of ponderable matter resulting from any chemical operation are expressed, viz.,

1. The absolute weight in grammes.
2. The relative weight or density as compared with the weight of the unit of hydrogen. This second series of numbers may also be regarded as expressing the absolute weight of the units of ponderable matter as estimated in "criths" \*.

*Combinations of the Prime Factors  $\alpha$  and  $\xi$ .*

Name of substance.	Prime factors.	Absolute weight, in grammes.	Relative weight.
		$\alpha$ $\xi$	0.089 0.715
	Symbol.		
Hydrogen .....	$\alpha$	0.089	1
Oxygen† .....	$\xi^2$	1.430	16
Water .....	$\alpha\xi$	0.805	9
Peroxide of hydrogen .....	$\alpha\xi^2$	1.520	17

\* Hofmann, *loc. cit.* (Sec. I (11)).

† In calculating the absolute weight, it is necessary to assume the absolute weight of the gaseous litre at  $0^\circ$  and 760 millims. pressure, of some one substance as accurately determined. The weight of a litre of oxygen is here assumed as the standard, and the other numbers are calculated from it.

(3.) *Symbol of Sulphur.*—It has been shown by the recent experiments of Deville and Troost that the density of the vapour of sulphur above a temperature of  $860^{\circ}$  C. becomes constant, and approximates to 32, the density of hydrogen being 1. This being the case, the ponderable matter of 2 units of sulphide of hydrogen is identical with the ponderable matter of 2 units of hydrogen and 1 unit of sulphur. Hence, putting  $\alpha^{m}\theta^{m_1}$  as the symbol of sulphide of hydrogen, and  $\alpha^n\theta^{n_1}$  as the symbol of sulphur,

$$2\alpha^{m}\theta^{m_1} = 2\alpha + \alpha^n\theta^{n_1},$$

and

$$(\alpha^{m}\theta^{m_1})^2 = \alpha^2\alpha^n\theta^{n_1},$$

and

$$2m = 2 + n, \quad 2m_1 = n_1,$$

whence

$$\begin{aligned} n &= 0, & m &= 1, \\ n_1 &= 2, & m_1 &= 1, \end{aligned}$$

a minimum.

And putting the density of sulphide of hydrogen as 17,

$$m + m_1w(\theta) = 17,$$

and

$$w(\theta) = 16.$$

Hence we have, as satisfying the conditions afforded by the above equation,

$$\begin{array}{l} \text{Symbol of sulphur} \quad . . . . . \theta^2, \\ \text{Symbol of sulphide of hydrogen} \quad \alpha\theta. \end{array}$$

If we assume the density of sulphur to be correct as determined before the recent experiments referred to, the simplest statement which can be made as to the decomposition of sulphide of hydrogen is, that 6 volumes of sulphide of hydrogen are decomposed into 6 volumes of hydrogen and 1 volume of sulphur-vapour; in which case

$$(\alpha^{m}\theta_1^{m_1})^6 = \alpha^6\alpha^n\theta_1^{n_1},$$

and

$$6m = 6 + n, \quad 6m_1 = n_1,$$

which gives as the minimum solution

$$\begin{aligned} n &= 0, & m &= 1, \\ n_1 &= 6, & m_1 &= 1, \end{aligned}$$

and

$$w(\theta_1) = 16.$$

Hence

$$\theta_1 = \theta.$$

The symbols, therefore, may be in either case expressed by the same prime factors.

In the latter case, we have

Symbol of sulphur . . . . .  $\theta^6$ ,  
 Symbol of sulphide of hydrogen as before  $\alpha\theta$ .

By similar reasoning to that employed in the determination of the symbol of the peroxide of hydrogen, we arrive at the following symbols.

*Combinations of the Prime Factors  $\alpha$ ,  $\xi$ , and  $\theta$ .*

Name of substance.	Prime factors.	Absolute weight, in grammes.	Relative weight.
	$\theta$		
	Symbol.		
Sulphur .....	$\theta^2$	2·861	32
Protosulphide of hydrogen ....	$\alpha\theta$	1·520	17
Bisulphide of hydrogen.....	$\alpha\theta^2$	2·950	33
Sulphurous anhydride .....	$\theta\xi^2$	2·861	32
Sulphuric anhydride .....	$\theta\xi^3$	3·576	40
Sulphurous acid.....	$\alpha\theta\xi^3$	3·665	41
Sulphuric acid .....	$\alpha\theta\xi^4$	4·380	49
Nordhausen sulphuric acid ....	$\alpha^2\theta\xi^7$	7·956	89
Hyposulphurous acid.....	$\alpha^2\theta\xi^3$	5·095	57
Dithionic acid.....	$\alpha^2\theta\xi^6$	7·241	81
Trithionic acid .....	$\alpha^3\theta\xi^6$	8·671	97
Tetrathionic acid .....	$\alpha^4\theta\xi^6$	10·101	113
Pentathionic acid .....	$\alpha^5\theta\xi^6$	11·532	129

(4.) *Symbol of Selenium.*—The vapour-density of selenium exhibits similar anomalies to the vapour-density of sulphur. But from the experiments of Deville there can be little doubt that at a sufficiently high temperature it would accord with theory. Deville found for the vapour-density of selenium at 860°, 8·2, and at 1040°, 6·37. On the hypothesis that 2 volumes of selenide of hydrogen are decomposed into 2 volumes of hydrogen and 1 volume of selenium, the vapour-density of selenium would be expressed by the number 5·44. I shall assume this as the correct number.

We have, then, putting  $\alpha^m \lambda^{n_1}$  as the symbol of selenide of hydrogen, and  $\alpha^n \lambda^{n_1}$  as the symbol of selenium,

$$2\alpha^m \lambda^{n_1} = 2\alpha + \alpha^n \lambda^{n_1},$$

whence, as in the last two examples,

$$2m = 2 + n, \quad 2m_1 = n_1,$$

and

$$\begin{aligned} n &= 0, & n_1 &= 2, \\ m &= 1, & m_1 &= 1, \end{aligned}$$

a minimum.

Assuming the density of selenide of hydrogen as 41,

$$w(\lambda) = 40.$$

*Combinations of the Prime Factors  $\alpha$ ,  $\xi$ ,  $\theta$ , and  $\lambda$ .*

Name of substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
		$\lambda$	3.576
	Symbol.		
Selenium.....	$\lambda^2$	7.151	80
Selenide of hydrogen .....	$\alpha\lambda$	3.665	41
Selenious anhydride .....	$\lambda\xi^2$	5.006	56
Selenic anhydride .....	$\lambda\xi^3$	5.721	64
Selenious acid.....	$\alpha\lambda\xi^3$	5.810	65
Selenic acid.....	$\alpha\lambda\xi^4$	6.526	73

(5.) *Symbol of Chlorine.*—It is ascertained by experiment that 2 volumes of hydrochloric acid can be decomposed into 1 volume of hydrogen and 1 volume of chlorine.

Hence, putting  $\alpha^m \chi^{m_1}$  as the symbol of the unit of hydrochloric acid, and  $\alpha^n \chi^{n_1}$  as the symbol of the unit of chlorine,

$$2\alpha^m \chi^{m_1} = \alpha + \alpha^n \chi^{n_1},$$

and

$$(\alpha^m \chi^{m_1})^2 = \alpha \alpha^n \chi^{n_1};$$

whence

$$2m = 1 + n,$$

$$2m_1 = n_1,$$

and

$$m = 1, \quad m_1 = 1,$$

$$n = 1, \quad n_1 = 2,$$

a minimum.

Since the density of hydrochloric acid is 18·25, we have to determine the absolute weight of the simple weight  $\chi$ ,

$$m + m_1 w(\chi) = 18\cdot25,$$

whence

$$w(\chi) = 17\cdot25,$$

which gives for the

Symbol of hydrochloric acid  $\alpha\chi$ ,  
 Symbol of chlorine.....  $\alpha\chi^2$ ,

in which case the above equation becomes

$$2\alpha\chi = \alpha + \alpha\chi^2.$$

The general solutions of the above equations, which contain all possible values of the indices of the symbols, give

$$\begin{aligned} m &= 1 + t, & m_1 &= 1 + t_1, \\ n &= 1 + 2t, & n_1 &= 2(1 + t_1), \end{aligned}$$

whence we arrive at the following general forms,

Hydrochloric acid  $\alpha^{1+t}\chi^{1+t_1}$ ,  
 Chlorine.....  $\alpha^{1+2t}\chi^{2(1+t_1)}$ ,

and

$$w(\chi) = \frac{17\cdot25 + t}{1 + t_1};$$

whence

$$t \text{ is not } > 17,$$

and

$$t_1 \text{ is not } < 0.$$

*Combinations of the Prime Factors  $\alpha$ ,  $\xi$ ,  $\theta$ ,  $\lambda$ , and  $\chi$ .*

Name of substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\chi$	1·542.	17·25
	Symbol.		
Chlorine .....	$\alpha\chi^2$	3·178	35·5
Hydrochloric acid .....	$\alpha\chi$	1·681	18·25
Protoxide of chlorine .....	$\alpha\chi^2\xi$	3·888	43·5
Teroxide of chlorine .....	$\alpha\chi^2\xi^2$	5·319	59·5
Tetroxide of chlorine .....	$\alpha\chi^2\xi^3$	6·084.	67·5
Hypochlorous acid.....	$\alpha\chi\xi$	2·346	26·25
Chlorous acid .....	$\alpha\chi\xi^2$	3·062	34·25
Chloric acid .....	$\alpha\chi\xi^3$	3·777	42·25
Perehloric acid .....	$\alpha\chi\xi^4$	4·492	50·25
Hydrate of chlorine .....	$\alpha\chi^2\xi^2\theta$	11·219	125·5
Protosulphide of chlorine.....	$\alpha\chi^2\theta$	4·604	52·5
Bisulphide of chlorine .....	$\alpha\chi^2\theta^2$	6·084	67·5
Biselenide of chlorine .....	$\alpha\chi^2\lambda^2$	10·325	115·5
Tetrachloride of selenium.....	$\alpha\chi^2\lambda^4$	9·922	111
Chlorosulphurous acid .....	$\alpha\chi^2\xi$	5·219	59·5
Hydrochlorosulphurous acid.....	$\alpha\chi^2\xi^2$	5·207	58·25
Chlorosulphuric acid.....	$\alpha\chi^2\theta\xi^2$	6·084	67·5

(6.) *Symbol of Iodine.*—Two volumes of hydriodic acid are decomposed into 1 volume of hydrogen and 1 volume of iodine.

Hence, putting  $\alpha^m\omega^m$  as the symbol of the unit of hydriodic acid, and  $\alpha^n\omega^n$  as the symbol of the unit of iodine,

$$2\alpha^m\omega^m = \alpha + \alpha^n\omega^n,$$

and

$$(\alpha^m\omega^m)^2 = \alpha\alpha^n\omega^n,$$

and

$$\begin{aligned} 2m &= 1 + n, & 2m_1 &= n_1, \\ m &= 1, & m_1 &= 1, \\ n &= 1, & n_1 &= 2, \end{aligned}$$

a minimum.

Assuming the density of iodine vapour to be 127,

$$\begin{aligned} 1 + 2w(\omega) &= 127, \\ w(\omega) &= 63, \end{aligned}$$

and the symbol of hydriodic acid is  $\alpha\omega$ , and of iodine  $\alpha\omega^2$ , in which case the above equation is thus expressed,

$$2\alpha\omega = \alpha + \alpha\omega^2.$$

*Combinations of the Prime Factors  $\alpha$ ,  $\xi$ ,  $\theta$ ,  $\lambda$ ,  $\chi$ , and  $\omega$ .*

Name of substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\omega$		
		5·632	63
	Symbol.		
Iodine .....	$\alpha\omega^3$	11·353	127
Hydriodic acid .....	$\alpha\omega$	5·721	64
Iodic anhydride .....	$\alpha\omega^2\xi^5$	14·923	167
Per-iodic anhydride .....	$\alpha\omega^3\xi^7$	16·359	183
Iodic acid .....	$\alpha\omega\xi^3$	7·866	88
Protochloride of iodine .....	$\alpha\omega\chi$	7·263	81·25
Terchloride of iodine .....	$\alpha^2\omega\chi^3$	10·436	116·75

(7.) *Symbol of Bromine.*—Two volumes of hydrobromic acid are decomposed into 1 volume of hydrogen and 1 volume of bromine.

Hence, putting  $\alpha^m\beta^m$  as the symbol of the unit of hydrobromic acid, and  $\alpha^m\beta^{m_1}$  as the symbol of the unit of bromine,

$$2\alpha^m\beta^m = \alpha + \alpha^m\beta^{m_1},$$

and by similar reasoning to that by which the symbols of chlorine and iodine have been ascertained, we have

$$\begin{aligned} \text{Symbol of hydrobromic acid } & \alpha\beta, \\ \text{Symbol of bromine.....} & \alpha\beta^2, \end{aligned}$$

and assuming 80 as the density of bromine,

$$w(\beta) = 39\cdot5.$$

*Combinations of the Prime Factors  $\alpha$ ,  $\xi$ ,  $\theta$ ,  $\lambda$ ,  $\chi$ ,  $\omega$ , and  $\beta$ .*

Name of substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\beta$		
		3·531	39·5
	Symbol.		
Bromine .....	$\alpha\beta^2$	7·151	80
Hydrobromic acid .....	$\alpha\beta$	3·620	40·5
Protoxide of bromine .....	$\alpha\beta^2\xi$	7·866	88
Hypobromous acid.....	$\alpha\beta\xi$	4·335	43·5
Bromic acid .....	$\alpha\beta\xi^3$	5·766	54·5

(8.) *Symbol of Nitrogen.*—Two volumes of ammonia can be



decomposed into 3 volumes of hydrogen and 1 volume of nitrogen.

Hence, putting  $\alpha^n \nu^m$  as the symbol of the unit of ammonia, and  $\alpha^n \nu^{n_1}$  as the symbol of the unit of nitrogen,

$$2\alpha^m \nu^{m_1} = 3\alpha + \alpha^n \nu^{n_1},$$

and

$$(\alpha^m \nu^{m_1})^2 = \alpha^2 \alpha^n \nu^{n_1};$$

whence

$$2m = 3 + n, \quad 2m_1 = n_1,$$

and

$$\begin{aligned} m &= 2, & m_1 &= 1, \\ n &= 1, & n_1 &= 2, \end{aligned}$$

a minimum.

Hence the symbol of nitrogen as determined from this equation is  $\alpha \nu^2$ , and the symbol of ammonia is  $\alpha^2 \nu$ .

Since the density of ammonia is 8.5,

$$2 + w(\nu) = 8.5,$$

and

$$w(\nu) = 6.5.$$

The general solutions of the above equations give

$$\begin{aligned} m &= 2 + t, & m_1 &= 1 + t_1, \\ n &= 1 + 2t, & n_1 &= 2(1 + t_1), \end{aligned}$$

whence we have as the

$$\begin{aligned} \text{Symbol of ammonia} &\dots\dots\dots \alpha^{2+t} \nu^{1+t_1}, \\ \text{Symbol of nitrogen} &\dots\dots\dots \alpha^{1+2t} \nu^{2(1+t_1)}, \end{aligned}$$

and

$$w(\nu) = \frac{6.5 - t}{1 + t_1},$$

where  $t$  is not  $> 6$ , and  $t_1$ , not  $< 0$ .

*Combinations of the Prime Factors  $\alpha, \xi, \theta, \chi, \lambda, \omega, \beta,$  and  $\nu$ .*

Name of substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\nu$	0.581	6.5
	Symbol.		
Nitrogen .....	$\alpha^2$	1.251	14
Ammonia .....	$\alpha^2\nu$	0.760	8.5
Protoxide of nitrogen .....	$\alpha^2\xi$	1.967	22
Binoxide of nitrogen* .....	$\alpha^2\xi^2$	2.682	30
Teroxide of nitrogen .....	$\alpha^2\xi^3$	3.397	38
Pentoxide of nitrogen .....	$\alpha^2\xi^4$	4.112	46
Nitrous acid .....	$\alpha\nu\xi^2$	4.827	54
Nitric acid .....	$\alpha\nu\xi^3$	2.101	23.5
Bisulphide of nitrogen .....	$\alpha\nu^2\xi^2$	2.816	31.5
Chloride of nitrogen .....	$\alpha^2\nu^2$	4.112	46
Nitrite of ammonium .....	$\alpha^2\nu^2\xi$	5.386	60.25
Nitrate of ammonium .....	$\alpha^2\nu^2\xi^2$	2.861	32
Sulph-hydrate of ammonium ..	$\alpha^2\nu^2\xi^3$	3.576	40
Protosulphide of ammonium ..	$\alpha^2\nu^2$	2.279	25.5
Bisulphide of ammonium .....	$\alpha^2\nu^2\xi$	3.039	34
Acid sulphite of ammonium ..	$\alpha^2\nu^2\xi^2$	4.470	50
Acid sulphate of ammonium ..	$\alpha^2\nu^2\xi^3$	4.424	49.5
Sulphite of ammonium .....	$\alpha^2\nu^2\xi^4$	5.139	57.5
Sulphate of ammonium .....	$\alpha^2\nu^2\xi^5$	5.285	58
Thionamic acid† .....	$\alpha^2\nu^2\xi^4$	6.000	66
Sulphamic acid .....	$\alpha^2\nu^2\xi^5$	3.620	40.5
Thionamide .....	$\alpha^2\nu^2\xi^6$	4.336	48.5
Sulphamide .....	$\alpha^2\nu^2\xi^7$	3.576	40
Acid sulphate of azotyl .....	$\alpha^2\nu^2\xi^8$	4.281	46
Neutral sulphate of azotyl .....	$\alpha\nu^2\xi^3$	5.676	63.5
Anhydro-sulphate of azotyl ..	$\alpha\nu^2\xi^4$	6.972	78
Chloride of ammonium* .....	$\alpha\nu^2\xi^5$	9.118	102
Chloride of azotyl† .....	$\alpha^2\nu^2\xi^6$	2.391	26.75
Chloride of nitryl† .....	$\alpha^2\nu^2\xi^7$	2.928	32.75
Bichloride of azotyl .....	$\alpha\nu^2\xi^8$	3.642	40.75
Chlorate of ammonium .....	$\alpha^2\nu^2\xi^9$	5.944	66.5
Iodide of ammonium .....	$\alpha^2\nu^2\xi^{10}$	4.537	50.75
Diniodamide .....	$\alpha^2\nu^2$	6.481	72.5
Bromide of ammonium .....	$\alpha^2\nu^2$	12.023	134.5
	$\alpha^2\nu^2$	4.380	49

(9.) *Symbol of Phosphorus.*—Let the symbol of the unit of phosphorus be  $\alpha^*\phi^m$ , and the symbol of the unit of gaseous phosphide of hydrogen  $\alpha^m\phi^m$ . Then, since 4 volumes of the gaseous phosphide of hydrogen are decomposed into 6 volumes of hydrogen and 1 volume of phosphorus-vapour,

$$4\alpha^m\phi^m = 6\alpha + \alpha^*\phi^m,$$

\* The symbols of nitric oxide, chloride of ammonium, and certain other substances, the densities of which are apparently anomalous, will be subsequently considered (see Section VIII).

† See Odling's "Chemistry," pages 269, 254, and 261.

and

$$(\alpha^m \phi^{m_1})^4 = \alpha^6 \alpha^n \phi^{n_1},$$

whence

$$4m = 6 + n, \quad 4m_1 = n_1,$$

and

$$m = 2, \quad m_1 = 1,$$

$$n = 2, \quad n_1 = 4,$$

a minimum; and we have for the

Symbol of phosphide of hydrogen  $\alpha^2 \phi$ ,

Symbol of phosphorus.....  $\alpha^2 \phi^4$ .

Assuming the density of phosphorus-vapour as 62,

$$2 + 4w(\phi) = 62,$$

$$w(\phi) = 15.$$

*Combinations of the Prime Factors  $\alpha, \xi, \theta, \lambda, \chi, \omega, \beta, \nu$ , and  $\phi$ .*

Name of substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\phi$	1·841	15
	Symbol.		
Phosphorus.....	$\alpha^2 \phi^4$	5·541	62
Phosphide of hydrogen.....	$\alpha^2 \phi$	1·519	17
Teroxide of phosphorus.....	$\alpha \phi^2 \xi^2$	4·916	55
Pentoxide of phosphorus.....	$\alpha \phi^2 \xi^5$	6·846	71
Hypophosphorous acid.....	$\alpha^2 \phi \xi^2$	2·949	33
Phosphorous acid.....	$\alpha^2 \phi \xi^3$	3·664	41
Orthophosphoric acid.....	$\alpha^2 \phi \xi^4$	4·379	49
Pyrophosphoric acid.....	$\alpha^2 \phi^2 \xi^7$	7·956	89
Metaphosphoric acid.....	$\alpha \phi \xi^3$	3·574	40
Protosulphide of phosphorus ..	$\alpha \phi^2 \theta$	4·201	48
Tersulphide of phosphorus ...	$\alpha \phi^3 \theta^3$	7·061	80
Tetrasulphide of phosphorus ..	$\alpha \phi^4 \theta^6$	9·921	112
Tetrachloride of phosphorus ...	$\alpha^2 \phi \chi^2$	6·145	68·75
Pentachloride of phosphorus ..	$\alpha^2 \phi \chi^3$	9·819	104·25
Oxychloride of phosphorus ....	$\alpha^2 \phi \chi^2 \xi$	6·869	76·75
Terbromide of phosphorus ....	$\alpha^2 \phi \beta^3$	12·112	135·5
Pentabromide of phosphorus ...	$\alpha^2 \phi \beta^5$	19·264	215·5
Oxybromide of phosphorus ....	$\alpha^2 \phi \beta^2 \xi$	12·827	143·5
Bromide of phosphonium.....	$\alpha^2 \phi \beta$	5·140	57·5
Biniodide of phosphorus.....	$\alpha^2 \phi \omega^2$	25·476	285
Teriodide of phosphorus.....	$\alpha^2 \phi \omega^3$	18·413	206
Iodide of phosphonium.....	$\alpha^2 \phi \omega$	7·240	81
Sulphochloride of phosphorus..	$\alpha^2 \phi \chi \theta$	7·575	84·75

(10.) *Symbol of Arsenic.*—The density of the chloride of arsenic has been determined by Dumas, the density of arsenic-vapour by Mitscherlich.

Four volumes of the chloride of arsenic are decomposed into 1 volume of arsenic and 6 volumes of chlorine.

Hence, putting  $\alpha^m \chi^{m_1} \xi^{m_2}$  as the symbol of the unit of chloride of arsenic, and  $\alpha^n \chi^{n_1} \xi^{n_2}$  as the symbol of the unit of arsenic, and  $\alpha \chi^3$  as the symbol of the unit of chlorine,

$$4\alpha^m \chi^{m_1} \xi^{m_2} = 6\alpha \chi^3 + \alpha^n \chi^{n_1} \xi^{n_2},$$

and

$$(\alpha^m \chi^{m_1} \xi^{m_2})^4 = (\alpha \chi^3)^6 \alpha^n \chi^{n_1} \xi^{n_2};$$

whence

$$4m = 6 + n, \quad 4m_1 = 12 + n_1, \quad 4m_2 = n_2.$$

The minimum solution of these equations gives

$$\begin{array}{ll} m = 2, & n = 2, \\ m_1 = 3, & n_1 = 0, \\ m_2 = 1, & n_2 = 4; \end{array}$$

and we have, as thus determined,

$$\begin{array}{ll} \text{Symbol of arsenic} & \dots\dots\dots \alpha^2 \xi^4, \\ \text{Symbol of terchloride of arsenic} & \dots \alpha^2 \chi^3 \xi. \end{array}$$

Assuming 150 as the density of the vapour of arsenic,

$$\begin{array}{l} 2 + 4w(\xi) = 150, \\ w(\xi) = 37. \end{array}$$

*Combinations of the Prime Factors  $\alpha$ ,  $\xi$ ,  $\theta$ ,  $\chi$ ,  $\dots$  and  $\rho$ .*

Name of substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\rho$	3·308	37
	Symbol.		
Arsenic .....	$\alpha^2 \xi^4$	13·408	150
Arsenide of hydrogen .....	$\alpha^2 \rho$	3·485	39
Teroxide of arsenic .....	$\alpha^2 \xi^4 \rho^5$	17·689	198
Pentoxide of arsenic .....	$\alpha^2 \xi^5$	10·279	115
Arsenious acid .....	$\alpha^2 \rho \xi^3$	5·630	63
Arsenic acid .....	$\alpha^2 \rho \xi^5$	6·345	71
Bisulphide of arsenic .....	$\alpha \rho^2 \xi^2$	9·563	107
Tersulphide of arsenic .....	$\alpha \rho^3 \xi^3$	10·995	123
Pentasulphide of arsenic .....	$\alpha \rho^5 \xi^5$	13·856	155
Terchloride of arsenic .....	$\alpha^3 \rho \chi^3$	8·111	90·75
Oxychloride of arsenic .....	$\alpha \rho \chi \xi$	5·653	63·25
Teriodide of arsenic .....	$\alpha^2 \rho \omega^3$	20·379	228
Terbromide of arsenic .....	$\alpha^2 \rho \delta^3$	14·078	157·5

(11.) *Symbol of Mercury.*—Assuming 100 as the density of the vapour of mercury, and 135.5 as the density of the vapour of mercuric chloride, 1 volume of mercuric chloride is decomposed into 1 volume of chlorine and 1 volume of mercury.

Hence, putting  $\alpha^m \chi^{m_1} \delta^{m_2}$  as the symbol of the unit of mercuric chloride, and  $\alpha^n \chi^{n_1} \delta^{n_2}$  as the symbol of the unit of mercury,

$$\alpha^m \chi^{m_1} \delta^{m_2} = \alpha \chi^2 + \alpha^n \chi^{n_1} \delta^{n_2},$$

and

$$\alpha^m \chi^{m_1} \delta^{m_2} = \alpha \chi^2 \alpha^{n_1} \chi^{n_1} \delta^{n_2};$$

whence

$$m = 1 + n, \quad m_1 = 2 + n_1, \quad m_2 = n_2.$$

The minimum solution of these equations gives

$$\begin{array}{ll} m = 1, & n = 0, \\ m_1 = 2, & n_1 = 0, \\ m_2 = 1, & n_2 = 1; \end{array}$$

whence we have

$$\begin{array}{ll} \text{Symbol of mercuric chloride} & \dots \alpha \chi^2 \delta, \\ \text{Symbol of mercury} & \dots \dots \delta, \end{array}$$

and

$$w(\delta) = 100.$$

*Combinations of the Prime Factors  $\alpha, \xi, \theta, \lambda, \chi, \dots$  and  $\delta$ .*

Name of substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\delta$	8·939	100
	Symbol.		
Mercury .....	$\delta$	8·939	100
Mercurous oxide .....	$\delta^2\xi$	18·593	208
Mercuric oxide .....	$\delta\xi$	9·654	108
Mercurous sulphide .....	$\delta^2\theta$	19·309	216
Mercuric sulphide .....	$\delta\theta$	10·369	116
Mercuric sulphite .....	$\delta\theta\xi^3$	12·514	140
Basic mercuric sulphite .....	$\delta^2\theta\xi^4$	22·169	248
Mercurous sulphate .....	$\delta^2\theta\xi^4$	22·169	248
Mercuric sulphate .....	$\delta\theta\xi^4$	13·280	148
Basic mercuric sulphate (Tur- peth's mineral) .....	$\delta^2\theta\xi^5$	32·539	364
Sulphate and sulphide of mercury	$\delta^2\theta^2\xi^4$	32·539	364
Selenide of mercury .....	$\delta\lambda$	12·515	140
Mercurous selenite .....	$\delta^2\lambda\xi^3$	23·600	264
Mercuric selenite .....	$\delta\lambda\xi^3$	14·661	164
Mercurous chloride .....	$\alpha\chi^2\theta^3$	21·051	235·5
Mercuric chloride .....	$\alpha\chi^2\theta$	12·118	135·5
Oxychloride of mercury, 1 .....	$\alpha\chi^2\theta^2\xi^3$	31·421	351·5
Oxychloride of mercury, 2 .....	$\alpha\chi^2\theta^2\xi^3$	41·075	459·5
Oxychloride of mercury, 3 .....	$\alpha\chi^2\theta^2\xi^4$	50·730	567·5
Mercurous chlorate .....	$\alpha\chi^2\theta^2\xi^5$	25·342	283·5
Mercuric chlorate .....	$\alpha\chi^2\theta^2\xi^5$	16·404	183·5
Mercurous perchlorate .....	$\alpha\chi^2\theta^2\xi^6$	26·772	299·5
Mercuric perchlorate .....	$\alpha\chi^2\theta^2\xi^6$	17·834	199·5
Chloride of mercury and sulphur	$\alpha\chi^4\theta^2\theta$	25·655	287
Mercurous iodide .....	$\alpha\omega^2\theta^2$	29·231	327
Intermediate iodide .....	$\alpha^3\omega^6\theta^4$	69·814	781
Mercuric iodide .....	$\alpha\omega^2\theta$	20·292	227
Mercurous iodate .....	$\alpha\omega^2\theta^2\xi^6$	33·521	375
Mercuric iodate .....	$\alpha\omega^2\theta^2\xi^6$	24·583	275
Mercurous bromide .....	$\alpha\zeta^2\theta^2$	25·029	280
Mercuric bromide .....	$\alpha\zeta^2\theta$	16·090	180
Trimercuramine .....	$\alpha\omega^2\theta^3$	28·069	314
Mercurous nitrate .....	$\alpha\omega^2\theta^2\xi^6$	23·420	262
Mercuric nitrate .....	$\alpha\omega^2\theta^2\xi^6$	14·481	162
Nitrate and sulphide of mercury	$\alpha\omega^2\theta^2\alpha^2\xi^6$	35·220	394
Nitrate and iodide of mercury ..	$\alpha\omega\omega\theta^2\xi^6$	17·386	194·5
Mercuramine .....	$\alpha^2\omega^2\theta^2\xi^3$	39·332	440
* A .....	$\alpha^2\omega\gamma\theta$	20·179	225·75
B .....	$\alpha^2\omega\gamma\theta$	11·240	125·75
C .....	$\alpha^2\omega\gamma^2\theta$	13·632	152·5
Mercurous phosphate .....	$\alpha\theta^2\theta^2\xi^6$	62·128	695
Mercuric phosphate .....	$\alpha\theta^2\theta^2\xi^6$	35·310	395

The preceding tables comprise a large number of the ascertained combinations of the prime factors to which they relate,

\* A. Formed by the action of ammonia on calomel. B. Formed by the action of ammonia on corrosive sublimate. C. Formed by the action of B on sal-ammoniac.

and afford sufficient illustration of the method. Hereafter I shall limit myself, in the case of each factor, to a few examples.

