

VI. *Inquiries respecting the Constitution of Salts. Of Oxalates, Nitrates, Phosphates, Sulphates, and Chlorides.* By THOMAS GRAHAM, Esq. F.R.S. Edin., Professor of Chemistry in the Andersonian University of Glasgow, Corr. Member of the Royal Academy of Sciences of Berlin, &c. Communicated by RICHARD PHILLIPS, Esq. F.R.S.

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FROM the results obtained in a former paper upon water as a constituent of sulphates, it seemed likely that a close analogy would generally be found to exist between any hydrated acid and the magnesian salt of that acid. The sulphate of water is constituted like the sulphate of magnesia; and so do I now find the oxalate of water to resemble the oxalate of magnesia, and the nitrate of water to resemble the nitrate of magnesia. Indeed it appears probable that the correspondence between water and the magnesian class of oxides (as we may call the metallic oxides isomorphous with magnesia) extends beyond their character as *bases*,—that in certain subsalts of the magnesian class of oxides we have the metallic oxide replacing the water of crystallization of the neutral salt, or discharging a function which was thought peculiar to water.

In the formation of a double sulphate a certain kind of substitution or displacement was observed, such as the displacement of an atom of water pertaining to the sulphate of magnesia, by an atom of sulphate of potash, to form the double sulphate of magnesia and potash. The same kind of displacement appears to occur likewise in the construction of double oxalates; and the tracing of it enables us to form an idea of the constitution both of the double and of the superoxalates, and to explain their derivation, as in the case of the sulphates.

I. *Of the Oxalates.*

The oxalates promised ample scope for investigation from their number and variety. For we have not only neutral oxalates, double oxalates, and binoxalates, but likewise an unparalleled combination, the quadroxalate of potash, of which the true constitution or proximate composition is a most interesting subject of inquiry.

1. *Oxalate of Water, or Hydrated Oxalic Acid.*



The recent and accurate experiments of BERZELIUS, GAY-LUSSAC, and TURNER, leave no doubt that the crystals of oxalic acid contain three atoms of water. I find

the acid to crystallize with this proportion of water in a variety of circumstances, and believe that it is never deposited from its aqueous solution in any other state. Of these three atoms of water one atom is basic, which is expressed in the formula by placing its symbol *before* that of the acid; while the other two atoms of water are attached to this oxalate of water, and may be termed the *constitutional* water of the oxalate of water. These two atoms of water are found in the oxalate of magnesia, the oxalate of zinc, and the other oxalates of the magnesian class, as well as in the oxalate of water.

It is well known that oxalic acid can likewise exist in combination with no more than one atom of water (its basic water), and is obtained in that state by drying it at a temperature a little above 212° FAHR., or on subliming the hydrated acid by a higher temperature. I have made many experiments in order to discover whether, in the case of the other two atoms of water, one is retained more strongly than the other, or whether an oxalate of water with one additional atom of water, instead of two, could be obtained. The common crystals were dried at various temperatures, both in air and in vacuo, but either none of the water was lost, or the entire two atomic proportions. There is certainly no intermediate hydrate.

2. *Oxalate of Zinc.*



In the oxalate of water we observe a contracted solubility, and all the oxalates of the magnesian class of oxides are very sparingly soluble in water. They may be obtained by precipitation, on mixing a solution of oxalate of potash with sulphate of zinc, &c. Cold solutions of the salts were always made use of in our experiments; and the precipitates, which were always granular and more or less distinctly crystalline, were washed with cold water, and dried by exposure to the air for a week or two, without the application of artificial heat.

The oxalate of zinc is admitted to possess two atoms of water, and these I find are retained pretty strongly, as in the case of oxalate of water. It was observed that 24.95 grains of the salt lost only 0.44 grain by three days exposure to 212° FAHR.; but by a few hours at 315° FAHR. the salt lost in all 4.87 grains of water, and appears to have become anhydrous.