With regard to the selection of letters by which the symbols of simple weights may be expressed, it is a mistake to confuse the objects of a symbolic system with those of a "memoria technica," and I am inclined to believe that a purely accidental distribution of letters among the weights to be expressed would be the best. In the selection here made, however, I have not proceeded rigidly upon this principle, a certain reminiscence of the name being retained in the symbol, as for example, the  $\xi$  of  $\delta\xi\upsilon\varsigma$ , the  $\theta$  of  $\theta\epsilon\acute{\iota}\omicron\nu$ , the  $\chi$  of  $\chi\lambda\alpha\rho\acute{\omicron}\varsigma$ , and the  $\delta$  of  $\acute{\iota}\delta\rho\acute{\alpha}\rho\gamma\upsilon\rho\omicron\varsigma$ . Facility of writing and reading the symbol is, however, far more important than any aid to memory which can be thus afforded, and these points are to be mainly considered. The unit of hydrogen, which occupies a peculiar position as the "modulus" of the system, is indicated by a special symbol,  $\alpha$ . With regard to names, I cannot pretend to be more successful than others. In the confusion which at present prevails on this point it is almost impossible to use a language which shall be universally understood, new names having been frequently and inconsiderately assigned to chemical substances as the expression of some transitory theory, or even individual speculation, rather than to fulfil the main purpose of words, as the common medium for the exchange of ideas. Hence, as in the language of barbarous tribes\* and from causes similar to those which there prevail, the same object comes to be denoted by a variety of appellations, and chemists of different schools can hardly understand one another. It is to be hoped that, as the science gradually assumes a more exact form, the use of symbols will enable the chemist to dispense, to a great extent, with any other nomenclature, and afford a satisfactory solution to this difficult problem.

### Group 2.—*Symbols of Carbon, Silicon, and Boron.*

(1.) *Symbol of Carbon.*—Although the density of the vapour of carbon has never been determined by experiment, we are yet

\* "Any feature that struck the observing mind as peculiarly characteristic could be made to furnish a new name. In common Sanskrit dictionaries we find five words for land, eleven for light, fifteen for cloud, twenty for moon, &c."—Max Müller, "Lectures on the Science of Language," Ed. v, p. 426. It would be easy to find parallel examples in the nomenclature of chemistry.

able to construct numerous chemical equations which connect the vapour-density of carbon with known vapour-densities, and in which the number of volumes of carbon-vapour which enters into the chemical equation appears as an indeterminate quantity. From these equations we are able to determine with a high degree of probability, though doubtless only by the aid of hypothesis, the symbols of many gaseous compounds of carbon, the prime factor of carbon, and, within certain limits, the symbol of the element itself.

It is known from experiment that marsh-gas can be decomposed into hydrogen and carbon, and that the number of volumes of hydrogen formed in this decomposition is twice the number of volumes of marsh-gas decomposed.

Hence, putting  $y$  as the number of units of marsh-gas thus decomposed, and  $x$  as the number of units of the vapour of carbon formed, and putting  $\alpha^m x^{m_1}$  as the symbol of marsh-gas, and  $\alpha^n x^{n_1}$  as the symbol of carbon,

$$y\alpha^m x^{m_1} = 2y\alpha + x\alpha^n x^{n_1}, \quad \dots \dots \dots (1)$$

whence

$$(\alpha^m x^{m_1})^y = \alpha^{2y} (\alpha^n x^{n_1})^x,$$

and

$$my = 2y + nx,$$

$$m_1 y = n_1 x.$$

Now, whatever be the values of  $y$  and  $x$ , these equations will admit of a minimum integral solution, provided only that  $y$  and  $x$  be integral numbers.

This solution is

$$\begin{array}{ll} m = 2, & m_1 = x, \\ n = 0, & n_1 = y. \end{array}$$

As determined, therefore, from this equation, we have

$$\begin{array}{ll} \text{Symbol of marsh-gas} \dots\dots\dots & \alpha^2 x^x, \\ \text{Symbol of carbon} \dots\dots\dots & x^y. \end{array}$$

Assuming 8 as the density of marsh-gas,

$$2 + xw(x) = 8,$$

whence

$$xw(x) = 6;$$

and putting  $W$  as the density of carbon-vapour,

$$W = \frac{6y}{x},$$



the above equation (1) being thus expressed,

$$y(\alpha^2 x^2) = 2y\alpha + x x^2.$$

We now should proceed to ascertain whether the same symbol,  $x^2$ , for carbon will satisfy the conditions afforded by other equations. I will give one or two examples of the process by which this is effected.

It is known from experiment that  $y_1$  volumes of olefiant gas are decomposed into  $2y_1$  volumes of hydrogen and  $x_1$  volumes of carbon-vapour. Hence the absolute weight of carbon formed by the decomposition of a unit of olefiant gas is

$$\frac{x_1 W}{y_1}.$$

But this weight is determined by experiment, and is equal to twice the weight of carbon formed by the decomposition of a unit of marsh-gas, which weight is equal to  $\frac{x}{y}W$ . Hence

$\frac{x_1}{y_1} = \frac{2x}{y}$ ; and putting  $\alpha^p x^p$  as the symbol of olefiant gas, and  $x^2$ , as before, as the symbol of carbon,

$$y\alpha^p x^p = 2y\alpha + 2x x^2,$$

and

$$p = 2, \quad p_1 = 2x,$$

whence we have the symbol of olefiant gas  $\alpha^2 x^2$ ; and the symbol of carbon can be expressed in this equation also as  $x^2$ , where  $y$  has the value given in equation (1).

Again, by similar reasoning, putting  $\alpha^q x^q$ , for example, as the symbol of styrol,

$$y\alpha^q x^q = 4y\alpha + (x)^{8x},$$

whence

$$q = 4, \quad q_1 = 8x,$$

and we have as the symbol of styrol  $\alpha^4 x^{8x}$ .

The following are the examples of symbols thus determined:—

Marsh-gas .....	$\alpha^2 x^2$ .
Acetylene .....	$\alpha x^{2x}$ .
Olefiant gas.....	$\alpha^2 x^{2x}$ .
Methyl.....	$\alpha^3 x^{2x}$ .
Propylene .....	$\alpha^3 x^{3x}$ .

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It is to be observed that the weight to be given to an argument of this kind may become very small, if the observations on which it is founded are few, and made exclusively on one class of substances. Thus, for example, if the course of chemical inquiry had been such as to make us acquainted only with the following substances: olefiant gas, methyl, ethyl, butylene, oxide of ethylene, glycol, alcohol, ether, acetic acid, and other substances of which the symbols can be expressed by the factor  $x^z$ , and of which the symbols are  $\alpha^2x_1^2$ ,  $\alpha^3x_1^3$ ,  $\alpha^6x_1^6$ ,  $\alpha^4x_1^4$ ,  $\alpha^3x_1^3\xi$ ,  $\alpha^2x_1^2\xi^2$ ,  $\alpha^3x_1^3\xi$ ,  $\alpha^6x_1^6\xi$ ,  $\alpha^2x_1^2\xi^2$ ,  $\alpha^3x_1^3\xi^2$ , and the like, where  $z = 2x$ , we should, by similar reasoning, have concluded that the symbols of the compounds of carbon could be expressed by the prime factor  $x_1$ , of which the absolute weight  $w(x_1) = 12$ , and that  $x_1$  was the symbol of a simple weight, a result which would not have been justified by a more extended experience.

We are able to bring to bear upon the symbol of carbon certain arguments of a very general application, and which are derived from direct experiment. If we compare the chemical equations into which enter the symbols of the units of volume of those elements of which the density can be experimentally determined, it will be perceived that, putting  $A$  as the smallest weight of the element which is in any case formed in the decomposition of the unit of any chemical substance, and  $V$  as the density of the element, either  $A = V$ , as in the case of mercury, or  $A = \frac{V}{2}$ , as in the case of hydrogen, chlorine, iodine, bromine, nitrogen, oxygen, sulphur, selenium, or  $A = \frac{V}{4}$ , as in the case of phosphorus and arsenic.

The truth of the above observation will be seen on inspecting the following equations, which have already been interpreted.

I.  $A = V$ . Mercury:—

$$\alpha\chi^3 = \alpha\chi^2 + \delta.$$

II.  $A = \frac{V}{2}$ . Hydrogen, chlorine, iodine, bromine, nitrogen, oxygen, sulphur, selenium:—

$$\begin{aligned} 2\alpha\chi &= \alpha + \alpha\chi^2, \\ 2\alpha\omega &= \alpha + \alpha\omega^2, \\ 2\alpha\beta &= \alpha + \alpha\beta^2, \\ 2\alpha\xi &= 2\alpha + \xi^2, \end{aligned}$$

$$\begin{aligned}2\alpha\theta &= 2\alpha + \theta^2, \\2\alpha\lambda &= 2\alpha + \lambda^2, \\2\alpha^2\nu &= 3\alpha + \alpha\nu^2.\end{aligned}$$

III.  $A = \frac{V}{4}$ . Phosphorus and arsenic:—

$$\begin{aligned}4\alpha^2\phi &= 6\alpha + \alpha^2\phi^4, \\4\alpha^2\chi^2\varrho &= 5\alpha\chi^2 + \alpha^2\varrho^4.\end{aligned}$$

This weight A, which may be regarded as the limit beyond which the chemical division of the weight of unit of the elemental body cannot be effected, is, it will be observed, half the atomic weight of the element on the most recent and approved system. And it is further true, as a matter of observation, that if X be the weight of an elemental body which is formed in the decomposition of the unit of volume of any chemical substance, X is a multiple of A, so that  $X = NA$ , where N is a positive integer. The relation which this weight holds to the thermal properties of the element will hereafter be pointed out.

From these considerations a certain probability is raised in regard to the value of V, where the value cannot be experimentally determined, in favour of the values  $V = A$ ,  $V = 2A$ ,  $V = 4A$ .

The smallest weight of carbon, A, which is formed by the decomposition of the unit of volume of any chemical substance, in regard to which the point can be experimentally ascertained, is that which is formed by the decomposition of the unit of volume of marsh-gas, formic acid, methylic alcohol, and a few other substances.

Now, the equation which asserts the identity of the unit of weight of marsh-gas with the units of hydrogen and carbon into which it is resolved, is

$$y\alpha^2x^2 = 2y\alpha + \alpha x^2,$$

whence

$$A = \frac{x}{y} V.$$

There are, therefore, from these considerations, three hypotheses more probable than others which may be made as to the value  $\frac{x}{y}$ .

1.  $A = V, \frac{x}{y} = 1, x = 1, y = 1 :—$

Symbol of carbon .....  $x$ ,  
 Symbol of marsh-gas.....  $\alpha^2x$ ,

in which case the equation is of the form,

$$\alpha^2x = 2\alpha + x.$$

2.  $A = \frac{V}{2}, \frac{x}{y} = \frac{1}{2}, x = 1, y = 2 :—$

Symbol of carbon .....  $x^2$ ,  
 Symbol of marsh-gas.....  $\alpha^2x$ ,

and

$$2\alpha^2x = 4\alpha + x^2.$$

3.  $A = \frac{V}{4}, \frac{x}{y} = \frac{1}{4}, x = 1, y = 4 :—$

Symbol of carbon .....  $x^4$ ,  
 Symbol of marsh-gas.....  $\alpha^2x$ ,

and

$$4\alpha^2x = 8\alpha + x^4.$$

The symbol of marsh-gas (and therefore the symbols of every other compound of carbon) is the same, whichever hypothesis be preferred; being, so far, independent of the form of the primary equation.

There is no class of symbols in regard to which the direct evidence of experiment either entirely or partially fails us, as to which we have more positive knowledge than the symbols of those substances of which the vapour-density can be experimentally determined, and which can be finally decomposed into carbon and the gaseous elements. The formulæ of these substances are usually given with unhesitating confidence, and even the vapour-density of carbon is treated as a reality. The evidence, however, on the former point is far more satisfactory than that on the latter; and with our present information, all that can be asserted with any high degree of probability is that the weight of the unit of carbon is a multiple of 6.

As the extreme limit of chemical certainty is marked by the equation

$$2\alpha\xi = 2\alpha + \xi^2,$$

so the equation

$$y\alpha^2x = 2y\alpha + x^y$$

may serve to indicate another degree in the same scale of chemical probability; the assumption here made being all that is truly required to determine the symbol of marsh-gas, by which the symbols of the other compounds of carbon are implicitly determined.

Between the forms of equation

$$\alpha^2 x = 2\alpha + x$$

and

$$2\alpha^2 x = 4\alpha + x^2,$$

we have no adequate means of selection.

*Combinations of the Prime Factors  $\alpha$ ,  $\xi$ ,  $\theta$ ,  $\lambda$ ,  $\chi$ ,  $\omega$ , . . . . and  $x$ .*

Name of substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$x$	0.536	6
	Symbol.		
Carbon*	$x$	$y \times 0.536$	$y \times 6$
Acetylene	$\alpha x^2$	1.161	13
Marsh-gas	$\alpha^2 x$	0.704	8
Olefiant gas	$\alpha^2 x^2$	1.251	14
Benzole	$\alpha^2 x^3$	3.486	39
Carbonic oxide	$x\xi$	1.251	14
Carbonic acid	$x\xi^2$	1.967	22
Alcohol	$\alpha^2 x^2 \xi$	2.056	23
Ether	$\alpha^2 x^4 \xi$	3.308	37
Allylic alcohol	$\alpha^2 x^2 \xi$	2.592	29
Benzyl alcohol	$\alpha^2 x^4 \xi$	4.827	54
Glycol	$\alpha^2 x^2 \xi^2$	2.771	31
Glycerine	$\alpha^2 x^4 \xi^2$	4.112	46
Anhydrous acetic acid	$\alpha^2 x^4 \xi^3$	4.559	51
Acetic peroxide	$\alpha^2 x^4 \xi^4$	5.274	59
Lactic acid	$\alpha^2 x^4 \xi^2 \theta$	4.028	45
Tetrachloride of carbon	$\alpha^2 x^4 \xi^2$	7.411	83
Chloride of ethylene	$\alpha^2 x^2 \xi^2$	4.425	49.5
Chloroform	$\alpha^2 x^4 \xi$	5.341	59.75
Chloride of acetyl	$\alpha^2 x^4 \xi^2$	3.509	39.25
Chloroacetic acid	$\alpha^2 x^4 \xi^2 \theta$	4.224	47.25
Trichloroacetic acid	$\alpha^2 x^4 \xi^2 \theta^2$	7.308	81.75
Chlorocarbonic acid	$\alpha^2 x^4 \xi^2$	4.425	49.5
Iodide of ethyl	$\alpha^2 \omega x^2$	6.973	78
Chloriodide of ethylene	$\alpha^2 \omega x^2 \xi^2$	8.515	95.25
Cyanogen	$\alpha^2 x^2$	2.324	26
Hydrocyanic acid	$\alpha x x$	1.207	13.5
Methylamine	$\alpha^2 x x$	1.386	15.5
Kakodyl	$\alpha^2 \theta^2 x^4$	9.386	105
Cyanide of kakodyl	$\alpha^2 \omega x^2$	5.855	65.5
Iodide of phosphotetreylium	$\alpha^4 \omega \theta x^2$	12.247	137
Mercuric ethide	$\alpha^2 x^4 \theta$	11.532	129

\*  $y$  being the number of units of marsh-gas in the equation (1), Sec. VII, Group 2 (1).

(2.) *Symbol of Silicon.*—In the decomposition of chloride of silicon it has been ascertained that the volume of chlorine formed is double the volume of the chloride of silicon decomposed.

Hence, putting  $\alpha^m \chi^{m_1} \sigma^{m_2}$  as the symbol of the unit of chloride of silicon, and  $\alpha^n \chi^{n_1} \sigma^{n_2}$  as the symbol of the unit of silicon, and  $z$  as the number of units of chloride of silicon decomposed, and  $z_1$  as the number of units of silicon formed, we have

$$z\alpha^m \chi^{m_1} \sigma^{m_2} = 2z\alpha \chi^2 + z_1 \alpha^n \chi^{n_1} \sigma^{n_2},$$

and

$$(\alpha^m \chi^{m_1} \sigma^{m_2})^z = (\alpha \chi^2)^{2z} (\alpha^n \chi^{n_1} \sigma^{n_2})^{z_1};$$

whence

$$zm = 2z + z_1 n,$$

$$zm_1 = 4z + z_1 n_1,$$

$$zm_2 = z_1 n_2,$$

which give

$$m = 2, \quad n = 0,$$

$$m_1 = 4, \quad n_1 = 0,$$

$$m_2 = z_1, \quad n_2 = z,$$

a minimum, whatever be the values of  $z$  and  $z_1$ , if only  $z$  and  $z_1$  be positive and integral.

This gives as the symbol of chloride of silicon  $\alpha^2 \chi^4 \sigma^{z_1}$ , and the symbol of silicon  $\sigma^z$ ; and assuming 85 as the density of the chloride of silicon,

$$2 + 4 \times 17.25 + z_1 w(\sigma) = 85,$$

and

$$w(\sigma) = \frac{14}{z_1}.$$

Again, in the decomposition of silicon-ethyl it has been experimentally ascertained that putting  $z_2$  as the number of volumes of silicon-ethyl decomposed, and  $z_3, z_4, z_5$  as the number of volumes of hydrogen, carbon, and silicon respectively formed by its decomposition,

$$\frac{z_3}{z} = 10, \quad \frac{z_4}{z} = \frac{8x}{y}, \quad \text{and} \quad \frac{z_5}{z} = \frac{z_1}{z},$$

where  $\frac{x}{y}$  is the ratio of the number of volumes of carbon formed to the number of volumes of marsh-gas decomposed, in the

equation expressing the result of the decomposition of that substance (Sec. VII. Group 2 (1)), and  $z$  and  $z_1$  have the values assigned to them in the previous equation. Hence, putting  $\alpha^m x^{m_1} \sigma^{m_2}$  as the symbol of silicon-ethyl,  $x^y$  as the symbol of carbon, and  $\sigma^z$  as the symbol of silicon, and substituting the above values for  $z_2, z_3, z_4, z_5$ , in the equation

$$z_2 \alpha^m x^{m_1} \sigma^{m_2} = z_3 \alpha + z_4 x^y + z_5 \sigma^z,$$

we have

$$yz \times \alpha^m x^{m_1} \sigma^{m_2} = 10yz \times \alpha + 8xz \times x^y + yz_1 \times \sigma^z,$$

whence

$$(\alpha^m x^{m_1} \sigma^{m_2})^{yz} = \alpha^{10yz} (x^y)^{8xz} (\sigma^z)^{yz_1},$$

and

$$m = 10, \quad m_1 = 8x, \quad m_2 = z_1;$$

and we have for the symbol of silicon-ethyl, as determined from experiment,  $\alpha^{10} x^{8z} \sigma^{z_1}$ , or, putting  $x = 1$  (Sec. VII. Group 2 (1)), as in the symbols of the other compounds of carbon,  $\alpha^{10} x^8 \sigma^{z_1}$ .

Proceeding in a similar manner with the other gaseous compounds of silicon, we have

	Symbol.
Chloride of silicon . . . . .	$\alpha^2 \chi^4 \sigma^{z_1}$ .
Silicon-ethyl . . . . .	$\alpha^{10} x^8 \sigma^{z_1}$ .
Silicate of ethyl . . . . .	$\alpha^{10} x^8 \xi^4 \sigma^{z_1}$ .
Silicate of amyl . . . . .	$\alpha^{32} x^{30} \xi^4 \sigma^{z_1}$ .
Monochlorhydrine of silicate of ethyl	$\alpha^8 \chi x^6 \xi^3 \sigma^{z_1}$ .

Now there is but one hypothesis which can be made as to the value of  $z_1$ , which is at once necessary and sufficient, namely that  $z_1 = 1$ . The reasoning here employed is of the same kind as that by which the symbols of the combinations of carbon were determined; but the observations being few, the conclusion is of a less certain character. By a similar argument also to that before used in regard to the value of  $A$ , it may be shown that there is great reason to believe that  $z_1 = 1$ , or = 2, or = 4. It is not necessary, however, to make any other assumption than that  $z = 1$ , in which case the density of silicon-vapour is a multiple of 14, which is all that can be asserted with probability.

Putting  $z_1 = 1$ , we have the following symbols:—



*Combinations of the Prime Factors  $\alpha, \xi, \theta, \chi, \dots$  and  $\sigma$ .*

Name of substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\sigma$	1.251	14
	Symbol.		
Silicon.....	$\sigma^2$	$z \times 1.251$	$z \times 14$
Silica .....	$\sigma\xi^2$	2.682	30
Monohydrated silicic acid.....	$\alpha\sigma\xi^3$	3.486	39
Sulphide of silicon.....	$\sigma\theta^2$	4.112	46
Chloride of silicon.....	$\alpha^2\chi^4\sigma$	7.598	85
Bromide of silicon.....	$\alpha^2\beta^4\sigma$	15.554	174
Silicon-ethyl .....	$\alpha^{10}\chi^8\sigma$	6.436	72
Silicate of ethyl .....	$\alpha^{10}\chi^8\xi^4\sigma$	9.297	104
Silicate of amyl .....	$\alpha^{22}\chi^{20}\xi^4\sigma$	11.442	128
Monochlorhydrin of silicate of ethyl .....	$\alpha^8\chi^8\xi^8\sigma$	8.872	99.25

(3.) *Symbol of Boron.*—In the decomposition of the chloride of boron into its elements, one volume of that substance is decomposed with the formation of  $1\frac{1}{2}$  volume of chlorine. Hence, if  $y_1$  be the smallest integral number of units of the chloride of boron decomposed, and  $y_2$  the number of units of boron formed in the decomposition,  $\frac{y_1}{y_2} = \frac{2}{3}$ ; and putting  $\alpha^m\chi^{m_1}\beta_1^{m_2}$  as the symbol of the terchloride of boron,  $\alpha^n\chi^{n_1}\beta_1^{n_2}$  as the symbol of boron,

$$2y_1\alpha^m\chi^{m_1}\beta_1^{m_2} = 3y_1\alpha\chi^2 + y_2\alpha^n\chi^{n_1}\beta_1^{n_2};$$

whence

$$(\alpha^m\chi^{m_1}\beta_1^{m_2})^{2y_1} = (\alpha\chi^2)^{3y_1}(\alpha^n\chi^{n_1}\beta_1^{n_2})^{y_2},$$

and

$$\begin{aligned} 2y_1m &= 3y_1 + y_2n, \\ 2y_1m_1 &= 6y_1 + y_2n_1, \\ 2y_1m_2 &= y_2n_2. \end{aligned}$$

From the first of these equations it appears (since  $y_2$  and  $y_1$  have no common measure) that  $y_2$  cannot be an even number, if the equation is to admit of an integral solution. Making this assumption, we have, putting  $y_2 = 1 + 2z$ ,

$$\begin{aligned} m &= 2 + z, & n &= y_1, \\ m_1 &= 3, & n_1 &= 0, \\ m_2 &= 1 + 2z, & n_2 &= 2y_1, \end{aligned}$$

a minimum, which give

Symbol of chloride of boron ..  $\alpha^{3+z}\chi^3\beta_1^{1+2z}$ ,  
 Symbol of boron .....  $\alpha^{21}\beta_1^{22}$ .

Also, since 5.5 parts of boron are formed by the decomposition of 1 volume of chloride of boron of the density 58.75, putting W as the density of boron-vapour;

$$\frac{y_2 W}{2y_1} = \frac{y_2(1 + 2w(\beta_1))}{2} = 5.5,$$

and putting  $y_2 = 1 + 2z$ ,

$$w(\beta_1) = \frac{5 - z}{1 + 2z}.$$

Again, putting  $\alpha^m x^m \beta_1^{2m}$  as the symbol of boric methide, and (as before)  $\frac{x}{y}$  as the number of volumes of carbon formed by the decomposition of one volume of marsh-gas, and giving to  $y_1$  and  $y_2$  the same values as in the last equation, it is known from experiment that

$$2yy_1 \alpha^m x^m \beta_1^{2m} = 9yy_1 \alpha + 6xy_1 x^y + yy_2 \alpha^{21} \beta_1^{22};$$

whence

$$\begin{aligned} 2m &= 9 + y_2, \\ 2m_1 &= 6x, \\ m_3 &= y_2; \end{aligned}$$

and putting  $y_2 = 1 + 2z$ , and  $x = 1$ ,

$$\begin{aligned} m &= 5 + z, \\ m_1 &= 3, \\ m_2 &= 1 + 2z, \end{aligned}$$

and we have for the symbol of boric methide  $\alpha^{5+z} x^3 \beta_1^{1+2z}$ .

Proceeding in a similar manner with the other gaseous combinations of boron, we arrive at the following symbols:—

	Symbol.
Boron .....	$\alpha^{21}\beta_1^{22}$ .
Chloride of boron .....	$\alpha^{3+z}\beta_1^{1+2z}\chi^3$ .
Boric methide .....	$\alpha^{5+z}\beta_1^{1+2z}x^3$ .
Boric ethide .....	$\alpha^{8+z}\beta_1^{1+2z}x^6$ .
Trimethylic borate .....	$\alpha^{5+z}\beta_1^{1+2z}x^3\xi^3$ .
Triethylic borate .....	$\alpha^{8+z}\beta_1^{1+2z}x^6\xi^3$ .
Triamyllic borate .....	$\alpha^{17+z}\beta_1^{1+2z}x^{15}\xi^3$ .

By similar reasoning to that employed in the case of silicon, we are led to assume in this system of symbols  $z = 0$ , which results in the system given in the following table.

*Combinations of the Prime Factors  $\alpha$ ,  $\xi$ ,  $\theta$ ,  $\chi$ , . . . . and  $\beta_1$ .*

Name of Substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\beta_1$	0.447	5
	Symbol.		
Boron . . . . .	$\alpha^2\beta_1^{2y}$	$y \times 0.988$	$y \times 11$
Teroxide of boron . . . . .	$\alpha\beta_1^2\xi^3$	3.129	35
Boracic acid . . . . .	$\alpha^2\beta_1\xi^3$	2.771	31
Terchloride of boron . . . . .	$\alpha^2\beta_1\chi^3$	5.252	58.75
Nitride of boron . . . . .	$\alpha\beta_1\gamma$	1.117	12.5
Boric methide . . . . .	$\alpha^2\beta_1\gamma^2$	2.503	28
Trimethyl borate . . . . .	$\alpha^2\beta_1\gamma^2\xi^3$	4.648	52
Triethyl borate . . . . .	$\alpha^2\beta_1\gamma^2\xi^3$	6.534	73
Triamyl borate . . . . .	$\alpha^{17}\beta_1\gamma^{15}\xi^3$	12.157	136
Boric ethide . . . . .	$\alpha^2\beta_1\gamma^6$	4.380	49

If we proceed to determine the most probable symbol of boron by aid of the hypothesis  $A = V$ , or  $A = \frac{V}{2}$ , or  $A = \frac{V}{4}$

(Sec. VII. Group 2 (1)), we have in case (i)  $A = V$ ,  $\frac{y_2}{2y_1} = 1$ , which admits of no integral solution,  $y_2$  being odd and  $y_1$  prime to  $y_2$ ; in case (ii)  $A = \frac{V}{2}$ ,  $\frac{y_2}{2y_1} = \frac{1}{2}$ , and  $y_2 = 1$ ,  $y_1 = 1$ ; in case

(iii)  $A = \frac{V}{4}$ ,  $\frac{y_2}{2y_1} = \frac{1}{4}$ , and  $y_2 = 1$ ,  $y_1 = 2$ . Hence the more probable symbols for boron (from these considerations) are  $\alpha\beta_1^2$  and  $\alpha^2\beta_1^2$ , between which we cannot decide.

The symbols which have been assigned to the gaseous compounds of the preceding elements, silicon and boron, are to be regarded as the symbolic expression of the most probable hypothesis as to their chemical constitution, which is consistent with the known facts of gaseous combination. What weight, we may ask, is to be attached to such conclusions? Now, it has already been remarked that the weight to be given to such hypotheses primarily depends upon the number of cases to which they are applicable. But in the case of these elements we are acquainted only with a very limited number of gaseous

compounds; and it must be admitted that, regarded exclusively from this point of view, but little value could be attached to any inference at which we thus arrive; for the conclusions drawn from six or seven instances, accidentally selected, would not improbably be negatived by a more extended experience. But our judgment is in truth based upon considerations of a far more complex character; and it would be unreasonable not to extend our view to the probabilities derived from other sources of the inferences to which the various hypotheses lead, and which often enable us to select among them.

For example, in the symbol of the chloride of boron,  $\alpha^{2+z}\chi^3\beta_1^{1+2z}$ , the value of  $z$  is necessarily limited only by the condition  $w(\beta_1) = \frac{5-z}{1+2z}$  whence  $z$  is less than 5. But if we

proceed to assign to  $z$  the different values 0, 1, 2, 3, 4, it will be found that on the first hypothesis,  $z = 0$ , the combinations of the prime factor  $\beta_1$  form a system strictly similar in the laws of their construction to the system of the combinations of the prime factors  $\nu$ ,  $\phi$ , and  $\xi$ ; whereas on the other hypotheses they are analogous to no existing system whatever.

Thus, putting  $z = 0$ , we have the following parallel systems, limiting our view for the moment to the gaseous compounds of boron.

$z = 0.$		
Boron . . . . .	$(\alpha\beta_1^2)^{\nu_1}$	Nitrogen . . . . . $\alpha\nu^2$
Chloride of boron . . . .	$\alpha^2\beta_1\chi^3$	Chloride of nitrogen $\alpha^2\nu\chi^3$
Boric methide . . . . .	$\alpha^5\beta_1x^3$	Methylamine . . . . . $\alpha^5\nu x^3$
Boric ethide . . . . .	$\alpha^8\beta_1x^6$	Ethylamine . . . . . $\alpha^8\nu x^6$
Triethyl borate . . . .	$\alpha^8\beta_1x^6\xi^3$	
Phosphorus . . . . .	$(\alpha\phi^2)^2$	Arsenic . . . . . $(\alpha\phi^2)^2$
Chloride of phosphorus	$\alpha^2\phi\chi^3$	Chloride of arsenic $\alpha^2\phi\chi^3$
Trimethyl-phosphine	$\alpha^5\phi x^3$	Trimethyl-arsine .. $\alpha^5\phi x^3$
Triethyl-phosphine ..	$\alpha^8\phi x^6$	Triethyl-arsine . . . . $\alpha^8\phi x^6$
Phosphite of ethyl ..	$\alpha^8\phi x^6\xi^3$	

If we put  $z = 1, 2, 3, 4$ , the system of the gaseous compounds of boron appears with the following symbols:—

	$z = 1.$	$z = 2.$	$z = 3.$	$z = 4.$
Chloride of boron..	$\alpha^3\beta^3\chi^3$	$\alpha^4\beta^5\chi^3$	$\alpha^5\beta^7\chi^3$	$\alpha^6\beta^9\chi^3$
Boric methide....	$\alpha^6\beta^3\kappa^3$	$\alpha^7\beta^5\kappa^3$	$\alpha^8\beta^7\kappa^3$	$\alpha^9\beta^9\kappa^3$
Boric ethide.....	$\alpha^9\beta^3\kappa^6$	$\alpha^{10}\beta^5\kappa^6$	$\alpha^{11}\beta^7\kappa^6$	$\alpha^{12}\beta^9\kappa^6$
Triethyl borate..	$\alpha^9\beta^3\kappa^6\xi^3$	$\alpha^{10}\beta^5\kappa^6\xi^3$	$\alpha^{11}\beta^7\kappa^6\xi^3$	$\alpha^{12}\beta^9\kappa^6\xi^3$

to which no parallel can be found among known and existing systems.

This coincidence cannot be regarded as of an accidental character. It is doubtless the result of the profound analogy of chemical properties by which this group of elements is connected, and which is revealed to us in the similarity of the symbolic forms of their combinations.

Group 3.--*Symbols of Antimony, Bismuth, Tin, Zinc, Cadmium, and Silver.*

It is evident that if some property of matter were discovered which admitted of accurate estimation, and which should vary with the gaseous density according to a known law, we should be able to infer the density from this property. Now in the numbers which represent the relative specific heats of chemical substances certain remarkable relations have been observed, which render it probable that general laws of this kind will hereafter be discovered, connecting the gaseous density of chemical substances with their specific heat, and which will afford a more solid foundation than we at present possess for the construction of a complete system of theoretical chemistry.

The law of Dulong and Petit is the most important of these numerical relations which has been as yet ascertained. This law may be regarded as an experimental truth, and thus stated:—

If  $A, A_1, A_2, \dots A_n$  be the smallest weights of the elemental bodies formed by the decomposition of the unit of any chemical substance, and if  $h, h_1, h_2, \dots h^n$  be the specific heats of these elements, either in the liquid or solid condition, then

$$hA = h_1A_1 = h_2A_2 = \dots h_nA_n.$$

In the following Table the value of the ratio  $\frac{hA}{h_1A_1}$  is given in the case of those elements of which the symbols have been considered, and of which the specific heats have been experi-

mentally determined, with the exception of the elements carbon, boron, and silicon, which do not appear to satisfy the condition. But these substances affect several allotropic forms, and have more than one specific heat; and it is not improbable that some variety of these elements may yet be discovered which shall conform to the law.

In the last column  $h_m A_m$  is assumed as the mean of the values given in the preceding column, namely, 3·289.

	A.	h.	hA.	$\frac{hA}{h_m A_m}$ .
Sulphur . . . . .	16	0·2026	3·241	0·985
Selenium . . . . .	40	0·0837	3·348	1·018
Iodine . . . . .	63·5	0·0541	3·436	1·045
Bromine . . . . .	40	0·0843	3·372	1·025
Phosphorus . . . .	15·5	0·2120	3·285	0·999
Arsenic . . . . .	37·5	0·0814	3·052	0·928

Hence if the specific heat,  $h$ , of an element be known, we are able, from the equation  $A = \frac{h_m A_m}{h} = \frac{3\cdot289}{h}$ , to calculate the value of A. The reasons have already been given which lead us to assume, with a certain probability, that  $W$  being the density of the element,  $A = W$ , or  $= \frac{W}{2}$ , or  $= \frac{W}{4}$ . Whence, if A be known,  $W$  is determined within certain limits.

*Symbol of Antimony.*—In the decomposition of the terchloride of antimony into its elements, if  $y$  be the number of units of the terchloride of antimony decomposed, and  $y_1$  the number of units of chlorine formed in the decomposition,

$$\frac{y}{y_1} = \frac{2}{3};$$

whence, if  $y_2$  be the greatest common measure of  $y$  and  $y_1$ ,  $y = 2y_2$ , and  $y_1 = 3y_2$ ; and putting  $y_3$  as the number of units of antimony formed,  $W$  as the density of antimony,  $V$  as the density of chlorine, and  $V_1$  as the density of terchloride of antimony,

$$y_3 W = y_2 (2V_1 - 3V),$$

and since  $V = 35\cdot5$ , and  $V_1 = 114\cdot25$ , as experimentally determined,

$$y_3 W = y_2 122.$$

Now the specific heat of antimony, as determined by Regnault, is 0.05077; whence, putting  $A = \frac{h_m A_m}{h}$ ,

$$A = \frac{3.289}{0.05077} = 64.8;$$

and since  $2 \times 64.4 = 128.8$  may be regarded as approximately equal to 122, we may assume, within the limits of error, that in the above decomposition

$$y_3 W = 2y_2 A.$$

Now three hypotheses may, as has been shown, be made as to the probable value of  $W$ .

1.  $W = A$ , in which case  $y_3 = 2y_2$ .
2.  $W = 2A$ , in which case  $y_3 = y_2$ .
3.  $W = 4A$ , in which case  $2y_3 = y_2$ .

Further, putting  $a^m \chi^m \sigma_1^m$  as the symbol of the trichloride of antimony,  $a \chi^3$  as the symbol of chlorine, and  $a^m \chi^m \sigma_1^m$  as the symbol of antimony, we have

$$2y_2 (a^m \chi^m \sigma_1^m) = 3y_2 a \chi^3 + y_3 a^m \chi^m \sigma_1^m,$$

$$(a^m \chi^m \sigma_1^m)^{2y_2} = (a \chi^3)^{3y_2} (a^m \chi^m \sigma_1^m)^{y_3};$$

whence

$$2m y_2 = 3y_2 + n y_3,$$

$$2m_1 y_2 = 6y_2 + n_1 y_3,$$

$$2m_2 y_2 = n_2 y_3.$$

1. Now on the first hypothesis,  $y_3 = 2y_2$ , which is incompatible with any solution in whole numbers of the first of these equations, which then becomes

$$2m = 3 + 2n:$$

this hypothesis is therefore to be rejected.

2. In the second case  $y_3 = y_2$ , and we have

$$2m = 3 + n,$$

$$2m_1 = 6 + n_1,$$

$$2m_2 = n_2,$$

the minimum integral solutions of which equations give

$$m = 2, \quad n = 1,$$

$$m_1 = 3, \quad n_1 = 0,$$

$$m_2 = 1, \quad n_2 = 2,$$

and we have as the

Symbol of terchloride of antimony.....  $\alpha^2\chi^3\sigma_1$ ,  
 Symbol of antimony.....  $\alpha\sigma_1^2$ .

3. On the third hypothesis  $2y_3 = y_2$ , and

$$\begin{aligned} 4m &= 6 + n, \\ 4m_1 &= 12 + n_1, \\ 4m_2 &= n_2, \end{aligned}$$

and

$$\begin{aligned} m &= 2, & n &= 2, \\ m_1 &= 3, & n_1 &= 0, \\ m_2 &= 1, & n_2 &= 4, \end{aligned}$$

a minimum, and the symbol of the terchloride is, as before,  $\alpha^2\chi^3\sigma_1$ , and the symbol of antimony  $\alpha^2\sigma_1^4$ , the equations on the two hypotheses being thus expressed:

$$\begin{aligned} \text{Hypothesis II} & \dots\dots\dots 2\alpha^2\chi^3\sigma_1 = 3\alpha\chi^2 + \alpha\sigma_1^2. \\ \text{Hypothesis III} & \dots\dots\dots 4\alpha^2\chi^3\sigma_1 = 6\alpha\chi^2 + \alpha^2\sigma_1^2. \end{aligned}$$

The symbol of the terchloride, and of all other compounds of antimony, is the same on either view.

*Combinations of the Prime Factors  $\alpha, \xi, \theta, \chi, \dots$  and  $\sigma_1$ .*

Name.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\sigma_1$	5.408	60.5
	Symbol.		
Antimony, Hypothesis 1 .....	$\alpha\sigma_1^2$	10.905	122
Antimony, Hypothesis 2 .....	$\alpha^2\sigma_1^4$	21.810	244
Terioxide of antimony .....	$\alpha\sigma_1^2\xi^3$	13.051	146
Tetroxide of antimony .....	$\alpha\sigma_1^2\xi^4$	13.767	154
Pentoxide of antimony .....	$\alpha\sigma_1^2\xi^5$	14.482	162
Tersulphide of antimony .....	$\alpha\sigma_1^2\theta^3$	15.198	170
Pentasulphide of antimony ....	$\alpha\sigma_1^2\theta^5$	18.057	202
Terchloride of antimony .....	$\alpha^2\sigma_1\chi^3$	10.213	114.25
Pentachloride of antimony ....	$\alpha^3\sigma_1\chi^5$	133.86	149.75
Oxychloride of antimony .....	$\alpha\sigma_1\chi\xi$	7.755	86.75

*Symbol of Bismuth.*—We are able to make precisely similar statements as to the relation which subsists between the densities of the terchloride of bismuth and its elements, chlorine and bismuth, to those which have been made respecting



terchloride of antimony ; and putting  $W$  as the density of bismuth,  $V$  the density of chlorine, and  $V_1$  the density of terchloride of bismuth, we have, as before,

$$y_3W = y_2(2V_1 - 3V);$$

and putting  $V = 35.5$  and  $V_1 = 157.25$ ,

$$y_3W = y_2 \times 208.$$

Now, the specific heat of bismuth,  $h$ , = 0.03084, and putting

$$A = \frac{3.289}{0.03084},$$

$$A = 106.6.$$

We may hence assume that  $y_3W = 2y_2A$ , and as before, putting

1.  $W = A, \quad y_3 = 2y_2;$
2.  $W = 2A, \quad y_3 = y_2;$
3.  $W = 4A, \quad 2y_3 = y_2;$

and by precisely similar reasoning to that in the last example, putting  $\alpha^m\chi^m\beta_2^m$  as the symbol of terchloride of bismuth, and  $\alpha^m\chi^m\beta_2^m$  as the symbol of bismuth, from the equation

$$(\alpha^m\chi^m\beta_2^m)^{2y_3} = (\alpha\chi^2)^{2y_3}(\alpha^m\chi^m\beta_2^m)^{y_2}$$

we arrive at the following symbols, rejecting, for the same reason as in the case of antimony, the first hypothesis.

On the second hypothesis,  $W = 2A$ ,

Symbol of bismuth .....  $\alpha\beta_2^2$ ,  
 Symbol of terchloride of bismuth .....  $\alpha^2\chi^2\beta_2$ .

On the third hypothesis,  $W = 4A$ ,

Symbol of bismuth .....  $\alpha\beta_2^4$ ,  
 Symbol of terchloride of bismuth .....  $\alpha^2\chi^2\beta_2$ .

We have hence the following system :—

Combinations of the Prime Factors  $\alpha$ ,  $\xi$ ,  $\theta$ ,  $\chi$ , . . . . and  $\beta_2$ .

Name.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\beta_2$	9.252	103.5
Bismuth, Hypothesis 1 . . . . .	Symbol.	18.594	208
Bismuth, Hypothesis 2 . . . . .	$\alpha\beta_2^3$	37.188	416
Teroxide of bismuth . . . . .	$\alpha^2\beta_2^4$	20.739	232
Pentoxide of bismuth . . . . .	$\alpha\beta_2^3\xi^5$	22.169	248
Hydrate of bismuth . . . . .	$\alpha\beta_2^2\xi^5$	10.772	120.5
Bismuthic acid . . . . .	$\alpha\beta_2^3\xi^5$	20.739	232
Bisulphide of bismuth . . . . .	$\alpha\beta_2^2\xi^5$	21.454	240
Tersulphide of bismuth . . . . .	$\alpha\beta_2^3\xi^5$	22.884	256
Terchloride of bismuth . . . . .	$\alpha^2\beta_2\xi^5$	13.967	156.25
Oxychloride of bismuth . . . . .	$\alpha\beta_2\xi^5$	11.598	129.75
Triethyl bismuth . . . . .	$\alpha^3\xi^5$	18.185	147.5
Chloride of protethyl bismuth..	$\alpha^4\beta_2\xi^5$	13.767	154

*Symbol of Tin.*—In the decomposition of the gaseous chloride of tin into tin and chlorine, the volume of chlorine formed is double the volume of the chloride decomposed. Hence, putting  $y_1$  as the number of units of stannic chloride decomposed, and  $\alpha^m\chi^{m_1}\xi^{n_1}$ ,  $\alpha^n\chi^{n_1}\xi^{n_2}$  as the symbols, respectively, of stannic chloride and of tin,

$$y_1\alpha^m\chi^{m_1}\xi^{n_1} = 2y_1\alpha\chi^2 + y_2\alpha^n\chi^{n_1}\xi^{n_2}$$

and

$$(\alpha^m\chi^{m_1}\xi^{n_1})^{y_1} = (\alpha\chi^2)^{2y_1}(\alpha^n\chi^{n_1}\xi^{n_2})^{y_2},$$

whence

$$y_1m = 2y_1 + y_2n,$$

$$y_1m_1 = 4y_1 + y_2n_1,$$

$$y_1n_1 = y_2n_2.$$

In all cases

$$m = 2, \quad n = 0,$$

$$m_1 = 4, \quad n_1 = 0,$$

$$m_2 = y_2, \quad n_2 = y_1,$$

a minimum, and we hence have, as determined from the above equation,

Symbol of tin . . . . .  $\alpha^2\xi^4$ ,

Symbol of bichloride of tin . . . . .  $\alpha^2\chi^4\xi^4$ ;

and, assuming 130 as the density of bichloride of tin,

$$2w(\alpha) + 4w(\chi) + y_2x = 130;$$

whence

$$y_2 w(x_1) = 59,$$

and

$$W = y_1 w(x_1) = \frac{y_1}{y_2} 59.$$

Now, proceeding to construct the symbols of the other known gaseous compounds of tin by processes precisely similar to those of which sufficient examples have already been given in the case of the elements silicon and boron, and which it is unnecessary here to repeat, we arrive at the following symbols:—

	Symbol.
Bichloride of tin.....	$\alpha^2 \chi^4 x_1^2$ .
Chloride of stannic dimethyl .....	$\alpha^4 \chi^2 x^2 x_1^2$ .
Chloride of stannic diethyl .....	$\alpha^6 \chi^2 x^4 x_1^2$ .
Bromide of stannic diethyl .....	$\alpha^6 \beta^2 x^4 x_1^2$ .
Iodide of stannic trimethyl .....	$\alpha^8 \omega x^3 x_1^2$ .
Chloride of stannic triethyl .....	$\alpha^8 \chi x^6 x_1^2$ .
Bromide of stannic triethyl .....	$\alpha^8 \beta x^6 x_1^2$ .
Stannic dimethyl-diethyl .....	$\alpha^8 x^6 x_1^2$ .
Stannic tetrethyl .....	$\alpha^{10} x^8 x_1^2$ .

As in the corresponding cases which have already been discussed, there is but one hypothesis that can be made as to the value of  $y_2$ , which is at once necessary and sufficient, namely, that  $y_2 = 1$ , which gives  $\alpha^2 \chi^4 x_1$  as the symbol of bichloride of tin.

Now the specific heat of tin is 0.05623. Hence  $A = \frac{3.289}{0.05623} = 58.5$ ; and it is known from experiment that  $\frac{y_2}{y_1} W = 59$ . It

may therefore be assumed that  $\frac{y_2}{y_1} W = A$ .

Hence (1) If  $A = W$ ,  $\frac{y_2}{y_1} = 1$ , and  $y_2 = 1, y_1 = 1$ .

(2) If  $A = \frac{W}{2}$ ,  $\frac{y_2}{y_1} = \frac{1}{2}$ , and  $y_2 = 1, y_1 = 2$ .

(3) If  $A = \frac{W}{4}$ ,  $\frac{y_2}{y_1} = \frac{1}{4}$ , and  $y_2 = 1, y_1 = 4$ .

Hence it appears that from these considerations also (whichever hypothesis be preferred)  $y_2 = 1$ , and the symbol of bichlo-

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ride of tin is  $\alpha^2\chi^4x_1$ . The symbol of tin is, from these data, either  $x_1$ ,  $x_1^2$ , or  $x_1^4$ , between which values we have no means of selecting.

*Combinations of the Prime Factors  $\alpha$ ,  $\xi$ ,  $\theta$ ,  $\chi$ , . . . and  $x_1$ .*

Name of substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$x_1$	5·274	59
	Symbol.		
Tin. Hypothesis 1 . . . . .	$x_1$	5·274	59
Tin. Hypothesis 2 . . . . .	$x_1^2$	10·548	118
Tin. Hypothesis 3 . . . . .	$x_1^4$	21·096	236
Protoxide of tin . . . . .	$x_1\xi$	5·989	67
Binoxide of tin . . . . .	$x_1\xi^2$	6·704	75
Hydrated stannic acid . . . . .	$\alpha x_1\xi^3$	7·509	84
Protosulphide of tin . . . . .	$x_1\theta$	6·704	75
Bisulphide of tin . . . . .	$x_1\theta^2$	8·135	91
Bichloride of tin . . . . .	$\alpha\gamma^2x_1$	8·448	94·5
Tetrachloride of tin . . . . .	$\alpha^2\chi^4x_1$	11·621	130
Chloride of stannic dimethyl . . . . .	$\alpha^4\gamma^2x_1^3x_1$	9·788	109·5
Chloride of stannic diethyl . . . . .	$\alpha^6\chi^2x_1^4x_1$	11·040	123·5
Bromide of stannic diethyl . . . . .	$\alpha^6\theta^2x_1^4x_1$	15·018	168
Iodide of stannic trimethyl . . . . .	$\alpha^6\omega x_1^3x_1$	12·962	145
Chloride of stannic triethyl . . . . .	$\alpha^8\gamma x_1^6x_1$	10·749	120·25
Bromide of stannic triethyl . . . . .	$\alpha^8\theta x_1^6x_1$	12·738	142·5
Stannic tetrethyl . . . . .	$\alpha^{10}\theta^2x_1$	10·459	117
Stannic dimethyl-diethyl . . . . .	$\alpha^8x_1^6x_1$	9·207	103

*Symbol of Zinc.*—It is known from experiment that one volume of zinc-ethyl, of which the density is 61·75, can be decomposed into 5 volumes of hydrogen, 24 parts by weight of carbon, and 32·5 parts by weight of zinc.

Now, since 6 parts by weight of carbon are formed by the decomposition of one volume of marsh-gas, putting  $y_1$  as the number of volumes of zinc-ethyl decomposed, and  $y_2$  as the number of volumes of vapour of carbon formed in this decomposition,

$$\frac{y_2}{y_1} = 4 \frac{x}{y},$$

where  $x$  and  $y$  have the values previously assigned to them (Sec. VII. Group 2 (1)), and assuming  $x = 1$ ,

$$\frac{y_2}{y_1} = \frac{4}{y};$$

whence, putting  $y_3$  as the number of volumes of zinc formed,

$\alpha^m x^{m_1} \zeta^{m_2}$  as the symbol of zinc-ethyl,  $\alpha^n x^{n_1} \zeta^{n_2}$  as the symbol of zinc,  $\alpha$  as the symbol of hydrogen, and  $x^y$  as the symbol of carbon,

$$yy_1(\alpha^m x^{m_1} \zeta^{m_2}) = 5yy_1\alpha + 4y_1x^y + yy_3\alpha^n x^{n_1} \zeta^{n_2},$$

and

$$(\alpha^m x^{m_1} \zeta^{m_2})^{y_1} = \alpha^{5y_1} (x^y)^{4y_1} (\alpha^n x^{n_1} \zeta^{n_2})^{y_3};$$

whence

$$\begin{aligned} y_1 m &= 5y_1 + y_3 n, \\ y_1 m_1 &= 4y_1 + y_3 n_1, \\ y_1 m_2 &= y_3 n_2 \end{aligned}$$

which equations have for all integral values of  $y_1$  and  $y_3$  the minimum solutions,

$$\begin{aligned} m &= 5, & n &= 0, \\ m_1 &= 4, & n_1 &= 0, \\ m_2 + y_3 & & n_2 &= y_1, \end{aligned}$$

which give the following expressions for the symbols,

Zinc-ethyl .....	$\alpha^5 x^4 \zeta^{y_3}$ ,
Zinc .....	$\zeta^{y_1}$ .

In a similar manner we arrive at  $\alpha^2 x^2 \zeta^{y_3}$  as the symbol of zinc-methyl.

These are the only gaseous compounds of zinc known.

The specific heat of zinc is 0.0955. Hence it may be assumed that

$$A = \frac{3.289}{0.0955} = 34.4.$$

Now, from the above equations

$$\frac{y_3 W}{y_1} = 32.75,$$

W being the density of zinc in the gaseous condition, and approximately

$$\frac{y_3 W}{y_1} = A.$$

- (1) If  $A = \frac{W}{y_1}$ ,  $y_3 = 1$ , and  $y_1 = 1$ .
- (2) If  $A = \frac{W}{2}$ ,  $y_3 = 1$ , and  $y_1 = 2$ .
- (3) If  $A = \frac{W}{4}$ ,  $y_3 = 1$ , and  $y_1 = 4$ .

On each hypothesis the value of  $y_3$  is the same. Hence we have—

Name of substance.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\zeta$		
		2·905	32·5
	Symbol.		
Zinc. Hypothesis 1 .....	$\zeta$	2·905	32·5
Zinc. Hypothesis 2 .....	$\zeta^2$	5·811	65
Zinc. Hypothesis 3 .....	$\zeta^3$	11·621	130
Oxide of zinc .....	$\zeta^2$	3·620	40·5
Hydrated oxide of zinc.....	$\alpha^2 \zeta^2$	4·425	49·5
Sulphide „ „ .....	$\zeta^3$	4·335	48·5
Sulphate „ „ .....	$\zeta^3 \theta^2$	7·196	80·5
Hyposulphite „ „ .....	$\zeta^3 \theta^2 \zeta^3$	7·911	85
Chloride „ „ .....	$\alpha \zeta^2$	6·079	68
Carbonate „ „ .....	$\zeta^2 \kappa^2$	5·587	62·5
Zinc-methyl .....	$\alpha^2 \zeta^2$	4·246	47·5
Zinc-ethyl .....	$\alpha^2 \kappa^2$	5·493	61·5
Zinc-amide .....	$\alpha^2 \zeta^2$	4·157	46·5

*Symbol of Cadmium.*—The density of the vapour of cadmium, as ascertained by Deville, and Troost, is 56·7 on the hydrogen scale, and in the decomposition of the chloride of cadmium equal volumes of chlorine and cadmium are formed.

Hence, putting

$\alpha^m \chi^{m_1} \kappa_2^{m_2}$  as the symbol of chloride of cadmium,  
 $\alpha^n \chi^{n_1} \kappa_2^{n_2}$  as the symbol of cadmium,  
 $\alpha \chi^2$  as the symbol of chlorine,

$$y_1 \alpha^m \chi^{m_1} \kappa_2^{m_2} = y_2 \alpha \chi^2 + y_3 \alpha^n \chi^{n_1} \kappa_2^{n_2},$$

and

$$(\alpha^m \chi^{m_1} \kappa_2^{m_2})^{y_1} = (\alpha \chi^2)^{y_2} (\alpha^n \chi^{n_1} \kappa_2^{n_2})^{y_3},$$

whence

$$\begin{aligned} y_1 m &= y_2 + y_3 n, \\ y_1 m_1 &= 2y_2 + y_3 n_1, \\ y_1 m_2 &= y_3 n_2. \end{aligned}$$

Now the specific heat of cadmium is 0·05669, whence the calculated value of  $A$  (putting  $A = \frac{3 \cdot 289}{0 \cdot 05669}$ ) is 58, and  $W = A$ .