3. *Oxalate of Magnesia.*



The oxalate of magnesia retains its two atoms of constitutional water very strongly, and it is doubtful whether they can be expelled without decomposing the salt; 13.74 grains of the salt lost only 0.32 grain by an exposure to 212°, protracted for several days; and by two days at 300° FAHR. the whole loss amounted only to 0.47 grain. 22.36 grains of the same salt, ignited, left 5.94 grains of caustic magnesia, or one part

of the salt contains 0·2656 magnesia. A salt constituted with two atoms of water should contain 0·2759 magnesia, of which the specimen analysed falls a little short, probably from containing some hygrometric moisture.

The *oxalate of manganese* lost nothing at 212°, and was found by analysis to contain 0·2416 water, which approaches very closely the quantity equivalent to two atoms, namely, 0·2474 water in one hydrated oxalate of manganese.

In regard to several other oxalates of this class, namely, the oxalate of the protoxide of iron, of oxide of nickel, of oxide of cobalt, and of oxide of copper, I believe it is impossible to obtain them in a state of sufficient purity for analysis. They appear to carry down with them portions of the precipitating salts; and they alter manifestly in appearance and composition during the progress of the washing, to which they must be submitted for the purpose of purification. In the case of oxalate of copper, which was examined most particularly, the results were so anomalous that no inference whatever could be drawn from them.

It will appear, however, that a neutral oxalate of copper with two atoms of water can exist but in combination with oxalate of potash, or with oxalate of ammonia, as a double salt.

None of the oxalates of the magnesian class of oxides is more soluble in oxalic acid than in water, and none of them combines with that acid to form a binoxalate. The crystals, which are obtained on mixing together solutions of binoxalate of potash and sulphate of magnesia, and which have been supposed to be a binoxalate of magnesia, are really a mixture of oxalate of magnesia and of quadroxalate of potash. Hence there is no combination of oxalate of magnesia with oxalate of water; which illustrates the fact that bodies of the same class, such as these two oxalates are, have no disposition to enter into union and form a new compound.

4. *Oxalate of Lime.*



The oxalate of lime contains two atoms of water, like the oxalate of magnesia, but parts with its water more freely than that salt. Thus 12·06 grains of the hydrated oxalate of lime were found to lose 1·6 grain of water at 212° FAHR. in the course of two days, 1·68 grain in three days, 1·84 grain in six days, and nothing more in nine days. The salt originally consisted of 100 oxalate of lime united to 27·85 water, of which last it has lost 19·53 parts, and retained 8·32 at 212°. It is probable therefore that the constitution of hydrated oxalate of lime is the same as that of hydrated oxalate of magnesia, that oxalate of lime forms only one definite hydrate, containing two atoms of water, but that it parts with the whole of its constitutional water at a moderate temperature.

5. *Oxalate of Barytes.*

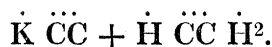
This oxalate differs from all the preceding, and contains only one atom of water. It was formed by digesting an excess of oxalic acid upon carbonate of barytes, and afterwards washing the resulting oxalate with cold water. 20·60 grains of the oxalate, calcined by a low red heat, left 16·45 grains carbonate of barytes, equivalent to 12·77 barytes. Hence it follows that the oxalate consisted of

		Composition of $\text{Ba } \ddot{\text{C}} \ddot{\text{C}} \text{H}.$
Barytes	100	100
Volatile matter	61·32	59·08
	<hr/>	<hr/>
	161·32	159·08

Before being washed this oxalate had a sour taste, and the volatile portion of it amounted to 67·01 parts instead of 61·32; but it was evidently the neutral oxalate with a little free oxalic acid. It was not a binoxalate; nor did such a salt present itself on digesting the neutral oxalate in oxalic acid, so that I am constrained to deny the existence of a binoxalate of barytes. Indeed it is scarcely a matter of doubt that no supersalt whatever exists of barytes, strontian, lime, or of the magnesian class of oxides.