Hence, assuming in conformity with the principle previously laid down, that  $\frac{y_2 W}{y_1} = XA$ , where  $X$  is a positive integer, since

$W = A$ , and  $y_1$  and  $y_2$  have no common measure,  $y_1 = 1$ , and the above equations become

$$\begin{aligned} m &= y_2 + y_2 n, \\ m_1 &= 2y_2 + y_2 n_1, \\ m_2 &= y_2 n_2 \end{aligned}$$

which in all cases admit of the minimum solutions,

$$\begin{aligned} m &= y_2, & n &= 0, \\ m_1 &= 2y_2, & n_1 &= 0, \\ m_2 &= y_2, & n_2 &= 1, \end{aligned}$$

and we have

Symbol of chloride of cadmium .....  $(\alpha\chi^2\kappa_2)^{\kappa_2}$ ,  
 Symbol of cadmium .....  $\kappa_2$ .

Or, assuming as the most probable hypothesis (in default of further information) that  $y_2 = 1$ , we have

Symbol of chloride of cadmium .....  $\alpha\chi^2\kappa_2$ .

We hence arrive at the following symbols:—

*Combinations of the Prime Factors  $\alpha, \xi, \theta, \chi, \dots$  and  $\kappa_2$ .*

Name.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\kappa_2$	5.006	56
	Symbol.		
Cadmium .....	$\kappa_2$	5.006	56
Oxide of cadmium .....	$\kappa_2\xi$	5.721	64
Sulphide of cadmium .....	$\kappa_2\theta$	6.436	72
Sulphate of cadmium .....	$\kappa_2\theta\xi^4$	9.297	104
Chloride of cadmium .....	$\alpha\chi^2\kappa_2$	8.179	91.5
Carbonate of cadmium .....	$\kappa_2\xi\theta^2$	7.688	86

*Symbol of Silver.*—Lastly, I will give one example of a class of symbols with regard to which we have even less positive knowledge, and are thrown almost exclusively upon hypothesis.

The specific heat of silver is 0.05701, whence the calculated value of A (putting  $A = \frac{3.289}{0.05701}$ ) is 57.6.

Now, the percentage composition of chloride of silver is

Silver .....	75.26
Chlorine .....	24.74
	100.00

whence, putting

$\alpha^m \chi^{m_1} g_1^{m_2}$  as the symbol of chloride of silver,

$\alpha^n \chi^{n_1} g_1^{n_2}$  as the symbol of silver,

$\alpha \chi^2$  as the symbol of chlorine,

and

$$y_1 \alpha^m \chi^{m_1} g_1^{m_2} = y_2 \alpha \chi^2 + y_3 \alpha^n \chi^{n_1} g_1^{n_2};$$

$$y_1 m = y_2 + y_3 n,$$

$$y_1 m_1 = 2y_2 + y_3 n_1,$$

$$y_1 m_2 = y_3 n_2,$$

and putting  $W$  as the density of the vapour of silver,

$$\frac{y_3 W}{y_2} = \frac{35.5 \times 75.24}{24.66} = 108,$$

whence we may infer that

$$\frac{y_3 W}{y_2} = 2A.$$

Also from the general conditions previously given,

$$\frac{y_3 W}{y_1} = XA,$$

where  $X$  is a positive integer.

Hypothesis I.—Let us assume that  $W = A$ . Then

$$\frac{y_3}{y_2} = 2, \quad \frac{y_3}{y_1} = X, \quad \text{and} \quad \frac{y_2}{y_1} = \frac{X}{2}.$$

There are two cases, according as  $X$  is assumed to be odd or even :

(1.) Let  $X = 2x + 1$ , an odd number. Then  $y_1 = 2$ ,  $y_2 = X$ ,  $y_3 = 2X$ ; and substituting these values in the equation

$$y_1 m = y_2 + y_3 n,$$

we have

$$2m = (2x + 1)(1 + 2n),$$

to which equation there is no integral solution. This hypothesis is therefore untenable.

(2.) Let  $X = 2x_1$ , an even number. Then  $y_1 = 1$ ,  $y_2 = x_1$ ,  $y_3 = 2x_1$ , and

$$m = x_1(1 + 2n),$$

$$m_1 = 2x_1(1 + n_1),$$

$$m_2 = 2x_1 n_2.$$



These equations in all cases admit of the minimum solution,

$$\begin{aligned} m &= x_1, & n &= 0, \\ m_1 &= 2x_1, & n_1 &= 0, \\ m_2 &= 2x_1, & n_2 &= 1. \end{aligned}$$

In which case the above equation becomes

$$(\alpha\chi^2g_1^2)^{x_1} = x_1(\alpha\chi^2 + 2g_1),$$

the symbols being thus expressed:

	Symbol.	Weight in grm.	Relative weight.
Silver.....	$g_1$	4·827	54
Chloride of silver..	$(\alpha\chi^2g_1^2)^{x_1}$	$x_1 \times 12·828$	$x_1 \times 143·5$ .

Hypothesis II.—Now, let  $W = 2A$ . Then

$$\frac{y_3}{y_2} = 1, \quad \frac{2y_3}{y_1} = X, \quad \text{and} \quad \frac{2y_2}{y_1} = X.$$

(1.) Let  $X$  be odd,  $= 2x + 1$ ; then  $y_1 = 2, y_2 = X, y_3 = X$ , and

$$\begin{aligned} 2m &= (2x + 1)(1 + n), \\ 2m_1 &= (2x + 1)(2 + n_1), \\ 2m_2 &= (2x + 1)n_2. \end{aligned}$$

These equations in all cases admit of the minimum solution,

$$\begin{aligned} m &= 2x + 1, & n &= 1, \\ m_1 &= 2x + 1, & n_1 &= 0, \\ m_2 &= 2x + 1, & n_2 &= 2, \end{aligned}$$

and the above equation becomes

$$2(\alpha\chi g_1)^{2x+1} = (2x + 1)(\alpha\chi^2 + \alpha g_1^2),$$

the symbols being thus expressed:

	Prime factor.	Weight in grm.	Relative weight.
	$g_1$ .	4·783	53·5
	Symbol.		
Silver.....	$\alpha g_1^2$	9·654	108
Chloride of silver..	$(\alpha\chi g_1)^{2x+1}$	$(2x + 1)6·423$	$(2x + 1)71·75$ .

(2.) If  $X = 2x_1$ , an even number,  $y_1 = 1, y_2 = x_1, y_3 = x_1$ , and

$$\begin{aligned} m &= x_1(1 + n), \\ m_1 &= x_1(2 + n_1), \\ m_2 &= x_1n_2, \end{aligned}$$

which admit of the minimum solution,

$$\begin{array}{ll} m = x_1, & n = 0, \\ m_1 = 2x_1, & n_1 = 0, \\ m_2 = x_1, & n_2 = 1. \end{array}$$

This hypothesis is, however, untenable for the following reason.

According to the definition given of the weight A (Sec. VII., Group 2 (1)), the weight A is the smallest weight of silver formed by the decomposition of the unit of any chemical substance. Hence, if  $y$  be the number of units of the substance decomposed, and  $x$  the number of units of silver in that equation in which the weight A appears,

$$\frac{xW}{y} = A.$$

And putting  $g_1$  as the symbol of silver,

$$yg_1^t = xg_1,$$

and

$$ty = x:$$

but since  $W = 2A$ ,  $y = 2x$ , whence  $2t = 1$ , to which equation there is no integral solution. This hypothesis is therefore to be rejected.

If, however, in the above equation we select 2 as the value of  $n_2$ ,

$$\begin{array}{l} m = x_1, \\ m_1 = 2x_1, \\ m_2 = 2x_1, \end{array}$$

in which case

$$(\alpha\chi^2g_1^2)^{n_1} = x_1(\alpha\chi^2 + g_1^2);$$

and we have

$$yg_1^t = xg_1^2,$$

and  $ty = 2x$  and  $t = 1$ .

It appears, therefore, that so far as any information extends which is afforded to us by the specific heat of silver, the symbol of this metal may be regarded as identical in form with that of zinc or mercury, the equation under consideration being expressed thus,

$$\alpha\chi^2g_1^2 = \alpha\chi^2 + 2g_1,$$

or as being similar to the equation which expresses the relation existing between mercurous chloride and its elements,

$$a\chi^{2\delta^2} = a\chi^2 + 2\delta.$$

Or again, it may also be regarded as identical in form with the symbols of chlorine and of nitrogen; in which case the above equation is thus expressed,

$$2a\chi\varrho_1 = a\chi^2 + a\varrho_1^2,$$

and is similar to the equation which connects the symbols of the chloride of iodine with those of chlorine and iodine,

$$2a\chi\omega = a\chi^2 + a\omega^2.$$

And lastly, the facts are not even inconsistent with the assumption that the symbol of silver is identical in form with the symbols of oxygen and sulphur, so that

$$a\chi^2\varrho_1^2 = a\chi^2 + \varrho_1^2,$$

which is similar to the equation which connects the symbol of the bisulphide of chlorine with the symbols of its elements

$$a\chi^{2\theta^2} = a\chi^2 + \theta^2.$$

The symbols of silver and its compounds appear, on the two more probable hypotheses, as follows:—

Hypothesis I.  $W = A, X = 2x_1.$

Name.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$\varrho$	4·827	54
	Symbol.		
Silver .....	$\varrho_1$	4·827	54
Oxide of silver .....	$\varrho_1^2\varrho$	10·369	116
Sulphide of silver .....	$\varrho_1^2\theta$	11·085	124
Sulphate of silver .....	$\varrho_1^2\theta\varrho^2$	18·945	156
Chloride of silver .....	$a\chi^2\varrho_1^2$	12·828	143·5
Nitrate of silver .....	$a\varrho^2\varrho_1^2\varrho^2$	15·197	170
Metaphosphate of silver .....	$a\varrho^2\varrho_1^2\varrho^2$	16·716	187
Pyrophosphate of silver .....	$a\varrho^2\varrho_1^2\varrho^2$	27·086	303
Orthophosphate of silver .....	$a\varrho^2\varrho_1^2\varrho^2$	37·455	419
Cyanide of silver .....	$a\varrho^2\varrho_1^2\chi^2$	11·979	134

Hypothesis II.  $W = 2A, X = 2x + 1$ .

Name.	Prime factor.	Absolute weight, in grammes.	Relative weight.
	$f_2$	4.782	53.5
	Symbol.		
Silver .....	$\alpha f_2^2$	9.654	108
Oxide of silver .....	$\alpha f_2^2 \xi$	10.869	116
Sulphide of silver .....	$\alpha f_2^2 \theta$	11.085	124
Sulphate of silver .....	$\alpha f_2^2 \theta \xi^4$	13.945	156
Chloride of silver .....	$\alpha \chi f_2$	6.414	71.75
Nitrate of silver .....	$\alpha \rho f_2^2 \theta$	7.598	85
Metaphosphate of silver .....	$\alpha \rho f_2^2 \theta^2$	8.358	98.5
Pyrophosphate of silver .....	$\alpha^2 f_2^2 f_2^4 \xi^2$	27.086	303
Orthophosphate of silver .....	$\alpha^2 \rho f_2^2 \theta^2$	18.728	209.5
Cyanide of silver .....	$\alpha \nu f_2 \xi$	5.989	67

This example may serve to show how inadequate are those considerations which are frequently regarded as affording a satisfactory solution of these important problems. If we are to pronounce an opinion on such slender data, the more probable hypothesis seems to be that which associates silver and the allied metals with the other electro-positive elements. In the two cases (namely mercury and cadmium) in which the fact can be experimentally determined,  $W = A$ . In other instances also, such as that of zinc, there is every reason to believe that this is the case.

As hypotheses thus accumulate, the probability diminishes of the conclusions which are based upon them. It is, however, to be remembered that such uncertainty is not peculiar to chemistry, but that in every inductive science our exact knowledge lies within a very narrow sphere, as compared with the total field of observation; and after every deduction has been made on this account, there remains, as the solid nucleus of the science, the combinations of carbon and the gaseous elements, which hold in the theory of chemistry a position somewhat analogous to that occupied in astronomy by our solar system, as the area of exact observation.

#### SECTION VIII.—ON THE APPARENT EXCEPTIONS TO THE LAW OF PRIME FACTORS.

(1.) On proceeding with the construction of the symbols of chemical substances, it will be found that in a certain limited

number of cases the primary equations are apparently of such a nature as to render impossible the expression in them of the symbols by means of the same system of prime factors  $\alpha, \chi, \xi, \dots$  by which the symbols in other cases can be expressed. It is probable that this anomaly admits of a very simple explanation, but it is not without interest to consider the modifications which such a fact, if it were truly established, would render necessary in our chemical ideas.

The density of sal-ammoniac in the gaseous condition, as experimentally determined, is 14.44, so that four volumes of sal-ammoniac are apparently decomposed into four volumes of hydrogen, one volume of chlorine, and one volume of nitrogen. Whence, putting  $\alpha^m \chi^{m_1} \nu^{m_2}$  as the symbol of the unit of sal-ammoniac,

$$(\alpha^m \chi^{m_1} \nu^{m_2})^4 + \alpha^4 \chi^2 \nu^2,$$

and

$$2m = 3,$$

$$2m_1 = 1,$$

$$2m_2 = 1,$$

and the symbol of sal-ammoniac is  $(\alpha^3 \chi \nu)^{\frac{1}{4}}$ , and cannot be expressed by an integral number of the prime factors  $\alpha, \chi, \nu$ .

We may now inquire whether, seeing this expression of the symbol of chloride of ammonium to be impossible on the assumption that the symbols of the elements hydrogen, chlorine, and nitrogen are of the forms  $\alpha, \alpha \chi^2, \alpha \nu^2$ , it be possible on any other hypothesis as to these symbols, consistent with known facts. Now every possible hypothesis as to these symbols consistent with their expression by an integral number of prime factors in the equations from which the symbols have been derived, and with the expression of the symbol of hydrogen by one prime factor,  $\alpha$ , is, as has been shown (Sec. VII. (5) and (8)), implicitly contained in the general forms of the symbols of chlorine and nitrogen, which are respectively  $\alpha^{1+2p} \chi^{2(1+p)}$  and  $\alpha^{1+2q} \nu^{2(1+q)}$ ; whence, putting

$$(\alpha^m \chi^{m_1} \nu^{m_2})^4 = \alpha^4 \alpha^{1+2p} \chi^{2(1+p)} \alpha^{1+2q} \nu^{2(1+q)},$$

$$2m = 3 + \overline{p + q},$$

$$2m_1 = 1 + p_1,$$

$$2m_2 = 1 + q_1,$$

and

$$\begin{array}{rcl} m & = & 2, \\ m_1 & = & 1, \\ m_2 & = & 1, \end{array} \qquad \begin{array}{rcl} p + q & = & 1, \\ p_1 & = & 1, \\ q_1 & = & 1, \end{array}$$

a minimum.

On the hypothesis,  $p = 0, q = 1$ , we have

$$\begin{array}{l} \text{Symbol of chlorine } \alpha\chi^4, \\ \text{Symbol of nitrogen } \alpha^3\nu^4. \end{array}$$

On the hypothesis,  $p = 1, q = 0$ , we have

$$\begin{array}{l} \text{Symbol of chlorine } \alpha^3\chi^4, \\ \text{Symbol of nitrogen } \alpha\nu^4. \end{array}$$

Neither hypothesis is absolutely inconsistent with any known fact, for it is possible thus to express the symbols of chlorine and nitrogen in every equation into which those symbols enter; and if it were placed beyond doubt that the true density of chloride of ammonium in the gaseous condition were 12.88, we might thus accept the fact and assert that the factors  $\chi$  and  $\nu$  were composite, so that either  $\chi = \chi_1^2$  and  $\nu = \alpha^2\nu_1^2$ , or  $\chi = \alpha^2\chi_1^2$  and  $\nu = \nu_1^2$ , and our view of the possible system of chemical substances, and of the laws of combination to which they were subject, would be profoundly modified. I am far from believing that such is the true solution of this apparent anomaly. Such a solution, although not absolutely precluded to us, is in the highest degree improbable; and the facts admit of an obvious and simple explanation on the hypothesis that chloride of ammonium is decomposed, at the temperature at which its vapour-density is supposed to have been taken, into equal volumes of hydrochloric acid and ammonia, of which very satisfactory evidence has been given.\*

(2.) Again, the density of the binoxide of nitrogen is 14.989, as determined by experiment. If this be correct, 2 volumes of binoxide of nitrogen are decomposed into 1 volume of nitrogen and 1 volume of oxygen: whence, putting  $\alpha^m\nu^{m_1}\xi^{m_2}$  as the symbol of the binoxide,  $\alpha\nu^2$  as the symbol of nitrogen, and  $\xi^2$  as the symbol of oxygen,

$$(\alpha^m\nu^{m_1}\xi^{m_2})^2 = \alpha\nu^2\xi^2,$$

and

$$\begin{array}{l} 2m = 1, \\ m_1 = 1, \\ m_2 = 1, \end{array}$$

\* See Pebal, Ann. Chem. Pharm., vol. cxxiii, p. 199.

and the symbol of the binoxide of nitrogen, as expressed by the factors  $\alpha, \nu, \xi$ , is  $\alpha^1 \nu \xi$ .

If we now inquire, as before, whether any hypothesis as to the symbols of nitrogen and oxygen can be made which shall be consistent with the fundamental assumption that the symbol of hydrogen is expressed by one factor, we have, putting  $\alpha^{2p} \xi^{2(1+p)}$  and  $\alpha^{1+2q} \nu^{2(1+q)}$  as the general symbols of oxygen and nitrogen (Sec. VII. (2) and (8)),

$$(\alpha^{m_1} \nu^{m_2} \xi^{m_3})^2 = \alpha^{1+2q} \nu^{2(1+q)} \alpha^{2p} \xi^{2(1+p)},$$

and

$$\begin{aligned} 2m &= 1 + 2(q + p), \\ m_1 &= 1 + q_1, \\ m_2 &= 1 + p_1. \end{aligned}$$

Now no positive and integral solution as regards  $m, q$ , and  $p$ , can be found which shall satisfy the first of these equations. The above equation, therefore, which expresses the relation which exists between the ponderable matter of the binoxide of nitrogen and its elements, is incompatible with the expression of the symbols by an integral number of prime factors, on the assumption that the symbol of hydrogen is  $\alpha$ .

The anomaly in the density of the binoxide of nitrogen was long since observed by Laurent and Gerhardt, who discovered the empirical law of even numbers. But such has been the influence upon the mind of chemists of an arbitrary hypothesis, as to the constitution of matter, and of an uncertain system of notation, that this anomaly, the most singular exception known to the general laws of chemistry, is even now imperfectly recognised, and has never yet been submitted to any serious or adequate investigation.

(3.) The following are the chief exceptions, real or apparent, to the law of prime factors\*. The second column contains the symbol, as expressed by the factors  $\alpha, \chi, \xi, \dots$ ; the third column the temperatures at which the observation is made; column A, the density of the substance, the density of air being assumed as 1; column B, the same density, the density of hydrogen being 1; column C contains the density as calculated from the symbols given in the first column.

\* See Laurent's "Chemical Method," p. 81; Watts's "Dictionary of Chemistry," vol. i, p. 469; "Gerhardt, *Traité de Chimie*," vol. i, p. 581, vol. iv, p. 897.

Substance.	Symbol.	Temp. C.	A.	B.	C.
Binoxide of nitrogen.....	$\alpha^2 \nu \xi$	..	1.088	14.989	15
Peroxide of nitrogen.....	$\alpha^2 \nu \xi^2$	..	1.527	22.050	23
" " .....	"	97.5	1.783	25.746	"
" " .....	"	24.5	2.520	36.389	"
" " .....	"	11.3	2.645	38.194	"
Mercurous chloride .....	$\alpha^2 \nu \xi$	..	8.35	120.574	117.75
Chloride of ammonium.....	$\alpha^2 \nu \xi \theta$	1040	1.00	14.44	13.375
Bromide of ammonium .....	$\alpha^2 \beta \nu \xi$	..	1.69	24.40	24.5
Iodide of ammonium .....	$\alpha^2 \omega \nu \xi$	..	2.68	38.77	36.25
Cyanide of ammonium .....	$\alpha^2 \nu \theta$	..	0.79	11.41	11
Hydrosulphate of ammonia....	$(\alpha^2 \theta)$	..	0.89	12.85	12.75
Iodide of phosphonium .....	$(\alpha^2 \omega \phi)$	..	2.77	39.999	40.5
Pentachloride of phosphorus....	$(\alpha^2 \chi^5 \phi)$	182	5.078	73.326	52.125
" " " " .....	"	386	3.656	52.793	"
Oxychloride of phosphorus ....	$(\alpha^2 \chi^3 \phi \xi)$	..	5.40	77.976	76.75
Sulphide of mercury .....	$(\theta \theta)$	..	5.51	79.564	77.33
Perchlorinated methylic ether ..	$\alpha^2 \chi^3 \nu \xi \theta$	..	4.67	67.435	63.25
Perchlorinated sulphide of methyl	$\alpha^2 \chi^3 \nu \xi \theta$	..	5.68	82.019	67.25

It will be seen on inspection of the preceding Table that, in many instances, the vapour-density, as determined by experiment, does not sufficiently agree with any hypothesis even remotely probable.

Many of these apparent exceptions obviously admit of a similar simple explanation to that which has been suggested in the case of chloride of ammonium. Indeed, it would be truly surprising if in the varied transformations of matter no example of such decomposition should occur. In more than one case actual evidence of it has been adduced;\* and while undoubtedly it must be allowed that the question is not to be answered by theoretical considerations alone, but that every case of such apparent anomaly should be submitted to the most rigid tests of experiment, there is every reason to believe that the simple weights  $\alpha$ ,  $\xi$ ,  $\theta$ ,  $\chi$ , . . . are the ultimate known components of the units of ponderable matter, and represent a limit to chemical decomposition which has not as yet been passed.

The atomic theory may be compared to a sort of "abacus" or simple mechanical instrument which chemists have invented to facilitate their calculations. It is useless to pretend that any demonstration can be given of this theory, which, at best, can

\* See Playfair and Wanklyn, Journ. Chemical Society, vol. xv, p. 142; Wanklyn and Robinson, "On Diffusion of Vapours," Proceedings, Royal Society, vol. xii, p. 507.



only be regarded as a possible hypothesis suggested by the facts; but nevertheless it has a very real claim upon our consideration from the practical advantages which it has afforded in the study of the science. The atoms of the chemist fulfil a similar purpose in his calculations to that fulfilled by balls in the estimation of probabilities. They afford a simple and not inaccurate image of the subject with which he is concerned, by which he is enabled to reduce his problems to a concrete form, and thus at once to realize and to isolate them. To forbid the use of such an image would be to impose a very unnecessary restriction upon scientific methods. A ball, as the concrete symbol of an indivisible whole, may advantageously represent, as occasion requires, a unit of weight, a simple weight, an event. We are perfectly free, when it suits our purpose, to make use of such conceptions. It is, however, a fatal illusion to mistake the suggestions of fancy for the realities of nature, and such a symbol becomes open to serious objection unless we carefully discriminate between conjecture and fact. Under the baneful influence of such hypotheses the methods of positive science lose their hold upon the mind, until at length we are actually informed by the consistent advocates of these ideas that the science of chemistry has no other field for its activity than the obscure region of atomic speculations.

Now a symbolic calculus affords the same indispensable aid which is given by the atomic theory, but in a more truthful and effectual way. In the place of molecules and atoms it offers, as the subject of scientific contemplation, a system of marks and combinations of letters, which, however, we are not free to arrange and to interpret according to the dictates of caprice, but of which each has a specific meaning assigned to it in the calculus, from which the laws are deduced according to which it is permitted to operate upon it. We are thus enabled to construct an accurate symbolic representation of the phenomena before us, on the fidelity of which we can rely. Such a system is indeed based, in the most absolute sense, upon fact, for it presents only two objects to our consideration, the symbol and the thing signified by the symbol, the object of thought and the object of sense; and it is not the least among the advantages which such a method affords, that through it we are enabled to dispense altogether with less truthful modes of representation, as no longer calculated to serve even a useful purpose.

Every mark or sign which we employ for the purposes of thought is in a certain sense a symbol, and in their actual system of chemical notation, chemists are already in possession of an imperfect symbolic method. It appeared to me inexpedient to attempt any interference with this method, which has already been subject to so many modifications, and which, moreover, satisfies certain real demands. I must confess also that it seemed to me incapable of development, as being destitute of those essential conceptions, in the growth of which the development of such a method consists.

Now it is the introduction of the conception of chemical operations, which, as has before been said, especially distinguishes this calculus. The symbols here employed are symbols not of quantities (which may be replaced by numbers), but of operations (which cannot be thus replaced), which are defined by their results; and the units of ponderable matter are primarily conceived of in this calculus as made up from their component weights by the successive performance upon the unit of space of the operations indicated by the symbols of those weights.

It is through this order of conceptions that we are enabled to introduce into the chemical calculus the zero-symbol 1, regarded as the symbol of the unit of space, the subject of chemical operations, without which symbol, as will hereafter be still more clearly evident, the construction of a chemical calculus would appear to be impossible, and the absence of which symbol, perhaps more than any other defect, marks the radical imperfection of the present notation.

It is moreover from this point of view that it has been found possible to assign to the composite symbol  $xy$ , as the symbol of a compound weight, an exact interpretation in harmony with symbolic analogies, and it is as symbols of operation that chemical symbols have been proved to possess the properties given in the equations

$$\begin{aligned} xy &= yx, \\ x(y + y_1) &= xy + xy_1, \\ xy &= x + y, \end{aligned}$$

which afford an adequate basis for a symbolic method, and enable us to apply to these symbols those algebraic processes through which symbols become an instrument of reasoning.

But further, symbols of this class afford the most real and the most obvious expression of the facts with which the chemist deals. That such operations as are here indicated are the primary and immediate object of his study, and therefore the most essential particular to be embodied in the symbol, has been already, to a certain extent, recognised by more than one master of the science, adverse to the atomic mode of representation. Thus Gerhardt, in the remarkable words which I have placed as a fitting motto to this paper, thus defines the object of a chemical formula:—"Les formules chimiques, comme nous l'avons dit, ne sont pas destinées à représenter l'arrangement des atomes, mais elles ont pour but de rendre évidentes, de la manière la plus simple et la plus exacte, les relations qui rattachent les corps entre eux sous le rapport des transformations."\* Now if this be the object of a formula, how unreasonable is it to attempt the expression of that formula by symbols which not only permit, but even compel us to regard it from the atomic point of view. We cannot adopt the atomic symbol and at the same time declare ourselves free from the atomic doctrines. The symbols which are here employed impose no such limitation upon our view. They are simply the symbols of the operations, from whatever point of view these operations may be regarded, by which chemical transformations are effected. In the symbol of the unit of water  $\alpha\xi$ , we assert an indisputable fact as to the operations by which that unit is composed and decomposed in the actual system of chemical transformations. The symbol asserts that the unit of water is composed by two indivisible operations—indivisible, that is, so far as our experience extends—operating successively upon the units of space, which are known to us through their results and are defined by their results. Again, we assert that the units of certain other substances are similarly composed, the units of hydrochloric acid and of hydrosulphuric acid, for example, of which  $\alpha\chi$  and  $\alpha\theta$  are the symbols, and that in this respect these substances are similar to water. Or, again, we say that the units of hydrogen, of water, and of peroxide of hydrogen are connected by a certain serial relation between the operations by which they are composed which is given by the interpretation of the symbols  $\alpha$ ,  $\alpha\xi$ ,  $\alpha\xi^2$ , and that this relation is similar to that which exists between the units of hydrogen, hydrochloric

\* *Chimie Organique*, Paris, 1856, vol. iv, p. 566.

acid, and chlorine,  $\alpha$ ,  $\alpha\chi$ ,  $\alpha\chi^2$ . Now these are those very relations "qui rattachent les corps entre eux sous le rapport des transformations," which Gerhardt discerned to be the true object of symbolic expression, but which are not indicated, except accidentally, by our present system, which is based upon a different order of ideas.

But there is another aspect of the science equally real with that in which Gerhardt regarded it, and which he declined to consider. Surely we may be permitted to ask with Dalton, not only by what operations water is composed, but what water *is*? What is the nature of ponderable matter as revealed to us by the science of chemistry? To this inquiry also, in the only form in which such an inquiry is real and intelligible, the symbol supplies an answer. This answer is given by interpreting the symbol with reference to the results of the operations. The unit of water (Sec. I., Def. 10), we may reply to such a question, is an integral compound weight (Sec. I., Def. 7) of which the whole is identical with the two simple weights (Sec. I., Def. 8)  $\alpha$  and  $\xi$  of Section VII., which we recognize as simple weights, from the fact that in the total system of chemical transformation these weights are not distributed (Sec. I., Def. 12). The science of chemistry we may add, affords no further information whatever as to the composition of water than that which is comprised in this assertion, which is not only the true, but the only real form of answer which it is possible to give to inquiries as to the chemical composition of ponderable matter. There is no difference whatever, as regards facts, between this and the preceding statement; the difference lies in the way in which the facts are regarded. From the former point of view we consider the operations, from the latter the result of the operations. The symbols of geometry have a similar double interpretation. They may be regarded, with equal truth, as the symbols of lines and surfaces, or of the operations by which lines and surfaces are generated.

A symbol, however, should be something more than a convenient and compendious expression of facts. It is, in the strictest sense, an instrument for the discovery of facts, and is of value mainly with reference to this end, by its adaptation to which it is to be judged. Now in the present paper I have considered not only the principles of the chemical calculus, as regards the formal construction of symbols, but also the primary appli-

cation of these principles to the construction of a special symbolic system. In the symbol of each chemical substance a distinct assertion is made as to the chemical properties of the substance, which any one is at liberty to test by an appeal to facts. Now as no symbolic system similar to the present has yet been devised, and as this system cannot be deduced from any existing system, every symbol not only makes an assertion but expresses a discovery as to the chemical properties of the substance symbolized. It is obvious, from the way in which the symbol is constructed, that the properties symbolized are the properties of that system of chemical equations into which the symbols enter, and from which the laws of the science are to be deduced. The further development of these ideas must be reserved for another communication, in which the nature of the numerical laws which are thus expressed will be more fully considered.

We may also regard the symbolic system as the expression, in the language of reason, of those conceptions as to the composition of ponderable matter to which we are inevitably brought by the contemplation of chemical phenomena. Our conclusions on this point are so remarkable, and so contrary to anticipation, that doubtless we could never trust them but for the simple and exact process by which they are deduced. Now the conceptions which we form of the nature of the elemental bodies constitute the fundamental theory of the science, for these conceptions comprise and determine every similar conception. The unit of the element hydrogen is here conceived of as a simple weight, and symbolized by the letter  $\alpha$ . That, to say the least, this view may be permitted is proved by constructing the symbols of chemical substances upon this hypothesis. There are, however, certain exceptions, be they real or apparent, in which this mode of expression is impossible, and it will be seen on reference to the table of exceptions (Sec. VIII. (4)), that this hypothesis rejects as inadmissible, not only the cases which are rejected by the atomic theory, but those also which are rejected by the empirical law of even numbers (p. 373). The symbolic system which is here given is the expression of these laws, by the truth of which it must stand or fall. The unit of the element mercury, and the units of several other metals, such as zinc, cadmium, and tin, so far as our imperfect experience extends, appear to be analogous in this respect to

hydrogen. But these are the only elements of this simple composition. The units of a second group, of which the element oxygen, symbolized as  $\xi^2$ , may be taken as a type, and to which belong sulphur,  $\theta^2$ , and selenium,  $\lambda^2$ , are composed of two identical simple weights, and the facts of the science do not permit us to assume these units as otherwise composed. Lastly, another group of elements appears in this system of a different and more complex composition, to which group belong the elements chlorine  $\alpha\chi^2$ , bromine  $\alpha\beta^2$ , iodine  $\alpha\omega^2$ , nitrogen  $\alpha\nu^2$ , phosphorus  $(\alpha\phi^2)^2$ , arsenic  $(\alpha\varrho^2)^2$ , and in all probability numerous other elements. The simplest view which, consistently with the fundamental hypothesis (Sec. VII., Group 1 (1)), can be taken of the composition of these elements, regard being had to the total system of chemical combinations, is that they are severally composed of a unit of hydrogen and of two identical simple weights, as, for example, in the case of chlorine, of the simple weight  $\alpha$  and two of the simple weights symbolized by  $\chi$ , so that the elements of this group are to be considered as combinations of elements of the two previous forms respectively. It is further found, as a matter of experience, that the unit of every chemical substance may be regarded as a combination of the same simple weights,  $\alpha, \xi, \theta, \chi, \omega, \nu, \dots$ , which are the component weights of the units of the elements. Now from the fundamental equation  $xy = x + y$ ,

$$\begin{aligned}\xi^2 &= 2\xi, \\ \alpha\chi^2 &= \alpha + 2\chi, \\ \alpha^2\phi^4 &= 2\alpha + 4\phi, \\ &\cdot \quad \cdot \quad \cdot \quad \cdot \\ &\cdot \quad \cdot \quad \cdot \quad \cdot\end{aligned}$$

whence we unavoidably have suggested to us as the ultimate origin of our actual system of combinations, and as affording an adequate and probable (doubtless we cannot say the only possible or conceivable) explanation of the peculiar phenomena there presented to us, a group of elements  $\xi, \theta, \chi, \beta, \omega, \nu, \phi, \dots$  of the densities indicated by these symbols, and which, though now revealed to us through the numerical properties of chemical equations only as "implicit and dependent existences," we cannot but surmise may some day become, or may in the past have been, "isolated and independent existences." Examples of these simple monad forms of material being are preserved

to us in such elements as hydrogen and mercury, which appear in the chemical system, as records suggestive of a state of things different from that which actually prevails, but which has passed away, and which we are unable to restore.

Such a hypothesis is not precluded to us, but nevertheless we are not to imagine that it is a necessary inference from the facts. So far as the principles or conclusions of this method are concerned, the "simple weights"  $\xi, \theta, \chi, \beta, \omega, \nu, \phi, \dots$  may be treated purely as "ideal" existences created and called into being to satisfy the demands of the intellect, to enable us to reason and to think in reference to chemical phenomena, but destined to vanish from the scene when their purpose has been served; and the existence of which as external realities we neither assume nor deny.

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### XLI.—*On Paraffin and the products of its Oxidation.*

By C. H. GILL and ED. MEUSEL.

THE paraffin used in this research was obtained from Messrs. Price. It had a melting point of 56° C., but by repeated crystallisation from carbonic disulphide the melting point was raised to 60° and over. It was, therefore, a mixture of various hydrocarbons. By analysis it gave:—

C. 85.5 per cent.  
H. 14.9       ,,

As it did not seem to be quite settled whether paraffin is a marsh gas or an olefine, we endeavoured to clear up this point by the following experiments:—

Paraffin digested with Nordhausen sulphuric acid blackens even in the cold, but gives no soluble baryta-salt. When treated with English acid of ordinary strength, it behaves in a similar manner. With oil of vitriol diluted with one-fifth its bulk of water, it blackens slightly on being heated to 60°—80° C. for seventeen days, but still gives no soluble baryta-salt.

Sealed up in long tubes with hydrochloric acid gas, and heated to temperatures varying from 50°—100° C. for intervals of 1½ hour to 15 days, it undergoes no change of melting point,



and absorbs none of the gas. Aqueous solution of hydrochloric acid is likewise without effect.

When heated or exposed to sunlight in contact with bromine and water, it becomes soft at the same time that the bromine disappears. However, all the bromine which enters into the paraffin does so by replacing hydrogen, none combining directly, as is shown by the following experiment:—

About 4 grms. paraffin and 14 grms. water were sealed up with 2.518 grms. bromine, and the whole was exposed to sunlight for three days, by which time the bromine had all disappeared, a very white soft product being left. The tube was opened and the bromine estimated, in the form of hydrobromic acid, by a standard solution of soda. The bromine so found was 1.26 grms., which is sensibly equal to  $\frac{2.510}{2} = 1.259$ .

Therefore neither bromine nor hydrobromic acid had combined directly.

Paraffin in a state of fine division was treated in the cold and at temperatures above its melting point with solutions of hypochlorous acid, of strength varying from 2 to 4 per cent. It underwent no alteration of melting point, nor could any action be observed. Cetene  $C_{16}H_{32}$ , as described by Carius, combines with hypochlorous acid, with evolution of heat. From these experiments, together with the fact that paraffin occurs in mineral oils not known to contain any hydrocarbons of the formula  $C_nH_{2n}$ ,\* we conclude that paraffin is a marsh-gas and not an olefine.

Paraffin resists the action of most oxidizing agents, but yields to nitric and to chromic acids.

#### *Oxidation by Chromic Acid.*

300 to 500 grms. of paraffin were placed in each of three large boltheads, and were boiled with 120 grms. potassic dichromate, and 180 grms. of sulphuric acid diluted with twice its volume of water. A small quantity of manganese dioxide was added to each flask to expedite the reaction, which it does to a remarkable extent. After three or four days' boiling, the chromic acid was completely reduced. The cakes on its surface were well washed and then boiled with a very dilute solution

\* Ann. Ch. Pharm., cxxvii, 195.

of carbonate of soda. By this means a creamy liquid containing soap and paraffin, and a floating layer of unaltered paraffin were obtained. The lower liquid separated from the layer of paraffin was raised to the boiling point, and mixed with nearly its own bulk of spirit of 88 per cent., which caused the separation of the suspended paraffin. After cooling, the paraffin was removed from the surface of the alcoholic liquid; the latter, which had gelatinized, was strained through linen; and the solid portions were submitted to strong pressure.

The solid soap so prepared contained acids melting at 62° C., while that in the liquid gave acids melting at 40° C.

By re-crystallisation of the hard soda soaps from weak alcohol, the melting point of the contained acids was raised to 65° C., when, suspecting the presence of some very high acid, we converted the whole into lead salts, and repeatedly exhausted these with strong boiling alcohol. A considerable portion of them dissolved; but some remained, and, after decomposition, gave acids melting at 74—75° C.; these, by many times repeated crystallisation from alcohol and ether, at last attained a constant melting point at 78° C., and were not then to be distinguished from pure cerotic acid prepared, for purposes of comparison, from Chinese wax.

A portion was converted into a silver salt by the process recommended by Brodie,\* then dried, weighed, and ignited—

0·1553 grms. of salt gave  
0·972 grms. silver, that is 20·41 per cent.

A portion of another preparation of the silver salt was burned in a current of oxygen, and the following results were obtained:—

0·2179 grms. substance gave  
0·1983 „ carbonic acid  
0·2022 „ water  
0·456 „ silver.

By allowing two atoms of oxygen for each atom of silver, we find 0·0135 grms. of oxygen.

These numbers correspond to the percentages given below in the table, which also shows the percentages required by the next higher and lower homologue of cerotic acid:—

\* Phil. Trans. for. 1848.

	$C_{26}H_{51}AgO_2$	$C_{27}H_{52}AgO_2$ Calculated.	Brodie.	Found.	$C_{28}H_{54}AgO_2$
C ..	62.02	62.66	62.5	62.36	63.27
H ..	10.01	10.25	—	10.31	10.37
Ag ..	21.46	20.9	20.69	20.92	20.34
O ..	—	6.19	—	6.21	—

The acid was therefore cerotic acid. In addition to this cerotic acid, there was a great number of the lower acids of the same series, some solid and others liquid and volatile; of these latter, acetic acid was the most abundant.

#### *Oxidation by Nitric Acid.*

Paraffin, as is well known, is powerfully attacked by strong nitric acid, with ultimate formation of succinic acid, as pointed out by Hofstädter.\* When, however, the action is regulated by using a more dilute acid, the result is different.

About a kilogramme of paraffin divided into three portions was boiled with five or six times its volume of commercial nitric acid, of sp. gr. 1.3, diluted with  $1\frac{1}{2}$  volume of water. The action, at first imperceptible, gradually became stronger, red fumes were evolved, and an odour like that of butyric acid developed itself. The action was continued till the paraffin was decidedly soft when cold. The three cakes thus obtained were washed out with dilute alkali, and the paraffin left was again treated with nitric acid, and so on, till a sufficient quantity of crude soaps was obtained on which to work. These were all boiled with water, and alcohol was then added, as before described, for the purpose of separating suspended paraffin. The soaps which crystallised out of the alcoholic liquid were, after strong pressure, again and again crystallised from dilute spirit, till they gave acids melting at  $56^\circ C$ .

These acids were very brown; we therefore distilled them in a current of superheated steam, whereby their melting point was raised to  $64^\circ C$ ., and their colour was entirely removed. They were then converted into lead soaps, as those procured from the chromic acid process of oxidation; only the final crystallisation from alcohol and ether was not continued after the melting point had been raised to  $76^\circ C$ .

\* Ann. Ch. Pharm., xci, 326.

A portion of this still impure acid was converted into a silver salt, which was found to contain 22.01 per cent. silver. The acid used was therefore probably cerotic acid, containing a portion of some lower acid, as its melting point indicated.

As cerotic acid had been proved to be the product of the oxidation of paraffin by chromic acid, we did not deem it worth while to attempt the further purification of this portion, our point being established.

A large quantity of the lower acids of the same series was obtained at the same time as the cerotic acid, including among the lower terms, acetic, butyric, valerianic, and cenanthylic acids, which were separated in the ordinary way by fractional saturation and distillation, then converted into silver salts, and the percentage of silver in each salt determined. We wish to remark that cenanthylic acid was present in considerable quantity.

The nitric acid which had been used for oxidising the paraffin was found to contain some bodies in solution. It was submitted to distillation, when a strong odour of prussic acid was noticed. The presence of this body was then proved by distilling it out at a very low temperature into water, and applying the ordinary tests. As the nitric acid became more concentrated, another reaction set in; we therefore stopped the distillation, neutralized the remaining acid with soda, and added solution of basic nitrate of lead, till no further precipitate could be obtained. The precipitate thus produced, gave, on decomposition by sulphuretted hydrogen, an acid melting at 117° C., forming soluble salts with sodium, potassium, and ammonium, and insoluble ones with silver, iron, lead, and barium, in presence of ammonia and alcohol. Thus the barium salt promised an easy means of separating the acid or acids; but we found that it was impossible to remove the barium completely by sulphuric acid, as an acid barium salt was always formed, which was not decomposed by dilute sulphuric acid. We therefore precipitated the acids as ferric salts by a solution of ferric chloride, then extracted them by boiling with ammonia, concentrated the liquid, and threw down the acids with nitric acid. They had a melting point of 106° C. They were treated by Arppe's process\* (slightly modified) four times, whereby we obtained two acids, the one nearly pure succinic acid, melt-

\* Ann. Ch. Pharm., cxxiv, p. 86.

ing at 172° C., and giving a silver salt with 63·4 per cent. of silver (succinic acid melts at 180°, and gives a silver salt with 64 per cent. of silver); the other, anchoic acid, melting at 117°—118° C., and giving the following numbers on combustion:—

0·1921 gr. substance gave 0·4021 gr. of carbonic acid and 0·1451 gr. water,

corresponding to the percentages given in the following table:—

	Sebacic.	Anchoic. Calculated.	Buckton.	Found.	Suberic. Calculated.
C ..	59·4	57·44	57·02	57·1	55·17
H ..	8·91	8·51	8·68	8·38	8·04

A silver salt yielded

from 0·1186 gr. substance, 0·0636 Ag. = 53·62 per cent. Ag. (theoretical percentage, 53·3).

These numbers, as will be seen, agree closely with those given by Buckton,\* and the properties of the acid are identical with those given by Buckton for anchoic acid.

We regard this acid as being a product of the oxidation of the cerotic acid previously formed from the paraffin.

Commercial nitric acid diluted with four times its volume of water acts very slowly on paraffin, but forms, in the course of twelve days' boiling, a small quantity of a fatty acid, which can readily be purified so far as to melt at 73° C. We were not able to observe the simultaneous formation of any other product either among the bibasic acids or the volatile monobasic ones, neither was there any prussic acid formed.

From the results of our experiments, above detailed, we conclude that paraffin is a mixture of hydrocarbons homologous with marsh-gas, some of which have a carbon condensation of not less than C<sub>27</sub>.

These experiments were carried out in the laboratory of University College, London.

\* Chem. Soc. Journ., vol. x, p. 167.

XLII.—*On the Hydride of Butyro-salicyl and Butyric Coumaric Acid.*

By W. H. PERKIN, F.R.S.

IN a previous communication\* it has been shown that in the formation of coumarin, by means of acetic anhydride and hydride of sodium-salicyl, the first product of the reaction is the hydride of aceto-salicyl, and that this body is subsequently transformed into coumarin by the separation of a molecule of water. Having obtained homologues of coumarin by substituting other anhydrides for the acetic, it appeared desirable to follow up the changes which take place in the formation of one of these new products, and at the same time to further establish its relationship to ordinary coumarin by the production of a new coumaric acid. I have therefore investigated the changes which take place in the formation of butyric coumarin and its corresponding acid.

*Hydride of Butyro-salicyl.*

A solution of butyric anhydride in anhydrous ether is left in contact with hydride of sodium-salicyl for two or three days, the reagents being used in equivalent quantities. The ethereal solution is then filtered off from the butyrate of sodium formed, and agitated with a small quantity of a dilute solution of carbonate of sodium. It is then dried over anhydrous carbonate of sodium and distilled. After the ether has passed over, the temperature gradually rises, but no very steady boiling point is observed; the principal product however comes over at about 260°—270° C., and is collected apart. Three combustions of this body gave the following numbers:—

- I. ·1925 of substance gave  
·4835 of CO<sub>2</sub>, and  
·1096 of H<sub>2</sub>O.
- II. ·2002 of substance gave  
·5026 of CO<sub>2</sub>, and  
·1116 of H<sub>2</sub>O.

\* Vol. vi, p. 181.

III. 2508 of substance gave  
 6289 of CO<sub>2</sub>, and  
 1392 of H<sub>2</sub>O.

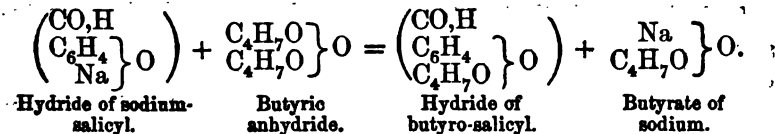
These results give percentages agreeing with the formula,



as the following comparisons show:—

	Theory.		Experiment.		
			I.	II.	III.
C <sub>11</sub> .....	132	68.75	68.50	68.46	68.38
H <sub>12</sub> .....	12	6.25	6.32	6.19	6.16
O <sub>3</sub> .....	48	25.00	—	—	—
	<hr/>	<hr/>			
	192	100.00			

The product therefore represents the hydride of salicyl, with an equivalent of hydrogen replaced by butyryl, its formation being analogous to that of the hydride of aceto-salicyl.



The hydride of butyro-salicyl is an oil boiling at about 260°—270° C. It has a slightly butyric odour mixed with that of the hydride of salicyl. It is soluble in all proportions in alcohol and ether.

With bisulphite it appears to decompose into butyric acid and hydride of salicyl, the latter combining with the bisulphite.

A strong solution of hydrate of potassium decomposes it immediately, forming a solid mass of the hydride of potassium-salicyl and butyrate of potassium; this decomposition is attended with a considerable elevation of temperature.

#### *Acetic Anhydride and Hydride of Butyro-salicyl*

A mixture of the hydride of butyro-salicyl and acetic anhydride, when heated in a sealed tube to 140° or 150° C. for a few hours, becomes slightly brown. On opening the tube and leaving the product in contact with water for a day or two;

crystals separate; these, when pressed between bibulous paper, and twice crystallised from alcohol, gave the following numbers on analysis:—

·2094 of substance gave—  
 ·4524 of  $C_2O_2$ ,  
 ·1057 of  $H_2O$ .

These results give numbers corresponding with those required by the formula

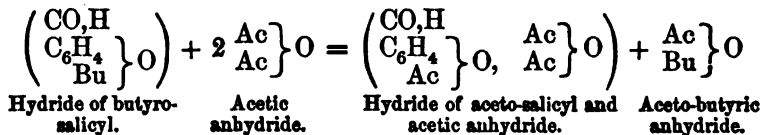


as the following comparisons will show:—

	Theory.		Experiment.
$C_{13}$ .....	156	58·64	58·92
$H_{14}$ ....	14	5·26	5·60
$O_6$ .....	96	36·10	—
	266	100·00	

This formula is that of the compound of the hydride of aceto-salicyl and acetic anhydride. Its identity was confirmed by the determination of its melting point.

In the formation of this product the radical butyryl has been replaced by acetyl, a mixed anhydride being probably formed at the same time, thus—



#### *Formation of Butyric Coumarin from Hydride of Butyro-salicyl.*

Hydride of butyro-salicyl when distilled alone does not appear to yield a coumarin, but if boiled with a mixture of butyric anhydride and butyrate of sodium for a short time, washed from saline matter with water, and then distilled, the last third of the distillate will be found to solidify on cooling. This solid product, when separated from oily matter by pressure between bibulous paper and then crystallised from alcohol, is



found to be pure butyric coumarin, possessing the correct melting point and characteristic odour.

The formation of this body is therefore perfectly analogous to that of ordinary coumarin.

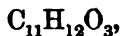
*Butyric Coumaric Acid.*

Butyric coumarin dissolves in boiling aqueous hydrate of potassium. Upon evaporating this solution, an oily layer forms, and if the liquid be then allowed to cool, this oily compound becomes a hard, tenacious mass, from which the alkaline solution may be easily decanted. This product is apparently a compound of one molecule of coumarin with one of hydrate of potassium, and is therefore isomeric with the potassium salt of a butyric coumaric acid. On heating this body in a dish, it fuses and boils up; it then becomes more pasty and frothy, and soon breaks up into soft masses.

This fused product is perfectly soluble in water, and on the addition of hydrochloric acid to its solution, it becomes a pure white mass of minute crystals. To separate any unchanged butyric coumarin from this product, it was dissolved in a little ammonia, filtered, thrown down with acid, washed well with water, and dried. Thus obtained it still contains a small quantity of butyric coumarin. This is easily separated by digestion with chloroform, in which the new body is very difficultly soluble. It is then further purified by crystallisation from dilute alcohol. A combustion of a specimen dried at 100° C. gave the following numbers:—

·1819 of substance gave—  
 ·4556 of CO<sub>2</sub>, and  
 ·1058 of H<sub>2</sub>O.

These numbers give percentages agreeing with the formula—



as the following comparisons will show:—

	Theory.		Experiment.
C <sub>11</sub> .....	132	68·75	68·30
H <sub>12</sub> ....	12	6·25	6·46
O <sub>3</sub> .....	48	25·00	—
	<hr/>	<hr/>	
	192	100·00	

This product is evidently butyric coumaric acid, the third of the series.

$C_9H_8O_3$  coumaric acid.

$C_{10}H_{10}O_3$  propionic coumaric acid (not known).

$C_{11}H_{12}O_3$  butyric coumaric acid.

It is also isomeric with the hydride of butyro-salicyl.

Butyric coumaric acid crystallises in flat prisms, having a brilliant lustre. It fuses at about  $174^\circ C.$ , but undergoes slight decomposition at that temperature. It is extremely soluble in alcohol and ether, but difficultly so in water and chloroform. It does not colour the solutions of the persalts of iron. It is but feebly acid in its characters, but will decompose a boiling solution of carbonate of sodium with effervescence.

Like ordinary coumaric acid, it forms only monometallic derivatives.

*Sodium salt.*—This body is prepared by boiling the acid with a solution of carbonate of sodium, keeping the acid in excess. The solution is then allowed to stand for a day, filtered, and evaporated. It is a crystalline and very soluble salt.

*Silver salt.*—A solution of the sodium salt gives a pale yellow precipitate with nitrate of silver; this, however, suddenly changes, becoming nearly white and crystalline. It is slightly soluble in water, and also in the above sodium salt. It requires careful drying for analysis, as it is apt to blacken at  $100^\circ C.$ , whilst a lower temperature does not appear to be sufficient for its complete desiccation. It gave the following results upon analysis:—

- I. .2012 of substance gave—
  - .3235 of  $CO_2$ ,
  - .0706 of  $H_2O$ , and
  - .0733 of Ag.
- II. .1338 of substance gave—
  - .0480 of Ag.

These numbers give percentages agreeing with the formula—



as the following comparisons will show:—

	Theory.		Experiment.	
			I.	II.
C <sub>11</sub> .....	132	44·14	43·85	—
H <sub>11</sub> .....	11	3·68	3·89	—
Ag .....	108	36·12	36·43	35·37
O <sub>3</sub> .....	48	16·06	—	—
	<hr/>	<hr/>		
	299	100·00		

*Ammonium Salt.*—Butyric coumaric acid dissolves easily in ammonia, but the resulting solution when evaporated decomposes, leaving nothing but the acid behind.

From these results there cannot be any doubt, I think, that the new coumarins are really true homologues of the natural body.

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XLIII.—*On the Vapour-Tension of Formate of Ethyl and of Acetate of Methyl.*

By W. DITTMAR.

By the experimental and speculative labours of H. Kopp, we have been made acquainted with a number of regularities regarding the correlation of chemical composition and boiling point in carbon-compounds. These regularities, although liable to exceptions, and in many cases only approximately in accordance with observation, clearly show that the constants determining the interdependence, in these compounds, of temperature and vapour-tension, must be dependent on, and deducible from, the atomic constitution of the molecule. It will take an enormous amount of experimental data, such as can only be furnished by the co-operation of a great number of investigators, before an approach towards the discovery of the great law expressing the correlation of chemical constitution, temperature, and vapour-tension will be possible. But chemists should not shrink from trying to accumulate these experimental data, the less so, as even a mere empirical knowledge of the tension-curves of a considerable number of compounds would be invaluable as a means for characterising them, and thus place in our hands a most powerful instrument of research.

Amongst the different boiling-point regularities pointed out by Kopp, there is one which, it seemed to me, might perhaps, at the expense of comparatively little experimental work, be expanded into a proposition regarding the dependence of vapour-tension generally, on chemical constitution.

We know that in the homologous series of ethers, formed by the union of fatty alcohols and fatty acids, a difference of  $n \times \text{CH}_2$  in the molecules of two terms corresponds to  $n \times a$  constant difference in the boiling points, and that consequently any two or more metameric ethers of the group must have the same boiling-point. Hence it would appear that the tension-curves of each group of metameric ethers have at least one point in common, and that, in case of all groups, this point always corresponds to the *accidentally* chosen pressure of 760 mm. It is certainly not going beyond the legitimate limits of induction to conjecture that, possibly, each such group has only *one* common tension-curve. In order to test this hypothesis, I decided upon undertaking a comparison, within a certain range of temperatures, of the tensions of the best known metameric ethers of this series, namely, of formate of ethyl and of acetate of methyl.

I have made two independent series of comparisons, employing in both of them methods which were in principle the same as Magnus's, only simplified so as to bring them within reach of my resources.

#### *First Series.*

In these experiments, which were finished about a year ago, the following apparatus was used:—A U-tube, of about 10 mm. inner diameter, was drawn out at a short distance from one end, so as to produce a narrow neck, into which was ground a well-fitting glass stopper. Each of the limbs was provided with a millimetre scale. The U-tube was placed in a vertical position, partly filled with mercury, and the levels of the mercury in both limbs were read, in order to find out which points in the two scales were situated in the same horizontal plane. More mercury was now added through *a*, so as

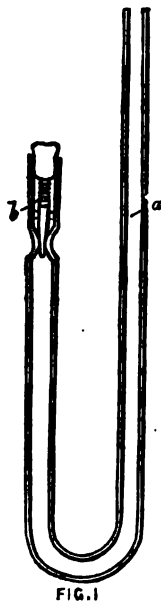


FIG. 1

to bring its level in *b* up to very near the neck. A quantity of formate of ethyl was poured into *b*, boiled for a short time, and then the stopper was inserted, so as to shut up a part of the liquid within the apparatus, and leave the rest in the funnel, *b*. Some mercury was now poured into this funnel, a spiral of steel wire introduced, and at last the opening closed with a well-fitting cork, so as to press the spiral against the top of the stopper, and at the same time hermetically close this end of the apparatus. At last the greater part of the mercury contained in limb *a* was taken out by means of a pipette. A similar apparatus was charged with acetate of methyl, and the open ends of both were connected with the same syphon-barometer, a branch off the connecting tube leading to a syringe, by means of which it was possible to rarefy, or condense, the atmosphere within the apparatus. The barometer was made out of a Frankland's gas-apparatus, and as the "pressure-tube" of this apparatus was more than 1 metre long, it was possible, by means of it, to measure pressures somewhat exceeding that of the atmosphere.

To execute the determinations, both U-tubes were plunged into the same water-bath (care being taken to make the tubes as exactly as possible vertical, and to bring the two ethers into close proximity to each other), and exposed to the desired temperature. The pressure within the apparatus was, by means of the syringe, adjusted so as to produce a convenient volume of each vapour; the water in the bath continually kept in motion by means of a current of carbonic acid; and after the temperature had been kept constant for a sufficient time to ensure equilibrium of temperature, the four levels of mercury in the U-tubes, and then the two in the barometer, were read off, and thus all the data were obtained for calculating the tensions of both vapours. Before giving the results, I will describe the methods used for preparing and testing the substances operated upon.