6. *Oxalate of Potash.*

Oxalate of potash is known to crystallize from solution with one atom of water, and with no other proportion. The crystals speedily become white and opake at 212° FAHR., from the loss of water, but cannot, I believe, be made quite anhydrous at that temperature; at least a portion of the salt, which had been exposed to 212° for four days, still retained water, consisting of 100 oxalate of potash and 3·4 water, which is rather less than a third of the water which the salt originally contained (10·8 parts). The oxalate of potash becomes quite anhydrous when dried at 300°. Of salt so dried 100 parts reabsorbed 10·63 water in a damp atmosphere with the greatest avidity. The oxalate of potash has therefore a certain attraction for a single atom of water, and this is an important feature of the salt.

7. *Binoxalate of Potash.*

This salt has hitherto been supposed to contain only two, but it certainly contains three atoms of water.

21·37 grains of the salt, calcined by a full red heat, which is necessary for complete

decomposition, left 10·14 grains of carbonate of potash. Allowing the potash an equivalent proportion of oxalic acid, the salt must consist by this experiment of

Potash	32·23
Oxalic acid	49·38
Water	18·39
	<hr/>
	100·

The water almost coincides with three atoms, which would amount to 18·42 per cent. of the salt.

In the formation of the binoxalate of potash, the constitutional atom of water of the neutral oxalate of potash appears to be displaced by an atom of hydrated oxalic acid; so that the formula of binoxalate of potash represents anhydrous oxalate of potash, followed by oxalate of water with two atoms of water, as given above. The same principle of derivation applies most happily to that anomalous salt, the quadroxalate of potash.

8. *Quadroxalate of Potash.*

Analytic formula . . . $\dot{\text{K}}(\ddot{\text{C}}\ddot{\text{C}})^4\dot{\text{H}}^7.$

Rational formula . . . $\dot{\text{K}}\ddot{\text{C}}\ddot{\text{C}} + \dot{\text{H}}\ddot{\text{C}}\ddot{\text{C}} + 2(\dot{\text{H}}\ddot{\text{C}}\ddot{\text{C}}\dot{\text{H}}^2).$

The formula of the preceding salt is terminated by two atoms of water: let us replace them by two atoms of hydrated oxalic acid, and we have the quadroxalate of potash. We thus derive the quadroxalate from the binoxalate, in the same way that the binoxalate itself is derived from the oxalate.

There can be no doubt, from the accurate analysis of BERZELIUS, that this salt contains seven atoms of water. He found 100 parts of the quadroxalate of potash to yield by ignition 27·225 carbonate of potash. In an experiment in which 17·3 grains of the salt were ignited by us, there resulted 4·7 carbonate of potash; which is 27·11 carbonate of potash from 100 quadroxalate. BERZELIUS determined the water directly by igniting the salt with oxide of copper, and found it to amount to 24·8 per cent. of the salt. Calculated from our experiment, the water comes out 25·05 per cent., while the theory of seven atoms of water in the salt requires 24·72 per cent.

10·87 grains of this salt, dried by a nitre-bath, of which the temperature was 240°, lost eventually 1·46 grains; or 100 salt lost 13·43. Four atoms of water amount to 14·12 per cent. of the salt, to which the experimental result approximates sufficiently to prove that this salt parts readily with four of its seven atoms of water. These four atoms of water are evidently the constitutional water of the two atoms of hydrated oxalic acid, which the quadroxalate contains. When the salt is still more strongly heated, oxalic acid itself goes off, partly as a sublimate and partly in a decomposed state.

9. *Oxalates of Ammonia.*

The oxalate and the binoxalate of ammonia agree exactly in composition with the corresponding salts of potash, the hypothetic oxide of ammonium being substituted for potash. It has been supposed that no quadroxalate of ammonia exists; but this is a mistake. Such a salt is formed, on dissolving together equal weights of binoxalate of ammonia and hydrated oxalic acid, and is analogous in form and composition to the quadroxalate of potash.