The formate of ethyl was prepared according to Löwig's method, *i.e.*, by distilling oxalate of ethyl (1 mol.) with dehydrated oxalic acid (1 mol.). In this process, the temporarily formed ethyl-oxalic acid breaks up into  $\text{CO}_2$  and formate of ethyl. The crude formate was purified by washing with water, then dehydrating with chloride of calcium, and at last distilling it in an apparatus constructed so that the vapours, before reaching

the condenser, had to pass through an ascending tube kept at about 56° C. The distillate was collected in fractions, and the fractions were separately tested by titration with standard baryta-water, when it turned out that the best fraction still contained about 1 per cent. of impurities. After an unsuccessful attempt to remove the latter, by repeated washing with water and drying with chloride of calcium, it was at last got rid of by digestion with, and distillation over dehydrated sulphate of copper. The ether thus purified giving, on titration, numbers corresponding to 100 per cent. of real formate, was considered sufficiently pure, and used for the tension experiments.

To prepare the *acetate of methyl*, a kind of purified wood-spirit, which at the time was to be had in commerce, under the name of "Eschwege's wood-spirit," served as raw material. The spirit was first dehydrated by means of lime, and then, by distillation with its own weight of dehydrated oxalic acid, changed into crystalline oxalate. The oxalate of methyl was, by means of a powerful press, freed from mother-liquor, and, for further purification, heated to near its boiling point in a current of hydrogen, when, however, no liquid distillate was obtained. This oxalate was originally intended to be next changed into methyl-alcohol, but I soon found out, and availed myself of a process for directly converting it into acetate. If glacial acetic acid and oxalate of methyl are heated together, there is scarcely any action observable; if, however, a small quantity of fuming hydrochloric acid be added, a complete double decomposition takes place, and acetate of methyl and oxalic acid are produced. The following *modus operandi* was ultimately adopted:—100 grs. of oxalate, 100 grs. of glacial acetic acid, 8 c.c. of (nearly saturated) hydrochloric acid were heated together in an apparatus in which the vapours formed had, before reaching the condenser, to pass through an ascending tube, placed in an open water-bath. The intermediate condenser was first, for a short time, kept cold, and its temperature then raised to, and kept at, about 56°, so that the acetate distilled over at the rate at which it was formed. The crude acetate was shaken with a solution of acetate of soda (which dissolves less of the ether than pure water does) kept in contact with and distilled over recently fused acetate of potash, and finally again distilled with fractional condensation at about 56°. The first fraction of the distillate titrated a few

tenths less than 100 p.c., and was used for the tension-determinations.

The following table gives the results of a series of tension-determinations executed in the manner above described:—

No. of experiment.	Temperature, Centigrade.	Vapour-tension reduced to 15° C.*		$f.-a.†$	Difference of temperature corresponding to $f.-a.$
		Formate f.	Acetate a.		
1	16·7	mm.	mm.	mm.	
1a	16·75	174·1	165·3	8·8	} 0·9°
2	25·0	174·5	165·2	9·3	
3	28·65	257·7	243·9	13·8	} 1·2
3a	28·6	} 300·3	282·3	17·7	
4	38·35		435·3	421·7	14·1
5	50·1	670·9	668·8	7·1	
5a	50·6	680·7	672·5	8·2	0·3
6	56·3	} 823·7	823·3	1·5	0·06
6a	56·2			—0·7	0·08

From these numbers it appears that the tension of the specimen of formate always exceeded that of the acetate; that from the temperature of 16° upwards, the difference of the tensions increased, until it attained a maximum, and then decreased again, so that at 56·2° it became practically = 0. It would have been extremely interesting to see, by a few experiments at higher temperatures, whether the tension-curves, from 56° upwards, continue to coincide or deviate again. An attempt towards this end unfortunately failed, and as I had just then to suspend work for some time, I was not in a position to repeat the experiment.

### Second Series.

Since Regnault has shown to how great an extent the vapour-tension of a substance may be affected by the admixture of even small quantities of impurities, it would be hasty to

\* The numbers in these two columns can only be considered as rough approximations; see end of memoir.

† Respecting the numbers in this column, it is to be remembered that they are independent of the manometer-readings.

apply to the *ideal substances*, results arrived at in experiments on one set of specimens. In resuming my experiments, therefore, I considered it necessary, first of all, to prepare new specimens, improving upon the methods of preparation and analysis, so as to bring the substances as nearly as possible to the state of absolute purity. I chiefly directed my attention to the titration of the ethers, and tried to give this process a higher degree of precision than I had previously been able to attain. The chief sources of error in the analysis of ethers by means of standard alkalies are those introduced:—

1. By the presence of free acid.
2. By the action of the alkalies on glass.
3. By the uncertainty, in case of weak organic acids, in the determination of the point of saturation.

Finding it extremely difficult to keep at least the formate of ethyl neutral for any length of time, I tried to find out a process for determining the amount of free acid in the ethers, and learned that this can be effected by means of a standard solution of ammonia, containing about  $\frac{1}{4}$  eq. ( $\frac{17}{4}$ ) grammes per litre. This liquid acts so slowly upon the ethers that, in employing it, it is easy to hit the point at which the *free* acid is saturated, and the ether begins to be acted upon.

Respecting the second source of error, it was found that, in case of the two compounds in question, it can practically be avoided by effecting the decomposition of the ethers (with alkali) in the cold. I have satisfied myself that, after a few hours' standing, the decomposition is quite complete. Caustic baryta and soda act about equally well; the latter, however, was found to offer this advantage, that the liquid, to the end of the titration, remained perfectly clear, while, in case of baryta, there was generally a slight precipitate formed, which carried down the litmus, and greatly diminished its sensibility as an indicator of alkalinity. A solution of pure soda (made of metal) containing about  $\frac{1}{2}$  equivalent, in grammes, per litre, and freed from  $\text{CO}_2$  by admixture with a slight excess of pure baryta, was ultimately found to be the most convenient standard alkali for the purpose.

Regarding the third source of error, I had no difficulty with the formate, the point of neutrality being quite sharply defined. In the titrations of the acetate, there was some degree of uncertainty, which I was not able entirely to remove. In order to



reduce the error, hereby introduced, to a minimum, the point of saturation was, in each case, determined several times, by successive addition of measured quantities of standard hydrochloric acid and saturation with standard alkali, and the mean of the results was taken.\*

In the preparation of the formate of ethyl for the new determinations, I first proceeded in the same way as before, with this difference only, that the crude formate was, previous to being washed with water, first shaken with ammonia, when a small quantity of oxamide separated out. The washed ether was dried, first with chloride of calcium, then with dehydrated sulphate of copper, distilled with partial condensation at 55°—56°, and collected in four fractions. Fractions I and III, when analysed by titration with baryta, gave numbers corresponding to, respectively:—

I.	III.
98·5	99·86 per cent. of real formate.

On titration with ammonia it was found that, while fraction I. contained only a trace of free acid, fraction III. contained a quantity corresponding to 1·4 p. c. of (decomposed) formate, so that in reality it was not any more pure than fraction I.

Seeing the impossibility of removing, by mere washing with water, the last traces of impurities, I tried to get rid of them by means of concentrated sulphuric acid. The ether was cautiously mixed with about one-fifth of its volume of distilled sulphuric acid, and the mixture was distilled from a paraffin bath at a temperature below 100°. The strongly acid distillate was treated with recently fused formate of potash and again distilled. In both distillations the vapour underwent partial condensation at 56°. The final product was found free from acid and titrated 100 p. c. (taken 922 mllgs.; found 922·3). It was preserved for the tension-determinations. Immediately before use it was tested with standard ammonia, when it was found to contain a quantity of free acid corresponding to  $\frac{1}{400}$  th

\* I hoped to be able completely to eliminate the uncertainty in the titration by decomposing the ether with excess of baryta, precipitating the excess with CO<sub>2</sub>, with the aid of heat, and determining the amount of carbonate precipitated. But finding that a solution of neutral acetate of barium (prepared by precipitating an acid solution of the salt with alcohol), when warmed and treated with CO<sub>2</sub>, gave a precipitate, I had to reject this method.

of its weight of decomposed formate. I did not think that this small amount of impurities could materially affect the results, and therefore used the ether as it was.

In the preparation of the acetate, the former process was improved upon in so far as the mixture of oxalate of methyl, acetic acid, and hydrochloric acid was heated in a paraffin bath, in order to avoid overheating, which might possibly have led to the formation of formate of methyl. The crude acetate was, this time, not washed, but at once poured on a large quantity of recently fused acetate of potash, the mixture allowed to stand for some hours, and then distilled from a paraffin-bath, with partial condensation, at 56—58°. The distillate was tested for, and found to be free from chlorine and oxalic acid, but titration showed it to contain 2.6 p. c. of other impurities. These were easily removed by successive distillations, firstly, with concentrated sulphuric acid, secondly, with recently fused acetate of potash, the operations being conducted exactly as in the case of the formate. The ultimate product was found, on titration with pure soda, to contain 99.8 p. c. of real acetate of methyl. (Taken 931.6 mllgs.; found 929.4.) It was perfectly neutral, and remained so up to the time of its being used.

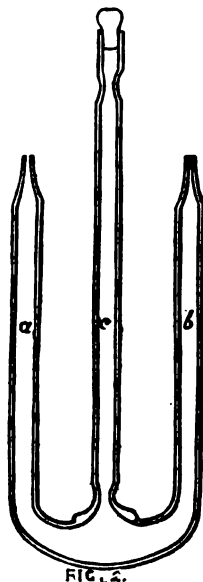


FIG. 2.

The improvements introduced in the physical part of the work consisted chiefly in this, that the two tubes containing the ethers were made to communicate, so that the two vapours pressed against each other through a continuous mass of mercury. The determination of the difference in tension was thus reduced to that of the difference of level of two menisci, a measurement which was effected by means of a cathetometer constructed by Dr. Meyerstein of Göttingen.

The water-bath used consisted of a rectangular iron case, provided on two opposite sides with plane glass plates, parallel to which the system of tubes containing the ethers was placed.

An apparatus, shaped like fig. 2, was made out of glass tubing of about 12 mm.

inner diameter. It was half filled with pure mercury, the open ends connected with an air-pump, and after exhaustion, the mercury was boiled for a considerable time. After cooling, *a* and *b* were drawn out near the ends, so as to produce very narrow-necked funnels, and more mercury was poured into the apparatus through the middle tube, the well-known precautions being taken to avoid, as much as possible, the formation of air-bubbles. Of the few bubbles formed, none were seen to travel over to the side tubes. About  $1\frac{1}{4}$  c. c. of formate of ethyl were now introduced into one of the side tubes, and the end of this tube was drawn out and broken off so as to produce a capillary orifice; the ether was then kept in ebullition for some time to expel the air, and the end of the tube sealed up. After the other side-tube had, in the same way, been charged with acetate of methyl, the greater part of the mercury contained in the middle tube was taken out with a pipette, and the end of this tube was closed with a perforated cork through which a glass tube passed, provided at the end with a cemented-on two-way stopcock of steel with two appendages, shaped so as to form one-half of a "Regnault's coupling." The apparatus was placed in the water-bath, and to one branch of the two-way cock there was coupled on a glass tube with soldered-on branches, connected severally, by means of black india-rubber tubing, with a syphon-manometer, a hollow copper ball of about 5 litres' capacity, and a syringe, constructed so as to serve for exhausting as well as condensing. The two-way cock afforded the means of making the W-tube communicate at will with the atmosphere or the manometer, or of shutting it off from either, and served to regulate the pressure within the apparatus. The object of the copper ball was to eliminate the influence of slight leakages in the joints, and of sudden changes in the temperature of the atmosphere. In the experiments at pressures exceeding one atmosphere, the cork in the middle tube was fastened down with wire, and the india-rubber joints were made pressure-proof by bandaging them over with strips of calico tied on with wire.

The *modus operandi* in the tension-determinations scarcely needs description.

After the desired temperature had been established in the water-bath, and the pressure within the apparatus properly adjusted, the temperature was kept constant and uniform by

well known means; and while one person kept the water in the bath continually in motion and observed the thermometers, another, by means of the cathetometer, took the levels of the menisci in the ether-tubes, first in *a*, then in *b*, and then again in *a*. In most cases the result was checked by altering the pressure within the apparatus, keeping the temperature as nearly as possible constant, and taking another series of readings. The temperatures up to  $50^{\circ}$  inclusive, were determined with a very sensitive thermometer, divided into fifths of degrees, obtained from Geisler, in Bonn, and corrected for a displacement (of  $+0.2^{\circ}$ ) in the zero-point of the instrument. The higher temperatures were taken with an ordinary laboratory-thermometer divided into whole degrees. This second thermometer had been compared with Geisler's at a series of temperatures below  $50^{\circ}$ ; and its indications having been found to exceed the latter by a constant difference of  $0.8^{\circ}$ , its readings above  $50^{\circ}$  were also corrected by deducting  $1^{\circ}$ . All this is, of course, no perfect guarantee for the exactness of the temperature-determinations;\* but considering that, as is seen from the table below, the differences of tension vary only very slowly with the temperature, a rectification of the errors in the scale of temperatures would probably not very materially alter its position towards that of the differences of tension.

The following table gives the results of thirty experiments carried out in the way described. "*t*" stands for the mean of the temperatures observed during the respective experiment; " $\Delta t$ " for the maximum deviation from this mean; "*f*" for the level of the meniscus in the formate-tube; "*a*" for that in the acetate-tube.† Consequently the column headed "*f—*a**," gives the excess of the tension of the formate over that of the acetate measured by a column of mercury of  $t^{\circ}$ ; the following column gives the same difference of pressure in mercury of  $15^{\circ}$  C.

\* I hope before long to be able to furnish a correction table for the temperatures given, founded on a calibration of the instruments or on comparisons with a "weight-thermometer."

† As observed with the cathetometer, the zero-point of which was at the upper end of the scale.

Experiment No.	<i>t.</i>	$\Delta t.$	<i>f</i> - <i>a.</i> mm.	<i>f</i> - <i>a.</i> reduced to 15°.
1	18·0	0	15·35	15·35
2	18·0	0	15·22	15·22
3	23·3	0·3	8·02(?)	18·02(?)
4	24·4	0	18·40	18·40
5	24·4	0	16·77	16·77
6	24·3	0·03	17·15	17·15
7	29·5	0·07	21·67	21·61
8	29·6	0·03	21·75	21·69
9	29·75	0·05	21·86	21·79
10	29·8	0	21·70	21·64
11	34·4	0	24·90	24·81
12	34·4	0	25·10	25·01
13	39·3	0·07	28·47	28·34
14	38·9	0·1	28·00	27·87
15	48·5	0·1	31·75	31·69
15 <sub>a</sub>	48·4	..	30·75	30·59
16	42·95	0·05	31·01	30·85
17	48·0	0·03	30·80	30·64
18	48·55	0·05	35·52	35·29
19	48·6	0	36·37	36·14
20	55·0	0	40·87	40·53
21	55·15	0·05	41·75	41·46
21 <sub>a</sub>	55·35	0·05	41·25	40·96
22	54·05	0·15	38·80	38·51
23	53·7	0·03	39·40	39·11
24	55·2	0·2	40·55	40·26
25	54·4	0·03	39·95	39·66
26	63·7	0	48·35	47·91
27	63·7	0·03	48·20	47·76
28	69·0	0	53·27	52·74
29	78·95	0·05	59·90	59·13
30	78·75	0·15	60·80	60·09*

It will be seen that the results of this series of determinations do not agree with those of the first. The differences cannot be accounted for by the more refined method of measurement employed in the second series, but must be owing to the different degree of purity of the two sets of substances used. Feeling sure that the ethers used in the second series of determinations were, at least, very nearly pure, I think we may safely assume that the results arrived at would substantially hold also for the ideal substances, and conclude that, at temperatures between 19° and 80° C, the vapour-tension of formate of ethyl is greater than that of acetate of methyl,

\* The absolute amount of the tensions at this temperature was about two atmospheres.

and that the difference is the greater the higher the temperature.\*

I cannot conclude without returning my cordial thanks to my friends, Mr. Cranston and Mr. Dewar, for the valuable assistance they have frequently given me in the course of this research.

University Laboratory,  
Edinburgh.

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#### XLIV.—*On a New Form of Constant Battery.*

By WARREN DE LA RUE and HUGO MÜLLER.

ALTHOUGH there are several voltaic batteries which possess the essential quality of continuous action, yet when a very large number of elements is required, it is found that they are all in some respects inconvenient. For example, it is very troublesome to charge a battery of several hundred elements, in which two liquids and a porous cell are required; moreover, diffusion of the two liquids eventually takes place, and produces a great amount of local action whenever the battery is left for a long time with the electrodes disconnected. We believe, therefore, that the instrument which we herein describe will be found useful to the chemist and the physicist as a ready source of dynamic electricity always at hand, and that, especially where from a few hundreds to several thousand elements are requisite, it will be found to be valuable, handy, and compact. In its construction no porous cell is needed, and the electrolyte is solid and very nearly insoluble, so that practically the electro-positive metal is scarcely attacked, even when the elements are left immersed with the electrodes disconnected for several weeks. We may state that this instrument was designed for the express

\* A few of the values for  $f-a$  were reduced to differences in temperature, the calculations being founded upon the absolute determinations of the tension of acetate, in series I.; the results, which I give only as rough approximations, were as follows. The temperatures of equal vapour-tensions are respectively :

For formate . . . .	20	26	33	43	53°	* 54.9
„ acetate . . . .	21.7	27.8	34.7	44.5	54°.4	56.3
Difference . . . . .	1.7	1.8	1.7	1.5	1°.4	1.4

\* According to H. Kopp.

object of facilitating experiments on the direct voltaic discharge in highly rarefied media, that is, as an "intensity" rather than as a "quantity" battery.

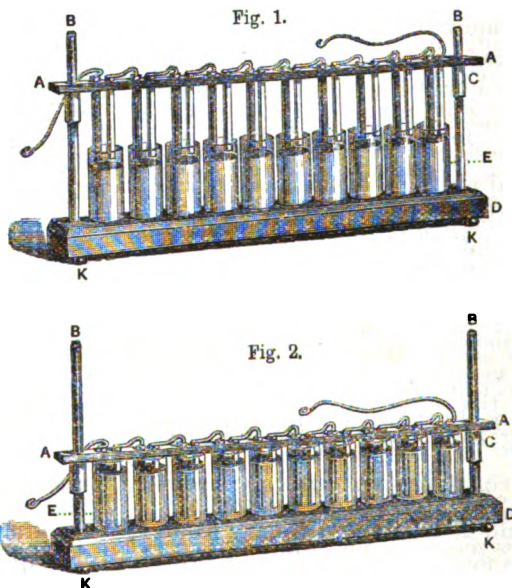
It will be recollected that a battery consisting of ten of our elements was described and exhibited in action, at the meeting of our Society, on February 6th last. At the soirée of the President of the Royal Society, on March 7th, one hundred elements were shown in action; and at that of the Chemical Society, on March 11th, and on several other occasions, two hundred elements were exhibited. But we have delayed giving a more detailed account of the instrument for publication, until we had an opportunity of making further experiments with it, and more especially of testing its electromotive force. In our battery, the generating or electro-positive metal is zinc, which it is better to amalgamate, although it is not essential to do so; the negative metal is silver, and the electrolyte solid chloride of silver, the whole being immersed in a solution of chloride of sodium or chloride of zinc. The solution we generally use contains 25 grammes of common salt to a litre of distilled water (219 grains to a pint). It is not desirable to use common water for dissolving the chloride of sodium, as the carbonates present cause a cloudiness by precipitating the zinc as carbonate, when the battery is in action.

The form of the battery which we have adopted is represented in Figs. 1 and 2, but where a very large number of elements is wanted, it is more economical and convenient to employ a modification presently to be described, and shown in Fig. 3. The zinc element is formed of Belgian zinc wire (English zinc being too impure to be used advantageously),  $2\frac{3}{4}$  inches (6 centimetres) long, and 0.2 inch (5.1 mm.) diameter. The electro-negative element consists of a wire of pure silver, 0.03 inch (0.77 mm.) in diameter; and round this is cast\* a cylinder of chloride of silver, 0.22 inch (5.6 mm.) in diameter. The silver wire projects about 0.2 inch (5 mm.) beyond the bottom end of the chloride of silver,

\* In making these cylinders, a mould which was designed for casting rods of lunar caustic (nitrate of silver) was found to be convenient. The mould contained a series of recesses which permitted of several rods being cast at a time. The silver wire was held firmly in the centre of the cylindrical recess by passing through a hole in the bottom of the mould, and by a series of arms projecting over the mouth of each recess at a sufficient distance to permit of the fused chloride being poured into them.

and about  $1\frac{1}{4}$  inch (3·8 centimetres) beyond the top end of it, so as to permit of its connection with the zinc of the next pair of elements. The cells are conveniently formed out of 1-ounce vials, by cutting off the necks with a diamond or an ignited splint-coal.

The zinc and chloride of silver rods pass through and are supported by a lath or bar of varnished mahogany A A, which is pierced for that purpose. The ends of this bar are also pierced

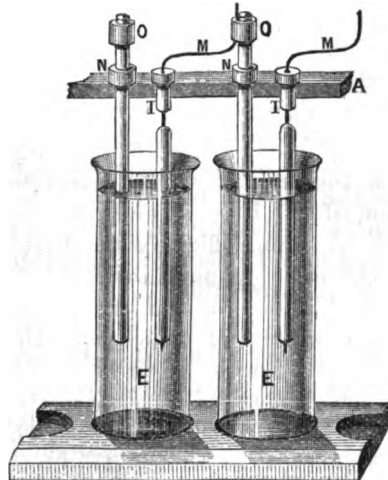


with two larger holes, through which the two supporting glass rods, B B, pass; it slides up and down these rods freely, and is retained in any required position by means of the vulcanized caoutchouc collars, C C, on which it rests; these grip the rods, B B, with adequate firmness, to support the bar, but at the same time permit of its being moved up and down with sufficient freedom to immerse the elements partially, or wholly, as in Fig. 2, or to raise them entirely out of the liquid, as in Fig. 1. The raising is conveniently performed by placing the two fore-fingers of each hand under the collars, C C, and pressing the thumbs on the top of the glass rods, B B; the lowering of the bar can be effected by pressing down the two ends. These glass rods should not be varnished on that portion over which



the vulcanized collars have to slide, as the varnish causes too much friction, and a liability to jerking; below this point they may be varnished with advantage. They are cemented into the base of varnished mahogany, D D, in which is made a series of recesses to fit the cells, E, and keep them in their places. This base rests on feet of vulcanite to increase the insulation. The rods of zinc and chloride of silver are prevented from falling through the holes in bar A A, by means of heads formed in the zinc by hammering the wire while it is held in a properly shaped tool, and on the chloride of silver by suitably shaping the upper end of the mould into which it is cast; a collar of caoutchouc is placed on the lower end of the zinc element to prevent contact between it and the rod of chloride of silver. Another plan of support is, however, more advantageous, where a very numerous series of elements is used, as shown in Fig. 3, for it permits both

Fig 3.



of economising the chloride of silver and of readily renewing it from time to time. Pieces of gutta-percha, or ebonite, I I, are well fitted into the bar A; they are pierced with a hole just large enough, to permit of the silver wire, M, being drawn through them. The zincs are held in position by means of the vulcanized collars, N, while a second collar, O, serves as a clip for making connection with the silver wires, M, which is done by passing the wire between the zinc and the collar, O.

It should be observed that as the chloride of silver becomes reduced, the resulting spongy silver is of greater diameter and less regular in form than the original rods of chloride; it is evident, therefore, that the reduced silver cannot be withdrawn through the holes in the bar, A A, with the arrangement shown in Figs. 1 and 2; moreover, that portion of the chloride which remains out of the liquid in the arrangement of Figs 1 and 2 is not reduced, and although no silver is ultimately lost, yet a portion of the useful effect of its chloride is sacrificed, and consequently the arrangement of Fig. 3 is both more economical and convenient. When the chlorine is more or less completely exhausted by the reduction of the cylinders through their entire thickness, the resulting rods of spongy silver should be placed in a vessel of water acidulated with hydrochloric acid and some rods of zinc, in order to reduce any undecomposed chloride, especially at their upper ends. After removal of the zinc, the spongy silver must be treated with dilute hydrochloric acid and well washed, to remove all traces of zinc. Very little, if any, loss of silver occurs, and the cost of renewal of the electrolyte is chiefly one of labour. If the battery be left in action after the complete reduction of the silver, there is always some reduction of chloride of zinc, and the amount of this secondary action we hope hereafter to investigate; but we confine ourselves, for the present, to a description of the effects of the primary action of the battery, and reserve for a future communication the total useful effect of the battery for an equivalent of zinc and chloride consumed.

Before entering on the details of the experiments, there are one or two matters worthy of notice. In the first place, the physical properties of chloride of silver render it especially advantageous as a solid electrolyte, for it is extremely tough, and therefore not liable to crumble away; it is sufficiently soft to be cut with a knife, and may even be rolled out in a rolling machine; although soft enough to be cut, yet it is so elastic as to give off musical sounds when struck. It conducts electricity so feebly that it must be classed with insulators; and it is on this account necessary that the silver wire should pass right through the chloride of silver, in order to touch the saline solution, and the circuit has to be closed for about a quarter to half an hour the first time the battery is used, in order to effect a sufficient reduction on the surface of the cylinders. When the action has once commenced

it may be continued until the whole of the chloride is decomposed. Although we have made batteries with plates of chloride of silver and zinc, instead of cylinders, the arrangements we have described are far more efficacious in proportion to their size.

In order to test the electromotive force of the battery, we availed ourselves of the kindness of Dr. Matthiessen and of Mr. Hockin, who placed at our disposal the apparatus they have employed in determining the conductivity of metals and alloys, and who were so good as to conduct the experiments, with which they are more familiar than ourselves. By way of comparison, a Daniell's battery was made, in which the electro-negative metal was pure electrotype copper, immersed in a solution of pure sulphate of copper, saturated at about 20° C. (68° F.), and the electro-positive metal was pure zinc, amalgamated and immersed in a solution containing 14 per cent. of pure sulphuric acid and 86 per cent. of water. The charge of the chloride of silver battery was 25 grammes of common salt to a litre of water (219 grs. to 1 pint). Two cells of the chloride of silver battery produced in a circuit of resistance of 31,170 Brit. Assoc. units a current of from 2 to 4 per cent. less than two of the Daniell's cells through the same resistance. But when the batteries were joined, zinc to zinc, and the negative elements were connected with the extremities of the coil, no current was apparent: the electro-motive force of the batteries was therefore identically the same, or, at all events, did not differ by 0.1 per cent. when only two cells of each battery were opposed. The internal resistance of 10 cells of the chloride of silver battery, estimated by the current produced through 31,200 B. A. units compared with the current produced by them through a circuit resistance of 10 units, besides their own resistance, was 56 units, giving 5½ units for each cell. In general terms, it may be said that the chloride of silver battery has about the same electro-motive force as a Daniell's battery.

During our experiments with the resistance coil, it was noticed that there occurred, in the readings of the galvanometer, pulsations which indicated a greater accumulation of force from time to time. The instrument could only show the pulsations of comparatively long interval; but this observation could not fail to point out that possibly periodic accumulations and discharges may occur in what we usually consider as a continuous current, whose periods are so small that it would require special

apparatus to reveal them. Their investigation might throw some light on the stratifications of discharges in highly rarefied media.

In order to test its constancy, a series of 10 cells was charged with a solution of common salt, and the circuit completed for half-an-hour. It was then connected, from time to time, with a voltameter, in which the electrodes were made of platinum wire, about  $\frac{1}{50}$ th (5.1 mm.) of an inch in thickness. When the current had become sensibly constant, the voltameter was read off, when it was found that the mixed gases were collected at the rate of 5.5 cubic inches (90.12 c.c.) per hour. The voltameter was then disconnected, and the circuit left unclosed for 14 days, the elements being allowed to remain immersed. At the end of this time, it was necessary to add water to replace that which had evaporated from the cells. On again completing the circuit, by means of the voltameter, 5.6 cubic inches (91.76 c.c.) of mixed gases per hour were collected, and this quantity was given off, from time to time, for several days, whenever the voltameter was made to close the circuit. A very slight local action had taken place on the zinc rods during the period of fourteen days that the elements had been left immersed and the circuit broken. Subsequently a trial was made with 100 cells, arranged so as to form a battery of 10 cells of ten times the surface, and connected with the same voltameter. On this occasion 53 cubic inches (868.46 c.c.) per hour were collected. Of course very little advantage was obtained in passing the current of 100 elements arranged in series through the voltameter over the current of 10 of the same elements. Some experiments were made by ourselves and Professor Abel with the battery, in order to test its value for igniting his artillery and blasting fuses. It required from 15 to 18 elements to fire the fuses with certainty; therefore 20 elements would be quite sufficient, for the purpose. 100 elements fired four of the fuses linked so as to form a chain.