10. *Oxalate of Soda.*

This salt is perhaps the least soluble of the salts of soda, and presents itself as a granular precipitate on saturating carbonate of soda with oxalic acid. Of the oxalate of soda dried in air without the application of heat, 23.44 grains left 18.52 carbonate of soda when strongly ignited, or 100 oxalate yield 79.01 carbonate of soda. Now 100 anhydrous oxalate of soda should yield 79.09 carbonate of soda. Hence the oxalate of soda is correctly stated to be anhydrous. It nevertheless combines with hydrated oxalic acid, and forms a binoxalate. In this compound we have simply the attachment of an atom of the oxalate of water, to the atom of oxalate of soda, without the displacement of an atom of water, as in the formation of the binoxalate of potash. Probably the absence of the atom of water in the oxalate of soda indicates an indifference on the part of this salt to enter into further combination. There is certainly a binoxalate of soda; but this binoxalate cannot support the further attachment to it of two atoms of hydrated oxalic acid, and there is no quadroxalate of soda.

11. *Binoxalate of Soda.*

This salt I find to resemble the binoxalate of potash, in containing three atoms of water. 22.11 grains, strongly ignited, left 8.05 grains fused carbonate of soda; or 100 binoxalate leave 40.67 carbonate of soda, equivalent to 23.84 soda; while a binoxalate with three atoms of water should yield 23.95 per cent. soda, or almost exactly the experimental result. The binoxalate of soda lost little more than 1 per cent. of its weight when kept at 212° FAHR. over sulphuric acid in vacuo. But by a heat approaching 300° FAHR. the salt lost 14.64 per cent. of water, which is a little more than two atomic proportions, namely, 13.78 per cent. Hence this salt retains the whole of its constitutional water at 212°, but loses two atoms of it at a higher temperature, retaining strongly the third atom of water, which is basic.

Double Oxalates.

The number of double oxalates is not so great as is generally supposed. On mixing a solution of binoxalate of potash either with the muriate or the sulphate of magnesia,

zinc, &c., the oxalate of magnesia or of zinc precipitates, while the quadroxalate of potash is formed, and remains in solution or crystallizes, being very sparingly soluble, according to circumstances. When binoxalate of potash is digested upon magnesia or upon oxide of zinc, a portion of the oxide is dissolved, but is quickly deposited again as an insoluble oxalate, and no double salt formed. But one member at least of the magnesian class of oxides, namely, oxide of copper, is dissolved by the binoxalates of the alkalies, and forms double salts, which were discovered and carefully examined by M. VOGEL of Bayreuth.

12. *Oxalate of Copper and Potash.*



and also

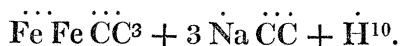
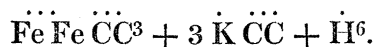
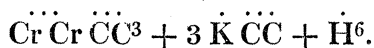


The binoxalate of potash, when considerably diluted, and digested with heat upon the oxide of copper, dissolves it easily, and a double salt of sparing solubility crystallizes, presenting itself generally in two forms, one of which contains two and the other four atoms of water, according to the analyses of M. VOGEL, which I have repeated and confirmed so far as the water is concerned. The crystals containing four atoms of water soon become opaque by exposure to the air, and lose two atoms of water by efflorescence.

Binoxalate of ammonia likewise dissolves oxide of copper, and does so still more readily than the binoxalate of potash, which may depend upon the circumstance that the resulting double salt of ammonia is considerably more soluble in water than the double salt of potash. The oxalate of copper and ammonia crystallized in plates of a blue colour, and seemed to affect one form only. Of these plates, 9.38 grains were readily decomposed by heat, and left 2.37 grains black oxide of copper, or 25.27 per cent., which is almost exactly the proportion of that of the oxide of copper, which a salt of two atoms water should contain, namely, 25.37 per cent. This salt loses water readily at 212° FAHR.; and of the 11.52 per cent. which it is supposed to have on the theory of its containing two atoms of water, 11.46 per cent. escaped by the exposure of the salt to that temperature. M. VOGEL describes two other double oxalates of copper and ammonia; but it is evident that they contain ammonia and not oxide of ammonium; so that they do not come under our consideration at present.

It is to be remarked that the oxalate of copper and potash is represented above by a formula quite analogous to that of binoxalate of potash, oxide of copper being simply substituted for basic water. We have oxalate of potash in both cases, to which there is attached oxalate of copper with two atoms of water in the one formula, and oxalate of water with two atoms of water in the other. It is to be remembered that in the case of the sulphates, the double sulphate of copper and potash was shown to have a similar analogy in constitution to the bisulphate of potash.

Oxalate of Chromium and Potash, of Peroxide of Iron and Potash, of Peroxide of Iron and Soda, &c.



This group of salts has not hitherto been submitted to analysis, although they occupy the same important position among the oxalates which the alums do among the sulphates.

13. *Oxalate of Chromium and Potash.*

This remarkable salt was first described by Dr. GREGORY, and its optical properties have been made the subject of a memoir by Sir DAVID BREWSTER*. It is easily prepared by the following process, which is Dr. GREGORY's, with the proportions slightly altered, from a knowledge of the composition of the salt. One part of bichromate of potash, two parts binoxolate of potash, and two parts hydrated oxalic acid, are dissolved together in hot water. There is a copious evolution of carbonic acid gas, arising from the deoxidation of the chromic acid, and nothing fixed remains except the salt in question; of which a pretty concentrated solution crystallizes upon cooling in prismatic crystals, which are black by reflected light, but of a splendid blue colour by transmitted light, when sufficiently thin to be translucent.

This salt, strongly dried without decomposition, was found to lose 11·67 per cent. of water.

The oxide of chromium cannot be precipitated from it completely by means of an alkaline carbonate, and it is very remarkable that only a small portion of the oxalic acid is thrown down from this salt by chloride of calcium.

To determine the proportion of oxalic acid, the salt was heated in strong sulphuric acid, and the gases allowed to escape through a tube containing chloride of calcium. 15·19 grains of the crystals lost 6·71 grains by this treatment, which loss is the weight of the oxalic acid. Hence this salt contains 44·17 per cent. of oxalic acid.

When this double oxalate is ignited, carbonic oxide escapes, and the residuary salt is a mixture of chromate and carbonate of potash, which is entirely soluble in water, and contains no oxide of chromium. In four experiments the fused residuary salt amounted to 0·5458, 0·5411, 0·5454, and 0·5425 of the weight of the crystals operated upon, while it should be 0·5433, provided this residuary salt is a mixture of two atoms chromate and one atom carbonate of potash, and that the composition of the crystals is as follows:

* Philosophical Transactions, 1835.

One atom oxide of chromium, $\text{Cr}\ddot{\text{O}}\text{Cr}$	1003·6	16·28
Three atoms potash, 3K	1769·7	28·70
Six atoms oxalic acid, $6\text{C}\ddot{\text{C}}$	2717·4	44·07
Six atoms water, 6H	675·	10·95
	<hr/> 6165·7	<hr/> 100·

The results in regard to the water and oxalic acid narrated above, agree completely with this view, and so does the determination of the oxide of chromium. 26·01 grains of the crystals left, when ignited, 14·08 grains of the mixed chromate and carbonate of potash, which were dissolved in water, and being acidulated with acetic acid, the chromic acid was precipitated by acetate of lead, and gave 17·45 grains chromate of lead, equivalent to 4·28 grains oxide of chromium. Hence by this experiment the crystals contain 16·46 per cent. of oxide of chromium, which approaches very nearly to the theoretical result. The fused residuary chromate and carbonate of potash amounted to 0·5425 of the weight of the crystals, which is so near the theoretical result, namely, 0·5433, that we may safely conclude that the quantity of potash in the salt agrees with our theoretical estimate.