A battery constructed as shown in fig. 3, gave, when the whole of the chloride of silver was immersed, 2 c.c. of mixed gases per minute, or 120 c.c. (73.2 cubic inches) per hour. The rods of chloride of silver weighed each 11.5 grammes; this corresponds to a total evolution of 1427.27 c.c. at 60° Fah. (15.6° C.), and the normal pressure, so that if used continuously at its maximum force, the chloride would be used up in 11.89

hours. It is easy, however, to regulate the consumption by immersing the elements a short distance at first, and gradually lowering them so as to make the chloride last for several days' continuous action. Moreover, for experiments, where the circuit is closed for a short interval only from time to time, the battery would remain available for several weeks without renewing the chloride. For special requirements the cylinders of chloride may be made of larger diameter.

One hundred elements gave a brilliant arc with boxwood charcoal points, which could be sustained when the points were withdrawn one-sixteenth of an inch (1.58 mm.); with a series of two hundred elements the arc could be maintained when the charcoal points were separated one-fourth of an inch (6.32 mm.). We have not hitherto constructed a larger series than that just described, as some slight improvements in construction have from time to time suggested themselves; but we anticipate that from 1,000 to 2,000 cells would permit of the investigation of the electric discharge in vacuo much more conveniently than with any other battery. Ten cells occupy a length of 15 inches (38.1 centimetres) and a width of 2 inches (5.1 centimetres), so that 1,000 elements would stand on five trays 18 inches (45.7 centimetres) wide and 48 inches (1.292 metre) long, and afford space for the supports. Although we have said that the battery was chiefly intended for use when "intensity" is desired, yet it will be seen that the amount of decomposition of water in the volta-meter shows that the amount of chemical force transmitted is very considerable in proportion to the size of the instrument. Lastly, it must be borne in mind that the source of power is the chloride of silver, and consequently that this is consumed as the sulphuric acid in Smee's battery, the sulphate of copper in Daniell's battery, and the nitric acid in Groves' battery, just in proportion to the amount of work done, and that it requires renewal just as these substances do; the chloride of silver battery, however, possesses this great advantage, that it is more simple to charge and bring into action than any porous cell-battery, and that it may be allowed to remain for a considerable time immersed without detriment. Notwithstanding this latter property, it will be better to remove the elements from the solution whenever the experiments are likely to be interrupted, particularly as the construction of the battery permits of this being done so readily.

XLV.—*Researches on Di-methyl.*

By WM. H. DARLING.

Being the results of an investigation for which the Dalton Chemical Scholarship at Owens College was awarded, October, 1867.

THE synthesis of carbon compounds forms perhaps the most important and interesting branch of modern chemical inquiry.

By the most recent developments of these synthetical processes it has been ascertained, that the chemical properties of a carbon compound depend upon the position of the atoms of which its molecule is built up.

From Frankland's original observations concerning the difference between the action of chlorine on the so-called di-methyl  $\left. \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \right\}$  obtained by the electrolysis of an alkaline acetate, and on the hydride of ethyl  $\left. \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{H} \end{array} \right\}$ , obtained from ethyl compounds, the existence of a difference in the four combining powers of a carbon atom was rendered probable.

The subsequent researches of Schorlemmer have, however, proved that only one hydrocarbon of the formula  $\text{C}_2\text{H}_6$  exists, inasmuch as he succeeded in preparing ethyl chloride from the hydrocarbon di-methyl  $\left. \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \right\}$ , obtained by the electrolytic decomposition of an alkaline acetate (Proc. R. Soc., xiii., 225); as well as from ethyl-hydride, obtained from ethyl compounds.\*

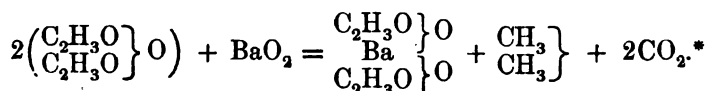
It appeared of great interest to repeat this synthesis, and to prepare the chloride in larger quantity, from which to obtain ethyl compounds and ascertain their chemical and physical properties.

At the request of Mr. Schorlemmer, I undertook this investigation. I take this opportunity to express my thanks to that gentleman, and also to Professor Roscoe, for the kind assistance rendered to me throughout this research.

\* Chem. Soc. J. [2], ii, 262.

### I. PREPARATION OF DI-METHYL BY SCHÜTZENBERGER'S PROCESS.

When peroxide of barium acts on acetic anhydride, a gas, stated to be di-methyl, is given off, the reaction being represented as follows:—



It was found that if the peroxide was heated with the anhydride, as Schützenberger directs, a violent explosion occurred, breaking the apparatus. In order to avoid this, the peroxide was mixed with dry sand; this had the desired effect, if the decomposition was allowed to begin at once. If, however, the flask containing the mixture was cooled to begin with, the action after a time became so violent, probably owing to the formation of peroxide of acetyl, that explosions occurred. 20 grms. of anhydride were weighed into a two-ounce flask, and an intimate mixture, consisting of 20 grms. of powdered peroxide of barium and 40 grms. of dry sand, was poured in, mixed by shaking and immediately connected with a bent glass tube, whereby all the air was displaced. The gas evolved was collected in a Pepys gas-holder, and afterwards displaced by pressure; it was purified by passing first through a strong solution of caustic potash to absorb the carbonic acid, afterwards through concentrated sulphuric acid to absorb any vapour of acetic anhydride present. The gas thus prepared burnt with a feebly luminous flame. In order to form the chloride, the gas thus prepared was treated with an equal volume of chlorine in the following manner:—A white glass bottle of about 2.5 litres capacity, full of water, was exactly half filled with the purified gas in a pneumatic trough, the remaining water displaced by pure chlorine, and the bottle tightly corked. The bottle thus filled was exposed, until nearly colourless, to diffused sunlight, after allowing time for the two gases to mix, and the action was completed by means of direct sunlight. The bottle was then opened under warm water; the hydrochloric acid absorbed was equal to half the capacity of the bottle. The remainder

\* Comptes Rendus, 1865, lxi, 487.

of the gaseous contents not absorbed was displaced by warm water into a receiver, in which a few pieces of stick potash were placed, and which was surrounded by a freezing mixture of salt and ice. In this tube a small quantity of liquid was condensed. After using the anhydride obtained from one pound of phosphorus, with the exception of a small quantity reserved for future analysis of the gas, the total volume of liquid obtained did not exceed 25 c.c., and began to boil at 40° C., the temperature rising up to 80° C. This quantity proved too small to admit of being fractionated, in order to separate any more highly chlorinated products.

In order to ascertain the cause of so small a yield of chloride, the gas was analysed, according to Bunsen's method, after freeing it from carbonic acid and vapour of anhydride by means of caustic potash. It was first tested for carbonic oxide, by means of cuprous chloride, and yielded the following result:—

## A.

	Volume.	Pressure.	Temp. C.	Vol. at 0° C. and 1m. Pressure.
Gas originally employed (moist)..	122.7	0.7151	14.0	83.47
After absorption of carbonic oxide (dry) .....	116.65	0.7273	17.0	79.86

The composition, as determined by analysis A, is

Carbonic oxide ..... 3.61

$\left. \begin{array}{l} C_n H_{2n} \\ C_2 H_6 \\ C H_4 \end{array} \right\} \dots\dots\dots 79.86$

83.47

The following absorption analysis B, was made with fuming sulphuric acid to determine the presence of olefines.

## B.

	Volume.	Pressure.	Temp. C.	Vol. at 0° C. and 1m. Pressure.
Original volume of gas (dry) ....	116.65	0.7273	17.0	79.86
After absorption with fuming sulphuric acid (dry) .....	119.40	0.7082	18.0	79.82



Hence the composition from B is

Carbonic oxide .....	3.61
$C_nH_{2n}$ .....	0.54
$C_2H_6$ } .....	79.32
$C^H_4$ }	83.47

For the determination of the remaining constituents, which could only consist of di-methyl and methyl hydride, a combustion analysis was made.

## C.

	Volume.	Pressure.	Temp. C.	Vol. at 0° C. and 1m. Pressure.
Original volume (moist) .....	203.5	0.1684	18.0	32.16
After addition of air (moist).....	527.1	0.4783	19.4	235.4
"  "  oxygen (moist) ..	618.5	0.5647	21.5	323.8
"  explosion (moist) .....	551.5	0.4992	20.2	256.4
"  absorption of carbonic acid (dry).....	495.2	0.4658	16.2	217.8

Original volume of gas .... 32.16 = A

Contraction .....

Carbonic acid .....

Since 1 volume of di-methyl gives 2.5 volumes of contraction and 2 volumes of carbonic acid, and 1 volume of methyl hydride gives 2 volumes of contraction and 1 volume of carbonic acid, then, if  $y$  represents the former gas and  $x$  the latter,

$$x + y = A$$

$$x + 2y = B$$

$$y = B - A \quad x = 2A - B.$$

By substituting the numerical values,

$$x + y = 32.16$$

$$y = 38.6 - 32.16$$

$$y = 6.44$$

$$x + 2y = 38.6$$

$$x = 64.32 - 38.6$$

$$x = 25.72.$$

The contraction C gives a third formula,

$$2x + \frac{5}{2}y = C$$

$$x + y = A$$

$$y = 2(C - 2A)$$

$$x = A - 2(C - 2A).$$

Again substituting values,

$$2x + \frac{5}{2}y = 67.4$$

$$x + y = 32.16$$

$$y = 2(67.4 - 64.32)$$

$$x = 32.16 - 2(67.4 - 64.32)$$

$$y = 6.16$$

$$x = 26.00.$$

Taking the mean of the results,

$$x = 25.86$$

$$y = 6.30.$$

From these analyses the following numbers were obtained :—

Carbonic oxide .....	3.58	4.29
Olefines .....	0.54	0.63
C <sub>2</sub> H <sub>6</sub> .....	15.49	18.57
C H <sub>4</sub> .....	63.84	76.51
	93.45	100.00

This analysis clearly shows that Schützenberger's description of the above decomposition is incorrect, the greater part of the gas consisting of hydride of methyl.

This method being found not to yield the required product, and not to be pure di-methyl, I endeavoured to procure this substance in quantity by the action of zinc upon methyl iodide.

## II. PREPARATION OF DI-METHYL BY FRANKLAND'S PROCESS.

In order to prepare pure di-methyl, I took advantage of the directions given by Schöyen\* for the preparation of pure di-ethyl.

Into stout glass tubes closed at one end, metallic zinc made rough on its surface was introduced; the open end was then softened before the blow-pipe, thickened, and drawn out into a strong capillary, which was bent twice at right angles, as described by Frankland. Through this capillary the methyl iodide was introduced, and afterwards the ether, equal in volume to that of the iodide, both of which had been dried as far as

\* Ann. Ch. Pharm., cxxx, 238.

possible over metallic sodium. The air in the tube was displaced by boiling the ether and closing the capillary, and the end was thickened after cooling the tube.

Tubes thus prepared were maintained at a temperature of  $130^{\circ}$  C., until all the zinc was dissolved, then allowed to cool, and afterwards opened by softening the end of the capillary before the blow-pipe, when any marsh-gas, which by presence of some moisture might have formed, escaped.

The tube, after heating until the contents began to boil, was again sealed, and heated at  $150^{\circ}$  C. for several hours.

After the tubes had attained the temperature of the room, they were immersed in a mixture of salt and ice; one end of a narrow tube of thick caoutchouc was drawn over the capillary, the other end being attached to a gas holder containing a saturated solution of common salt; and the end of the capillary was broken off. The gas then rushed into the holder, the internal pressure frequently projecting some of the liquid contents into the holder, where, in contact with the water, decomposition took place, it being almost impossible to decompose all the zinc-methyl.

The di-methyl obtained from iodide of methyl and zinc by this process, and purified by fuming sulphuric acid and caustic potash, was treated with chlorine, as in the previous case, whereby a liquid was condensed which began to boil at  $11^{\circ}$  C., and rose above  $80^{\circ}$  C. The quantity obtained was, however, but small, in consequence, no doubt, of the presence of marsh-gas from zinc-methyl which was carried over; and as it became apparent that considerable difficulty would be encountered in preparing large quantities of the pure gas, this method was abandoned.

To substitute mercury for the solution of salt would not be desirable, as the mass of mercury then required would be unmanageable.

That pure di-methyl is obtainable by this method is clearly shown by the following analysis; this gas was, however, collected in a mercury gas holder, as described in Bunsen's Gasometry.

The following analysis of di-methyl thus prepared was made according to Bunsen's method:—

	Volume.	Pressure.	Temp. C.	Vol. at 0° C. and 1m. Pressure.
Original volume of gas (moist) ..	145·62	0·1205	11·0	16·71
After addition of oxygen (moist)..	283·87	0·2563	11·8	69·74
„ „ air (moist).....	539·23	0·5075	11·8	262·3
„ explosion (moist).....	495·06	0·4637	11·5	220·3
„ absorption of carbonic acid (dry) .....	456·53	0·4268	11·9	186·8
„ addition of hydrogen (dry) .	579·12	0·5461	13·2	301·8
„ explosion (dry).....	476·92	0·4351	11·4	199·4

	Found.	Calculated.
Gas employed .....	16·71	—
Contraction .....	42·30	41·77
Carbonic acid.....	33·50	33·42

### III. PREPARATION OF DI-METHYL BY ELECTROLYSIS OF AN ALKALINE ACETATE.

I prepared the di-methyl by the electrolytic decomposition of acetate of potash, according to the process described by Kolbe. The gas, evolved from a platinum plate contained in a porous cell, was passed, first through a solution of caustic potash, to absorb the carbonic acid, afterwards through Nordhausen acid, and over pumice-stone moistened with oil of vitriol, to free it from a trace of oxide of methyl or hydrocarbon absorbable by this acid, and finally through a solution of caustic potash, to absorb acid fumes, any carbonic acid which had escaped the first wash bottle, or traces of sulphurous acid. The gas thus prepared had a very slight odour, and burnt with a non-luminous flame.

The following analysis of di-methyl was made according to Bunsen's method:—

	Volume.	Pressure.	Temp. C.	Vol. at 0° C. and 1m. Pressure.
(1) Original vol. of gas (moist) ..	188·48	0·1402	8·5	24·94
(2) After add. of oxygen „ ..	333·41	0·3919	8·0	127·00
(3) „ „ air „ ..	567·52	0·5221	8·5	237·5
(4) „ explosion „ ..	505·38	0·4591	9·2	224·7
(5) „ absorption of carbonic acid (dry) .....	447·58	0·4156	12·3	178·9

Contraction observed ..	62·80 ..	calculated for $C_2H_6$ ..	62·85
Carbonic acid ..	50·80 ..	.. ..	49·83

On similar treatment with chlorine as in the previous cases, and subsequent displacement with warm water into a receiver containing pieces of potash and surrounded by a freezing mixture of salt and ice, a colourless volatile liquid was condensed in the tube. If the gas or the chlorine was not pure, being mixed with air, very little or no liquid was condensed, being carried off by the current. The same fact was noticed by Mr. Schorlemmer. This will probably account for Frankland's observation that no liquid was condensed at  $-18^\circ C$ .

One hundred grammes of chloride were prepared by the repetition of this process. This first product was separated by distillation into two parts, one which distilled below  $30^\circ C$ ., and the other above  $30^\circ C$ . On still further fractionating the first distillate, a portion was obtained boiling at  $11-13^\circ C$ ., whose specific gravity was 0·9253 at  $0^\circ C$ . Pierre found the specific gravity of ethyl chloride to be 0·9241 at the same temperature.

The chloride boiling below  $30^\circ C$ . gave, on heating in sealed tubes with acetate of potash and glacial acetic acid to a temperature of  $130-140^\circ C$ . for three or four hours, a volatile fragrant liquid, having the characteristic odour of acetic ether, which, after drying over chloride of calcium and magnesia, boiled at  $74\cdot0-75\cdot5^\circ C$ . Kopp gives the boiling point of ethyl acetate at  $74\cdot3$  under a pressure of 760 mm. of mercury.

In order to prepare the alcohol, the acetate was heated with crystals of baryta hydrate in sealed tubes for one or two hours, to a temperature of  $120^\circ C$ . After cooling, the liquid was distilled, and the distillate treated with dry carbonate of potash until it separated into two layers; and the upper one was decanted upon fused carbonate and afterwards upon anhydrous baryta, from which it was distilled, when it had assumed a light amber colour. It began to boil at  $78\cdot1^\circ$ , the whole coming over before the temperature exceeded  $79\cdot0^\circ C$ . Kopp gives the boiling point of ethyl alcohol prepared by fermentation at  $78\cdot4^\circ C$ . under a pressure of 760 mm. mercury, and the specific gravity at  $0^\circ C$ ., as 0·8095; calculating by means of his coefficient of expansion, the specific gravity at  $6^\circ C$ . would be 0·80446, whilst I found the same to be 0·80302 at the same temperature.

The alcohol thus prepared had very little odour, agreeing in

this respect with the observation of Mendelejeff\* though the specific gravity is slightly higher than his at the same temperature, calculated from his coefficient of expansion, viz., 0·80123.

On submitting this liquid to combustion analysis, the following numbers were obtained:—

No. 1. 0·2834 grm. of liquid gave 0·5357 grm. of carbonic acid, and 0·3314 grm. of water.

No. 2. 0·5533 grm. of liquid gave 1·0481 grm. of carbonic acid, and 0·6480 grm. of water.

	No. 1.	Percentage	No. 2.		Calculated from the formula $C_2H_6O$ .
C ..	51·56	....	51·65	....	52·17
H ..	12·99	....	13·02	....	13·04
O ..	35·45	....	35·33	....	34·79
	<u>100·00</u>		<u>100·00</u>		<u>100·00</u>

The numbers are not all that could be desired when compared with the calculated composition; this is, however, owing to the difficulty in burning so volatile a liquid, and to the small quantities taken. Dumas and Boullay† state that, in order to obtain accordant results upwards of a grm. of liquid was necessary; in one combustion 1·742 grms. was used; with ether a still greater quantity was required.

The alcohol still remaining in the carbonate of potash and in the dilute solution was separated by distillation; this distillate was oxidized by a mixture of bichromate of potash and sulphuric acid, when the characteristic odour of aldehyde was recognised; and the oxidation was continued until it had disappeared. On distilling to dryness, an acid distillate was obtained: this was neutralized with pure carbonate of soda, and yielded on evaporation needle-shaped crystals of acetate of soda. The mother-liquor was distilled to dryness with sulphuric acid; and the distillate was neutralized with pure carbonate of silver, and filtered boiling. On cooling it yielded colourless transparent flat needles, which, after drying over sulphuric acid, gave on analysis the following numbers:—

No. 1. 0·4142 grm. of salt gave 0·2663 grm. of metallic silver.

\* Zeitschrift für Chemie, 1865, p. 257.

† Ann. Ch. Phys., 1827 [3], xxxvi, 299.

- No. 2. 0.5095 grm. of salt gave 0.3274 grm. of metallic silver.  
 No. 3. 0.3650 grm. of salt gave, after drying at 100° C. in a water-bath for one hour, 0.2349 grm. of metallic silver.  
 No. 4. 0.2483 grm. of salt gave, after drying at 100° C. in a water-bath for two days, 0.1604 grm. of metallic silver.

Estimation No. 1 gave 64.30 per cent. of silver.

"	2	"	64.25	"
"	3	"	64.36	"
"	4	"	64.60	"

Calculated from the formula  $\left. \begin{matrix} C_2H_3O \\ Ag. \end{matrix} \right\} O$ , acetate of silver yields 64.68 per cent. of silver.

That portion of the mixed chlorides which distilled above 30° C. was fractionated, when two-thirds of the total volume distilled over between 57°—59° C., and consist, as the following analyses prove, of the monochlorinated chloride of ethyl. The specific gravity of this liquid was found to be 1.198 at 6.5° C. Regnault found the sp. gr. to be 1.174 at 17° C., and the boiling point to be 64° C.\*

Beilstein† has shown that mono-chlorinated ethyl chloride, and chloride of ethylidene obtained by acting on aldehyde with perchloride of phosphorus, are identical; the boiling point of the latter, as observed by Wurtz, is 58-59°, and the specific gravity, as determined by Geuther, is 1.189 at 4.3° C.;—these numbers agree with those I found. Beilstein remarks that the higher boiling point, as observed by Regnault, would result from the presence of more highly chlorinated products.

The following numbers were obtained by analysis:—

- No. 1. 0.5206 grm. gave 0.3691 grm. of chlorine.  
 No. 2. 0.4491 " " 0.3186 "  
 No. 3. 0.4292 " " after drying over solid caustic potash for a week, 0.3010 grm. of chlorine.

Percentage of chlorine found by No. 1, 70.89

"	"	"	2, 70.94
"	"	"	3, 71.76

\* Ann. Ch. Phys. [2], lxxi, 355.

† Ann. Ch. Pharm., cxiii, 110.

The percentage required by the formula of monochlorinated ethyl chloride  $\left. \begin{matrix} \text{C}_2\text{H}_4\text{Cl} \\ \text{Cl} \end{matrix} \right\}$  is 71.73.

Hence the mono-chlorinated ethyl chloride was formed in quantity by the action of excess of chlorine on di-methyl.

The foregoing results confirm the conclusion that only one hydrocarbon,  $\text{C}_2\text{H}_6$ , exists, and that this substance, from whatever source it may be prepared, always yields ethyl chloride when treated with chlorine.

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*XLVI.—On the Application of Chlorine Gas to the Toughening and Refining of Gold.*

By FRANCIS BOWYER MILLER, F.C.S., Assayer in the Sydney Branch of the Royal Mint.

THE methods at present in use for refining gold, viz., by alloying it with a certain proportion of silver, and treating the metal so alloyed, either by sulphuric or nitric acid, necessitate a large and costly plant, besides causing a considerable delay before arriving at the desired end; whilst the processes used for toughening brittle gold are all more or less objectionable; the use of mercuric chloride, on account of its expense, as well as its obnoxious vapours; and the employment of oxide of copper, or of nitre and borax, from their corrosive action on the melting pots, and the unavoidable introduction, in the former case, of copper into the gold so toughened.

The consideration of these facts and objections suggested the desirability of instituting experiments for the purpose of determining whether it was not possible in one operation to satisfy all the requirements of the case more simply and cheaply.

The chemical part played by the mercuric chloride in the common process of toughening brittle gold, due as it is to the action of its chlorine upon the baser metals, which are thereby converted into more or less volatile chlorides, naturally suggested the use of chlorine gas; and the well known property of this gas to form argentic chloride when passed over red-hot



silver, encouraged the anticipation that it might, when applied to the alloys of gold and silver, give rise to the same compound.

The chief difficulties which presented themselves as opposing the practical adoption of such a method, were the volatility of the so formed argentic chloride when exposed for a considerable time to a very high temperature, and its liability to be absorbed by, and filter through, the pores of clay crucibles.

To overcome these difficulties, and thus to open a way for a practical application of chlorine gas to the before mentioned purposes, the following experiments were made.

A clay crucible was dipped into a hot saturated solution of borax in water, so as to be thoroughly impregnated therewith. Into this crucible, when dry, argentic chloride was introduced, and a well-fitting lid luted to it, and the whole was submitted to a high temperature in a furnace for 25 minutes. It was then removed from the fire, and when cold, broken. No absorption of chloride by the crucible was found to have occurred, and the residual cake of argentic chloride weighed nearly the same as before the operation.

Thus a ready means was indicated for obviating the infiltration and consequent loss of the fused chloride when treated in an ordinary clay pot.

The next and not less important question which had to be experimentally decided was the volatility of the argentic chloride at high temperatures. Indeed, so much does this question seem to involve the whole success of the application of chlorine gas to the purposes in view, that there can be little doubt but that a foregone conclusion on this point has hitherto prevented such a process from receiving earlier attention and trial.

The following experiments, however, were sufficient to set this question at rest.

I. 922.63 grains of argentic chloride, together with 1,660 grains of fused borax were introduced into a weighed porcelain crucible, loosely covered with a porcelain lid, and the whole was submitted to the highest heat of an assay muffle for 1 hour and 35 minutes. The crucible and its contents were found to weigh after this operation only  $5\frac{1}{4}$  grains less than they did before the experiment was begun.

II. 102 ounces of fine silver, and 3 ounces of fused borax were melted in a clay crucible, previously prepared by dipping it into a solution of borax, as before described, and covered with

a well fitting but not luted lid, through a hole in the centre of which, a clay pipe, reaching down to the bottom of the pot, was introduced as soon as the whole contents were in a state of fusion. Through this pipe a current of chlorine gas was allowed to pass for upwards of an hour, which was effected quietly and without any projection of globules.

At the end of this time the crucible was withdrawn, and allowed to cool. On breaking the crucible, a cake of silver was found at the bottom; on this rested a layer of argentic chloride; and on this, again, a thin stratum of borax, tinged with a delicate pink colour.

The argentic chloride thus produced weighed 14.93 ounces, yielding on reduction 10.81 ounces of silver.

An ingot of silver was obtained unacted on by the chlorine, weighing 90.83 ounces.

The pot on being crushed and washed, gave of silver 0.08 ounces.

And the borax yielded 0.06 ounces; summarized thus:—

Weight before experiment .....	102 ounces.
	Ounces.
Silver recovered as ingot .....	90.83
"    "    fr. chloride .....	10.81
"    "    fr. pot .....	0.08
"    "    fr. borax .....	0.06
	101.78
Loss .....	0.22
	102.00
	oz. 102.00

In these experiments the small addition of borax appears to have prevented all but a very minute volatilization of argentic chloride.

Encouraged by these results, as well as by those obtained with small quantities of alloys of gold and silver similarly treated, trials on a large scale were instituted.

From these trials, the results of which are appended in a tabular form, it will be seen that, with the imperfect apparatus employed, the time required for the operation was only a few hours, in order to bring the gold to a fineness of, say, 993 parts in 1,000, and that the *apparent* loss of gold is very little more than what is known to occur in ordinary gold melting, being

$2\frac{2}{10}$  parts in 10,000, whereas in ordinary Mint melting the *apparent* waste is about 2 parts in 10,000. By "*apparent loss*" is meant the loss at the end of an operation, without taking into account the amount recoverable from "*sweep*," &c.

The *apparent* waste of silver it will be seen is about  $\frac{1}{4}$  per cent. of the gross weight operated on, or 3 per cent. of the silver contained in the alloy: but a large proportion of this is recoverable from the flue, more especially if a small condensing chamber is constructed in its course.

In the experiments referred to in the table, the gold to be operated on was melted with a little borax, in French clay crucibles, duly prepared by dipping into a solution of borax, in order to render them less liable to absorb the melted argentic chloride.

It was found that black-lead pots would not answer for the purpose, as they exert a reducing action on the chloride, probably from a small quantity of hydrogen contained in the materials of which they are composed.

The crucible was covered with a closely fitting but unluted lid, with a small hole bored through it, and when the metal was melted, a long, ordinary tobacco-pipe stem (no suitable clay tubes being then procurable in the colony) was inserted through this hole, so as to dip into the molten gold down to the bottom of the pot. The upper end of the pipe stem was connected by a vulcanized india-rubber pipe, with a large stone bottle (warmed by a water-bath), in which chlorine was generated, and with this simple arrangement quantities of gold, weighing upwards of 400 ounces, were refined. The gas was used undried, just as it issued from the generator, no advantage being obtained when dry chlorine was employed.

The chlorine generator was fitted with a safety tube, 7 feet long, dipping at its lower end into the liquid in the generator; and the liquid standing in this tube at such a height as was necessary to overcome the pressure of the column of melted gold in the crucible, afforded a ready means of detecting at once if any accident had happened to the clay pipe, by the immediate alteration of the height of the column. One inch depth of gold in the crucible was equivalent to about 16 inches of liquid in the safety tube.

The india-rubber pipe when protected from the direct radiation of the fire, was found to stand the heat well; and if plunged

into weak ammonia at the end of each operation, lasted uninjured for some time.

No difficulty was experienced from the projection of globules of gold, as might perhaps have been anticipated would be the case. The greater part of the chlorine appears to be absorbed at once, and no violent ebullition consequently takes place. It was found advisable not to introduce the stream of gas into the molten metal until all the atmospheric air had been expelled from the generator, and only pure chlorine gas was issuing from the eduction pipe; for the *air* passed through the gold without being absorbed, and caused rather more bubbling of the molten gold, and possible loss by projection, than was the case with pure chlorine, which was almost wholly taken up by the silver.