This salt is clearly, therefore, a compound of one atom oxalate of chromium, containing three atoms oxygen in the oxide and nine atoms oxygen in the acid, with three atoms oxalate of potash; and the salt has six atoms of water of crystallization. The oxygen in the oxide of chromium being 1, that in the potash is also 1, that in the water 2, and that in the oxalic acid 6.

I made several attempts to crystallize the oxalate of chromium itself, but without success, so that I had no opportunity of studying its constitution in relation to the constitution of the preceding double salt.

14. *Oxalate of Peroxide of Iron and Potash.*

This salt, which has not hitherto been described, is formed by dissolving the hydrated peroxide of iron to saturation in binoxalate of potash. There is no effervescence, but a sap-green solution results, which, when concentrated, deposits the salt in question in tabular crystals, of which the form has no resemblance to that of the corresponding oxalate of chromium and potash, and which are of a beautiful grass-green colour. These crystals are permanent in the air, unless it is very dry, when they lose water by efflorescence and become brown and opake. The solution of the salt is decomposed by ammonia, and the peroxide of iron completely thrown down. The salt, when ignited, leaves peroxide of iron and carbonate of potash. It loses 10·56 per cent. of water at a temperature not exceeding 230° FAHR., but is partially decomposed at 300°. Below, the theoretical composition of this salt is placed in juxtaposition with the results of an analysis.

	Theory.	Experiment.
One atom peroxide of iron . . .	15·93	16·13
Three atoms potash	28·82	29·07
Six atoms oxalic acid	44·25	43·74
Six atoms water	11·00	10·56
	<hr/> 100·	<hr/> 99·50

Hence its composition is the same as that of the preceding salt, iron being substituted for chromium.

15. *Oxalate of Peroxide of Iron and Soda.*

This salt is formed by dissolving the hydrated peroxide of iron in binoxalate of soda. It crystallizes in solid green crystals. It is composed as follows, the water being calculated from the loss on the analysis:

	Theory.	Experiment.
One atom peroxide of iron . . .	16·32	16·56
Three atoms soda	19·57	19·66
Six atoms oxalic acid	45·34	45·51
Ten atoms water	18·77	18·27
	<hr/> 100·	<hr/> 100·

Of the ten atoms water which this salt contains it readily loses six at 212° FAHR., and retains four atoms water at that temperature. It differs, therefore, in composition, and it does so also in form, from either of the preceding double oxalates.

A corresponding oxalate of chromium and soda was produced by a similar process, and crystallized with some difficulty in solid dark crystals, which appeared to have the same form as the preceding soda-salt, and were found, like it, to contain ten atoms of water.

There is also a double oxalate of alumina and potash, which may be made by dissolving hydrated alumina in binoxalate of potash, and crystallizes in white tables of a pearly lustre, which have the same form as the oxalate of iron and potash.

II. *Of Nitrates.*

1. *Hydrated Nitric Acid, the Nitrate of Water.*



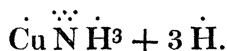
Nitric acid combines with one atom of water as base, and with three atoms more by a less powerful affinity. The well-defined character of the combination containing four atoms water, which is the acid of specific gravity 1·42, is evinced in its high boiling point and in an appearance of saturation which it exhibits. The true and complete nitrate of water has therefore three atoms of constitutional water attached to it. And in the case of the nitrates of those metallic oxides which correspond with

water in their basic character, we find the water of crystallization likewise to be three atoms, or a multiple of three, and no other number.

2. Nitrate of Copper.



and also



There are two nitrates of copper, one of which crystallizes in prisms, and the other in rhomboidal plates of a lighter blue colour than the prisms; the first of which I find to contain three and the other six atoms of water. Both are deliquescent to a certain degree, the salt which contains the large proportion of water being more so than the other.

(1.) Of the dark blue prisms, 28.12 grains carefully calcined left 8.98 grains black oxide, or 31.94 per cent. In a second experiment, 22.9 grains left 7.34 grains oxide, or 32.05 per cent. The salt being neutral in composition, the quantity of nitric acid may be inferred from the oxide of copper, and the difference between their sum and the weight of the salt operated upon is the water. By the first analysis the water amounts to 3.38, and by the second to 3.28 atomic proportions. The excess above three atoms is probably hygrometric moisture, to remove which from this salt we cannot employ the ordinary means. In a third experiment upon a portion of the same salt, which had been dried over sulphuric acid till it began to effloresce, 33.19 grains of nitrate left 11.04 grains oxide, which gives 2.83 atomic proportions of water to the salt, or the result is a little below the three atoms. Hence this nitrate may safely be supposed to possess three atoms of water.

(2.) Of the lighter coloured crystals in plates, 10.60 grains left 2.78 grains oxide of copper when ignited, or 27.36 per cent. Hence the salt is composed of

			With six atoms water.
Nitrate of copper . . .	6.57	100.	100.
Water	4.03	61.33	57.54
	<hr/> 10.6	<hr/> 161.33	<hr/> 157.54

The experimental determination is a little above the theoretical estimate, as might be expected from the deliquescent nature of the salt.

The crystals speedily became opaque over sulphuric acid in vacuo, and 10.6 grains lost 2.18 grains water in a night, retaining 1.85 water; which is 28.16 water retained to 100 anhydrous salt, or almost exactly three atoms of water. Hence this salt parts easily with half its water. The other three atoms of water are retained more strongly; for by a second day's exposure over sulphuric acid there was an additional loss of only 0.15 grain water; or the water retained was reduced to 25.87 parts united to 100 anhydrous salt.

3. *Subnitrate of Copper.*

It is well known that when the nitrate of copper is heated to the temperature of 400° or 500° FAHR., it is decomposed, nitric acid and water being expelled, and a subnitrate remaining, which consists of one atom of nitric acid, one atom of water, and three atoms of oxide of copper. This decomposition I find to take place and be completed at a very moderate temperature, not exceeding 150° FAHR. ; and it appears, besides, that none of the three constitutional atoms of water of the nitrate of copper can be expelled without a certain corresponding loss of acid : that on heating the salt in question, nitric acid and water go off together, in the form of nitrate of water with its three atoms water. Thus, three atoms of crystallized nitrate of copper, containing three atoms acid, three atoms oxide, and nine atoms of water, are resolved into two atoms nitrate of water, each containing one atom acid and four water ; and one atom of subnitrate of copper, which contains one atom acid, one water, and three oxide of copper.

Experiment.—In a stove of which the temperature never exceeded 150° FAHR., 27·54 grains crystallized nitrate of copper, containing three atoms of water, exposed on a capsule, suffered the following gradual reduction of weight : a loss of 2·59 grains in one day, of 9·62 in six days, of 11·1 in seven days, of 13·35 in eleven days, of 13·47 in twelve days, of 13·58 in sixteen days, of 13·60 in eighteen days, and nothing more afterwards by a heat of 300° FAHR., continued for several hours. Of the crystallized nitrate, 27·54 grains have left 13·94 grains subnitrate ; or we have 0·5062 subnitrate from 1 nitrate. By calculation the residuary subnitrate should be 0·5026, with which the experimental result closely corresponds.

Another portion of the same nitrate of copper, dried exactly in the same way, lost 1 per cent. of its weight when afterwards heated to 400° FAHR. ; and thereafter, being ignited, was found to consist of

	Experiment.	Theory.
Oxide of copper	100·	100·
Volatile matter	53·19	53·1
	<hr/> 153·19	<hr/> 153·1

I am satisfied that no other subnitrate except the preceding, which contains three atoms of oxide of copper, can be obtained by the decomposition of the neutral nitrate by means of heat. For a quantity of the subnitrate of copper of the first experiment narrated above being gradually exposed in a platinum crucible to a heat above the melting point of lead, by means of a sand-bath, so as actually to reduce a portion of the subsalt in contact with the bottom of the crucible to the state of black oxide, yet the major portion of the subsalt, which still retained its green colour, was found to be little altered in composition. After this extreme heating the subsalt consisted of

Oxide of copper	. . 100·
Volatile matter	. . 50·6
	<hr/> 150·6

Or the proportion of volatile matter in the subsalt has suffered only a small reduction, namely, from 53·1 to 50·6 parts. This last subnitrate afforded drops of nitric acid with fumes of nitrous acid when heated in a tube, so that the subnitrate of copper retains water even at a temperature above the melting point of lead.