It is difficult to obtain proper apparatus in the colony; but with the defective arrangement here described, about 8 ounces of metallic silver per hour were separated as chloride from gold alloyed with it, and at nearly a uniform rate, whether the gold contained much silver or little.

An assay of the contents of the pot was taken from time to time by dipping into it a clay pipe warmed, to prevent it from cracking when plunged into the molten metal. A little column of gold rose in the bore, and the pipe, if at once withdrawn after the manner of a pipette, while the gold was partially cooled within it, retained a sample in the form of a little wire of gold; this was rapidly alloyed approximately, and thus the progress of the operation was ascertained.

When the refining was complete, the crucible was withdrawn from the fire and allowed to cool until the gold therein had set, and the still liquid chlorides were then poured from its surface into a mould, so as to form a slab. The borax was in this operation retained in the crucible: in effecting this no difficulty was experienced, as the borax was quite viscid, and consequently much less fluid than the chlorides.

The fused argentic chloride appeared to have the property while hot of holding a little chlorine gas in solution, which escaped from it with sluggish effervescence, as it cooled.

The fine gold remaining in the crucible was re-melted, and cast into ingots.

The reduction of the chloride of silver to the metallic state was effected by placing the slab between two flat pieces of

wrought iron, and immersing them in water acidulated with sulphuric acid, where it was left for 24 hours, by which time the reduction was usually complete, but the metal thus obtained always contained *a little* gold; it was therefore necessary to dissolve the reduced silver in nitric acid, when the undissolved gold was separated by decantation and melted, while the silver was precipitated as chloride, and again reduced to the metallic state.

[Since these experiments were completed, however, it has been found that the chloride of silver can be obtained free from gold without the necessity of dissolving the reduced silver, a matter of much importance in a practical point of view.]

On reducing the slab of argentic chloride with iron, as above described, and dissolving the spongy reduced silver in nitric acid, the gold remained as a flaky residue resembling precipitated metal, and not in rounded globules, as would probably have been the case had it been mechanically thrown up from the molten alloy by the gas during the operation. This fact rather appeared to indicate that a chemical combination of gold, silver, and chlorine had been formed, a view of the case which was further confirmed by the quantity of the two metals obtained from the slab of chlorides, as compared with the amount that should have resulted from calculation and from the circumstance that the residual gold was nearly pure.

It was found that a part of the gold was readily separated in the metallic state, and obtained as a button on submitting the slab of chlorides to fusion at a red heat, but that a portion still remained with the chloride of silver. This leads to the conclusion that if some agent could be found that would reduce the chloride of gold without affecting the chloride of silver, the whole of the gold might be separated by simple fusion. The only substance likely to effect this reduction seemed to be metallic silver; this, therefore, was tried, and found completely to effect the desired object, when tried on a small scale; experiments on larger amounts are necessary, and will immediately be made.

The mode of operation adopted was as follows:—A slab of argentic chloride, containing a small quantity of gold obtained from the refining of silvery gold by chlorine, and weighing 13·22 ounces, was fused in a borax-prepared clay crucible, at a bright red heat for five minutes; half an ounce of carbonate of

potash was then gradually dusted into the crucible, which was allowed to remain in the furnace for twenty minutes longer. The effect of the carbonate of potash was, by reducing a small quantity of chloride, to produce a shower of minute globules of metallic silver, which, as it descended through the fused argentic chloride, exerted its reducing action on any chloride of gold that might exist therein.

After withdrawing the crucible from the furnace, it was allowed to cool until the chlorides appeared black, but were still quite liquid; these were then poured off into a mould, and there remained at the bottom of the crucible a button of silvery gold, together with a spongy mass appearing to consist of subchloride of silver, which is less fusible than the chloride. The crucible was now replaced in the furnace with the silvery button and the spongy residue, and a little carbonate of soda added to reduce any silver chloride, &c., and the whole was brought to a red heat for five minutes. A button of silvery gold was thus obtained, weighing  $\frac{5.5}{100}$  of an ounce, and containing 0.28 oz. of gold and 0.27 oz. of silver.

On reducing the slab of argentic chloride to the metallic state, and dissolving the silver obtained in nitric acid, it was found to be *quite free from gold*.

It seems therefore probable that this plan will afford a convenient means of separating the small quantity of gold existing in the chlorides obtained in the method of refining above described, without the necessity of dissolving the reduced metal in acid and again reducing the dissolved silver to the metallic state.

With regard to the amount of chlorine wasted and passing up the chimney in the operations described in the earlier part of this paper, it appears, calculating from the materials employed in the generator, that the quantity so wasted does not exceed in amount that required to chloridize the silver in the alloy operated on. One cubic foot of chlorine will, theoretically, convert eight and a quarter ounces of silver into argentic chloride; not more than twice this quantity is actually required in practice, and probably less. Thus in refining 1,000 ounces of gold containing 5 per cent. (or 50 ounces) of silver, six cubic feet of chlorine would theoretically be required, and practically twelve cubic feet are amply sufficient; and this waste six feet, is not all vomited forth from the chimney at

once, but is gradually evolved during several hours. It can be readily intercepted in a small chamber furnished with a trickling stream of milk of lime. To determine approximately the amount of chlorine required to effect the refining, the following experiment was made:—

A known quantity, viz., 8·65 gallons of chlorine was passed through an alloy of gold and silver, containing an excess of the latter, that is to say, more than the chlorine employed would theoretically be able to convert into argentic chloride. At the end of the experiment 9·23 ounces of chloride of silver were obtained, so that the 8·65 gallons of chlorine converted 6·62 oz. of silver into chloride, whereas this amount of chlorine was theoretically capable of chloridizing 11·62 oz. of silver. The waste, therefore, of chlorine in this operation amounted to 44 per cent. of the quantity employed.

I am greatly indebted to my brother officer, Mr. Robert Hunt, the gentleman in charge of the melting department, and to Dr. Adolph Leibius, my colleague in the Assay Office of the Sydney Mint, for their valuable suggestions and assistance in reducing this plan of refining to a practical and workable method, and for their earnest encouragement under difficulties.

*Table showing results of Experiments in Refining Gold by Chlorine Gas.*

Fra. Bowyer Miller's Patent, Royal Mint, Sydney.

Number of experiment.	Gross weight of gold alloy operated on			Weight of silver extracted.	Weight of alloy left after the operation.				Apparent loss in operating.		Assay of alloy operated on.	Assay of refined gold.
	containing according to Assay.				containing according to Assay.				Gold.	Silver.		
	Gold.	Silver.			Gold.	Silver.	Gold.	Silver.				
	ozs.	ozs.	ozs.	ozs.	ozs.	ozs.	ozs.	ozs.	ozs.	ozs.		
1	135·35	129·95	5·40	4·700	130·460	129·840	0·620	0·010	0·120	959·4	995·2	
2	194·925	166·076	28·300	27·173	166·801	165·966	0·835	0·110	0·292	852·0	996·0	
3	276·499	255·165	20·765	18·135	256·820	255·080	1·800	0·085	0·830	822·8	993·0	
4	377·96	336·309	39·651	32·950	341·090	336·212	4·874	0·093	1·827	889·8	987·9	
5	409·25	375·280	32·740	29·600	377·050	375·111	1·939	0·169	1·201	917·0	995·0	
6	229·80	212·100	17·510	15·580	213·620	212·090	1·530	0·010	0·400	923·0	993·0	
	Before refining.				After refining.							

NOTE.—By "Apparent loss" is meant the loss shown at the end of each experiment, without taking into account the amount recoverable from "sweep" and fuses, which is a considerable proportion of the whole loss

XLVII.—*Note on the Specific Gravity and Boiling Point of Chromyl Dichloride.*

By T. E. THORPE.

IN the course of an investigation, the results of which will shortly be made public, I had occasion to prepare a considerable quantity of pure chromyl dichloride,  $\text{CrO}_2 \begin{Bmatrix} \text{Cl} \\ \text{Cl} \end{Bmatrix}$ , and consequently took the opportunity of repeating the determination of the boiling point and specific gravity of this substance. To the best of my knowledge, the only determinations hitherto published were made some years ago by Walter.\* The following results but incompletely confirm those obtained by that chemist.

The chromyl dichloride employed in these experiments was prepared by distilling an intimate fused mixture of 10 parts sodium chloride and 12 parts potassium dichromate, with 30 parts strong sulphuric acid. In order to ensure the expulsion of the free chlorine, the liquid was repeatedly distilled in a current of dry carbonic acid, and on the fifth distillation it was received in a flask provided with a long, narrow neck into the side of which, near its upper extremity, a tube had been fused in order to convey the vapours into Liebig's condenser. The determination of the boiling point was made in this flask, the thermometer being so disposed that the entire length of the mercurial column was within the vapour. The weight of the liquid employed was about 60 grammes. Under a barometric pressure of 733 millimetres it began to boil at  $114^\circ \text{C}$ ., the height of the column quickly rose to  $116^\circ \text{C}$ ., and remained perfectly constant at  $116^\circ.8 \text{C}$ ., the quantity distilling over at this latter point being about five-sixths of the whole. Walter observed  $118^\circ \text{C}$ . under a pressure of 760 millimetres. When the necessary allowance is made for the difference in the pressures, the two determinations may be said to agree completely. It appears, however, not to be possible to distil chromyl dichloride without slight decomposition.

To determine its specific gravity, a portion of the distillate

\* Ann. Chim. Phys. [2], lxxvi, 387; Pogg. Ann. xlv, 154.



obtained during the observation of the boiling point was transferred to a small weighed bulb, the neck of which was narrowed and provided with an accurately fitting stopper, to prevent the decomposition of the liquid by atmospheric moisture.

The following are the results of the various weighings:—

Weight of specific gravity bottle .....	3.5312	grms.
Bottle and water. Temp. 25° C. ....	7.6549	„
Weight of bottle after emptying and drying it, and before the introduction of the chromyl- dichloride .....	3.5311	„
Bottle and chromyl dichloride. Temp. 25° C. . .	11.4692	„

On calculation, these numbers give 1.920 as the specific gravity of chromyl dichloride at a temperature of 25° C. At 21° C., Walter observed 1.71. I may state, as some confirmation of the former number, that the accidental observation that this body immediately sinks on being dropped into strong sulphuric acid, originally led me to re-determine its specific gravity. It is worthy of remark that the atomic volume of this compound, calculated from the corrected number, agrees perfectly with that of its analogue, sulphuryl dichloride.

	At. wt.	Sp. gr.	At. vol.
Sulphuryl Dichloride, SO <sub>2</sub> { Cl	135.0	1.66	81.8
{ Cl			
Chromyl Dichloride, CrO <sub>2</sub> { Cl	155.5	1.92	81.2
{ Cl			

Heidelberg, September, 1868.

XLVIII.—*Analysis of the Ashes of a diseased Orange Tree (Citrus Aurantium).*

By T. E. THORPE, Dalton Scholar in the Laboratory of Owens' College, Manchester.

THE orange plantations along the south-eastern coast of Spain, and in the adjacent Balearic Isles, have recently been visited with a severe epidemic, the rapid progress of which was

naturally viewed with no little anxiety by the people, since the culture and exportation of oranges constitute one of their principal industries. This disease is said to have made its appearance at Valentia, and to have spread to the islands during the summer of last year. The first symptoms of the sickening manifest themselves in the leaves, which turn yellow and in time drop from the branches. During the progress of the disease, the roots exhale a most disgusting odour, and within a very few days after the attack the tree succumbs. But the true nature of this remarkable disease, hitherto unknown in these parts, is very imperfectly understood; its origin is involved in complete obscurity, and as yet it has baffled all attempts at remedial measures. Happily, however, its violence, which at one time threatened destruction to the entire plantations in the islands, has, within the present year, considerably abated, and the disease seems to be gradually dying out.

For these particulars I am indebted to the kindness of Professor Bunsen, who visited the Balearic Isles during the summer vacation of last year, and as it appeared interesting to ascertain the nature of the inorganic constituents of the diseased trees, and to compare it with that of the ashes left by the combustion of perfectly healthy specimens, procured all the necessary materials for analysis. Accordingly analyses of the ashes of the roots, stem, branches, and fruit were made in the laboratory of the University of Heidelberg, under Professor Bunsen's direction and superintendence. The results of these analyses form the subject of the present communication.

The following was the method of analysis adopted:—From 4 to 5 grammes of the ash, obtained by burning in a muffle at the lowest possible temperature, were placed in a glass cylinder of about 500 c.c. capacity, provided with a well fitting stopper. About 50 c.c. of distilled water was then added, and carbonic acid passed into the cylinder, the delivery tube of the apparatus (which did not dip below the surface of the liquid) being frequently withdrawn, the stopper inserted, and the liquid shaken, in order to promote the absorption of the gas. When the caustic bases were completely neutralized, and the solution saturated (which was evidenced by the cessation of the partial vacuum, and also by the bubbles passing "*upwards*" between the bottle and its stopper when the latter was cautiously lifted after vigorously shaking the liquid) the total contents of the cylinder

were washed into a porcelain dish, evaporated to complete dryness, again heated with a small quantity of water, just about sufficient to dissolve the soluble portion, and after standing a short time filtered through a weighed filter. The filtrate, together with the washings, was again evaporated nearly to dryness, and allowed to stand for some time to effect, as far as possible, the complete precipitation of the calcium sulphate, which was separated, and when its amount was but small weighed immediately; if large, it was added to the main quantity of the insoluble portion of the ash, which was then dried at 100° C. and weighed.

### I. *Analysis of the Insoluble Portion.*

In the insoluble portion are contained lime, magnesia, ferric oxide, silica, phosphoric, sulphuric, and carbonic acids. The carbonic acid was estimated by the usual method, that is, by determining the loss of weight which a known quantity of the ash suffered on treatment with dilute hydrochloric acid; the sulphuric acid was afterwards determined in this solution by precipitation as barium sulphate. The phosphoric acid was separated by means of tin. For its estimation, together with that of the bases and the silica, about 1 gramme of the insoluble portion was dissolved in nitric acid, and after separation of the silica in the usual manner, the solution was again evaporated nearly to dryness, and dilute nitric acid added, until the bases were completely dissolved; strong fuming nitric acid was then added, until the calcium nitrate began to separate, when the slight precipitate was immediately re-dissolved by the addition of a few drops of dilute acid. The nitric acid solution of the bases was thus in the highest possible state of concentration, and on warming such a solution, the tin-foil is rapidly oxidized to the maximum degree of oxidation, whilst the supernatant liquid remains perfectly clear. The preliminary heating of the solution is absolutely necessary, since in the cold the metal becomes passive, and refuses to oxidize. The quantity of tin foil added amounted to about six times the weight of the phosphoric acid that could possibly be present, and care was always taken to keep the nitric acid in sufficient excess, in order to prevent the formation of the monoxide, which renders the solution inconveniently turbid. When all action was at an end, and

the tin fully oxidized, the contents of the dish were evaporated nearly to dryness, in order to remove the excess of nitric acid; water was then added, and the solution filtered. The precipitate contains all the phosphoric acid; the bases are found in the filtrate. This precipitate, detached as far as possible from the filter, was digested in the smallest possible quantity of highly concentrated potash-solution; on the addition of water this mixture dissolves to a perfectly clear liquid, provided no great excess of the alkali has been employed. The trifling amount of the precipitate still adhering to the filter was dissolved in the same manner, and added to the main portion of the solution. The liquid was then saturated with sulphuretted hydrogen, acetic acid added in very slight excess, and the precipitated tin sulphide separated by means of Bunsen's filter pump. The filtrate was next concentrated to a small bulk, the slight amount of tin sulphide, which invariably precipitates on evaporation, being removed, and the phosphoric acid determined in the usual manner as magnesium pyrophosphate. This slight departure from the indirect method usually employed is only rendered possible by the aid of the filtering apparatus invented by Bunsen; it has the advantage that the whole of the phosphoric acid admits of direct determination, a point of some importance when its amount is but relatively small, and moreover the saving of time it effects is considerable. The filtrate from the tin oxide, containing the ferric oxide, lime, and magnesia, may also contain no inconsiderable quantity of foreign metals, for example, lead and copper, existing as impurities in the foil; these were removed by sulphuretted hydrogen before the determination of the bases, which were then separated in the usual way, the iron by ammonia, and the lime and magnesia respectively by ammonium oxalate and sodium phosphate.

## II. *Analysis of the Soluble Portion.*

The solution of the soluble portion of the ash was filtered from the calcium sulphate (separated by evaporation in the manner above described) through as small a filter as possible, into a weighed flask provided with a tubulus drawn out at the side, to admit of the more convenient weighing off of aliquot portions of the weighed liquid. The total quantity of liquid was divided as near as possible into six equal parts, to serve for

the determination of the sulphuric acid, alkalis, chlorine, soluble phosphoric acid and carbonic acid, the sixth portion being reserved in case of accident.

The carbonic acid was determined volumetrically by  $\frac{1}{4}$  normal sulphuric acid and litmus solutions; the sulphuric acid and chlorine in the ordinary way, by precipitation as barium sulphate and silver chloride, and the phosphoric acid separated after considerable concentration of the solution, as the double salt of magnesium and ammonium, and weighed as pyrophosphate. In order to determine the amount of the alkalis, the solution was boiled with excess of baryta-water in a porcelain dish, filtered, and the excess of baryta removed by ammonium carbonate and ammonia; the solution was then evaporated to dryness in a platinum dish, gently heated, re-dissolved in a few drops of water; ammonia and ammonium carbonate again added; and after standing a considerable time, the solution was again filtered and evaporated to dryness, heated, and by the cautious addition of hydrochloric acid, converted into chlorides, in which form the alkalis were weighed. The potassium chloride was then separated in the usual way by platinum chloride. In cases where the amount of the soluble portion of the ash was comparatively large, more than traces of magnesia still remained in solution with the alkaline chlorides, even after repeated treatment with ammonium carbonate and ammonia. This small quantity of magnesia was found in the filtrate from the double salt of potassium and platinum; its amount was easily estimated by evaporating the alcoholic solution to dryness, re-dissolving in water, and transferring the solution to a small flask provided with a tightly fitting cork, pierced with two holes, to admit of the introduction of glass tubes. This little piece of apparatus has the disposition seen in the annexed figure. Hydrogen is led through the tube (A), and the end of the exit tube (B), within the flask is sufficiently long to reach just above the surface of the liquid, so as to ensure the complete expulsion of the air by the gas. When the vessel is completely full of hydrogen, the ends of the tubes (A) and (B) are closed during the actual transmission of the gas, either by screw-clamps or by glass rods, and the whole is placed in the direct sunlight, when the platinum is quickly reduced to the metallic state, and the solution ultimately becomes perfectly



colourless. The process of reduction may, if necessary, be facilitated by heating the solution on a water-bath before the transmission of the gas. If the capacity of the flask is small, it may be requisite to re-fill it once or twice with hydrogen, to ensure the complete reduction of the platinum; it is then desirable to displace the remaining gas by a rapid current of carbonic acid; otherwise an explosion might possibly occur, particularly if the contents of the flask are warm, owing to the surface action of the finely divided metal on a mixture of air and hydrogen. The clear solution was then filtered from the finely divided platinum, and after concentration the magnesia was precipitated in the usual way by sodium phosphate and ammonia, and its weight deducted from that of the mixed chlorides. This method is recommended to be used in all accurate separations of the alkalis from magnesia; it moreover offers a rapid and easy mode of recovering the excess of platinum used in the determination of potash.

(A.) *Analysis of the Ash of the Roots.*

413.4 grms. of the roots, freed as far as possible from adhering sand and soil, left on burning 5.686 grms. of ash. Amount taken for analysis, 4.9315 grms. After treatment with carbonic acid, the insoluble portion weighed 5.0816 grms., the solution of the soluble portion, 66.2125 grms.

I. Composition of the Insoluble Portion.

grms.		grms.	Amount in total insoluble portion.	grms.
1.1434	gave Silica .....	0.0710	Silica .....	0.31554
	Magnesium Pyrophosphate ....	0.1735	Magnesia .....	0.27787
	Ferric oxide .....	0.0100	Ferric oxide ..	0.04444
	Lime .....	0.5021	Lime .....	2.28145
	Magnesium pyrophosphate ....	0.0199	Phosphoric acid	0.05658
1.2273	Do. do. ....	0.0214	Do. ....	0.05063
0.5868	lost on treatment with dilute acid ..	0.2289	Carbonic acid ..	1.98230
	Total weight of Calcium Sulphate .....		.....	0.0050

II. Composition of the Soluble Portion.

grms.		grms.	Amount in total soluble portion.	grms.
10.1446	solution gave Barium sulphate .....	0.0751	Sulphuric acid..	0.16827
9.6667	„ „ Silver chloride .....	0.0191	Chlorine .....	0.03236
10.8218	„ „ Mixed chlorides .....	0.1290	Potash .....	0.24331
	Platinum-salt .....	0.1968	Soda .....	0.23455
9.2180	„ required 11 c.c. $\text{SO}_4\text{H}_2$ sol. (11 $\times$ 0.0022)		Carbonic acid ..	0.17332

(B.) *Analysis of the Ash of the Stem.*

Made by Herr Gütschow. 122.5 grms. of the wood left 4.00 grms. of ash. Amount taken for analysis, 2.9551 grms. After treatment with carbonic acid, the insoluble portion weighed 2.6687 grms.: the solution of the soluble portion weighed 40.5786 grms.

## I. Composition of the Insoluble Portion.

grms.		grms.	Amount in total insoluble portion.	grms.
0.8945	gave Magnesium pyrophosphate . . . . .	0.0955	Magnesia . . . . .	0.10269
	Do. do. . . . .	0.0175	Phosphoric acid . . . . .	0.08340
	„ Lime . . . . .	0.4465	Lime . . . . .	1.33210
0.4719	lost on treatment with acid . . . . .	0.1923	Carbonic acid ..	1.08750

## II. Composition of the Soluble Portion.

grms.		grms.	Amount in total solution.	grms.
8.4638	solution gave Silver chloride . . . . .	0.0552	Chlorine . . . . .	0.06542
8.1861	„ „ Barium sulphate . . . . .	0.0420	Sulphuric acid..	0.07147
7.7051	„ „ Magnesium pyrophosphate . . . . .	0.0050	Phosphoric acid.	0.01684
8.1500	„ „ Mixed chlorides . . . . .	0.0882	Potash . . . . .	0.20225
	Platinum salt . . . . .	0.2104	Soda . . . . .	0.06081
	Magnesium pyrophosphate . . . . .	0.0030	Carbonic acid ..	0.05916
8.0736	„ required 10.7 c.c. $\text{SO}_3\text{H}_2$ solution (10.7 $\times$ 0.0011)			

(C.) *Analysis of the Ash of the Branches.*

Made by Herr H. Knopf. Amount taken for analysis, 5.0115 grms. After treatment with carbonic acid, the insoluble portion weighed 4.8286 grms; the solution of the soluble portion, 47.7822 grms.

## I. Composition of the Insoluble Portion.

grms.		grms.	Amount in total insoluble portion.	grms.
1.3815	gave Silica . . . . .	0.0260	Silica . . . . .	0.09087
	Magnesium pyrophosphate . . . . .	0.0622	Phosphoric acid.	0.14004
	Ferric oxide . . . . .	0.0042	Ferric oxide....	0.01460
	Lime . . . . .	0.6837	Lime . . . . .	2.38950
	Magnesium pyrophosphate . . . . .	0.0992	Magnesia . . . . .	0.12498
0.3525	lost on treatment with acid . . . . .	0.2194	Carbonic acid ..	1.63340

## II. Composition of the Soluble Portion.

grms.		grms.		grms.
11·0056	solution required 5 c.c. $\frac{1}{10}$ normal HCl solution.			Carbonic acid .. 0·0476
6·9950	" gave Mixed chlorides .....	0·0293		Soda..... 0·02186
	Platinum salt .....	0·0770		Potash..... 0·10110
6·9592	" " Barium sulphate .....	0·0050		Sulphuric acid.. 0·0116
7·0647	" " Silver chloride .....	0·0016		Chlorine..... 0·0027

(D.) *Analysis of the Ash of the Fruit.*

Amount taken for analysis, 5·5482 grms. After treatment with carbonic acid, the weight of the insoluble portion was 2·2948 grms.: that of the solution of the soluble portion was 59·9210 grms.

## I. Composition of the Insoluble Portion.

grms.		grms.	Amount in total insoluble portion.	grms.
0·9339	gave Silica .....	0·0085	Silica .....	0·02062
	Magnesium pyrophosphate .....	9·2970	Phosphoric acid.	0·46085
	Ferric oxide .....	0·0023	Ferric oxide....	0·00560
	Lime .....	0·3834	Lime.....	0·24191
	Magnesium pyrophosphate.....	0·2021	Magnesia.....	0·17667
0·5149	lost on treatment with dilute HCl ....	0·1045	Carbonic acid ..	0·45978
	Total weight of calcium sulphate .....			0·02930

## II. Composition of the Soluble Portion.

grms.		grms.	Amount in total solution.	grms.
6·0410	solution gave Barium sulphate.....	0·0395	Sulphuric acid..	0·13442
5·1163	" " Silver chloride.....	0·0304	Chlorine .....	0·08805
2·8770	" " Magnesium pyrophosphate	0·0059	Phosphoric acid.	0·02305
7·9500	" " Mixed chlorides .....	0·4497	Potash .....	2·06950
	Platinum salt .....	1·4246	Soda.....	0·05800
	Magnesium pyrophosphate	0·0017		
6·2297	" required 42·1 c.c. $\text{SO}_4\text{H}_2$ solution (42·1 $\times$ 0·0022).		Carbonic acid ..	0·39086

Reducing all these results to percentages, after deducting the amount of carbonic acid, the composition of the ash of the root, stem, branches, and fruit is found to be as follows :—



	Root.	Stem.	Branches.	Fruit.
Potash.....	6.74	10.79	3.49	51.64
Soda.....	6.50	3.22	0.75	1.45
Lime.....	61.82	70.67	82.49	23.50
Magnesia.....	7.70	5.92	4.31	4.41
Ferric oxide.....	1.23		0.51	0.14
Chlorine.....	0.90	3.48	0.09	2.19
Phosphoric acid.....	1.57	2.66	4.88	12.07
Sulphuric acid.....	4.66	3.26	0.40	3.85
Silicic acid.....	3.74		3.13	0.52
Calcium sulphate.....	0.14		..	0.73
	100.00	100.00	100.00	100.00

For the sake of comparison, I here append the results of a similar series of analyses made some years ago by Messrs. Rowney and How, of ashes obtained from perfectly healthy trees grown in the island of St. Michael.\* In the last column I also add an analysis of the entire fruit by Dr. Richardson.† The results of these analyses are here represented in percentages, after deduction of the unessential constituents, *i.e.*, carbonic acid, sand, and charcoal.

	Root.	Stem.	Leaves.	Fruit.	Seed.	Fruit (Richardson).
Amount of ash left by } 100 pts..... }	4.48	2.74	13.73	3.94	3.30	..
Potash.....	15.43	11.69	16.51	36.42	40.28	33.72
Soda.....	4.52	3.07	1.68	11.42	0.92	7.64
Lime.....	49.39	55.13	56.38	24.52	18.97	22.99
Magnesia.....	6.91	6.34	5.72	3.06	3.74	6.55
Ferric oxide.....	1.02	0.57	0.52	0.46	0.80	1.74‡
Sodium chloride.....	1.18	0.25	6.66	3.87	0.32	trace
Phosphoric acid.....	13.47	17.09	3.27	11.07	23.24	14.17
Sulphuric acid.....	5.78	4.64	4.43	3.74	5.10	2.95
Silicic acid.....	1.75	1.22	4.33	0.44	1.13	5.25
	99.95	100.00	100.00	100.00	100.00	100.00

It will at once be noticed, on instituting the comparison, that the composition of the ashes of the healthy tree differs widely

\* Reports, &c., Royal College of Chemistry, 1847, Journal of Chemical Society.

† Ann. Ch. Pharm., lxxvii, 377, 1848.

‡ Ferric phosphate.

from that of the diseased specimens. The want of analogy is more particularly seen in the undue proportion of lime, and the comparative lack of phosphoric acid in all parts of the unhealthy tree, with the exception of the fruit; but the concentration of potash in the latter is remarkable. Whether, however, these deviations may in any way be connected with the source of the disease, or are themselves its results, remains still to be demonstrated. Hitherto the culture of the orange has nowhere been carried to a greater degree of perfection than in the Balearic Isles; but the yield of fruit seems to have been forced by excessive manuring to a most unnatural extent; and probably in this injudicious overworking of the trees may be found the cause of their sickening.

Heidelberg, September, 1868.

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