The subnitrate of copper merits a careful consideration; for the subsalts of the magnesian class of oxides, which can be had of a definite composition, are really much fewer in number than is generally supposed. What constitution ought to be assigned to this salt? It will be observed that I have represented it by the singular formula



implying that the single atom of water which it contains is really the base of the salt, and that the three atoms of oxide of copper are in the place of the constitutional water of this nitrate of water. This opens a new view of the constitution of subsalts. The excess of metallic oxide which they contain may not be basic at all in certain cases like the present, but discharge a function in the constitution of the salt which has hitherto been recognised only as executed by water. For if we find water and oxide of copper strongly resembling each other as bases, why may not the analogy between them extend further, and oxide of copper be capable of discharging the function of constitutional water or water of crystallization in the composition of a salt? Indeed the speculation that all salts whatever are neutral in composition is highly probable. Where the metallic oxide is in excess, as in what are called subsalts, we can attribute another function than that of base to the whole or a portion of the metallic oxide, and thus preserve the salt neutral in composition, or according to its formula. To this subject I shall again recur.

The following observation is particularly favourable to the view which we are taking of the constitution of subnitrate of copper. When the black oxide of copper is drenched with the strongest nitric acid, it is a subnitrate of copper which is formed, although the nitric acid may be in great excess. The black oxide is converted into a green powder, from which the excess of nitric acid should be drained off as well as possible, and the powder will be found to be in great part insoluble in water. The explanation seems to be, that the concentrated nitric acid employed does not contain the constitutional water which the neutral nitrate of copper requires, and accordingly that salt is not formed; but the nitrate of water supplies itself with oxide of copper in the place of its deficient constitutional water; so that the result is a nitrate of water with three atoms of oxide of copper attached. But when nitric acid of a specific gravity not exceeding 1·42 is digested upon the same black oxide of copper, the neutral nitrate of copper only is formed, and no subnitrate.

This view seems likewise to be necessary to account for the great force with which the single atom of water is retained by the subnitrate of copper. The water cannot be expelled without decomposing the salt, notwithstanding the great excess of oxide of copper present.

4. Nitrate and Subnitrate of Bismuth.



The neutral nitrate is admitted to contain three atoms of water, like the nitrate of copper, and its constitution appears to be similar.

No portion of the constitutional water of this salt can be expelled without decomposing the salt. Indeed this salt loses acid by exposure to dry air at a temperature not exceeding 80° FAHR. The crystals of the salt are resolved by a heat of 212° into a solid and fluid portion, the first of which is probably the subnitrate, while the last is hydrated nitric acid containing much nitrate of bismuth in solution, and not a supernitrate of bismuth. But the fluid portion fixes so readily upon cooling that the solid product cannot be obtained in a definite state.

Experiment. 28·61 grains of nitrate of bismuth in good crystals, being exposed to a gradual ignition, left 14·16 grains of fused oxide of bismuth. This result accords with the view which is taken above of the composition of this salt:

		Experiment.	Theory.
Oxide of bismuth	14·16	100·	100·
Nitric acid and water	14·45	102·04	102·72
	<hr/> 28·61	<hr/> 202·04	<hr/> 202·72

It appears likewise that three atoms of the hydrated nitrate of bismuth are resolved, when dried at a high temperature, into two atoms hydrated nitrate of water and one atom subnitrate of bismuth, which last is of the same constitution as the subnitrate of copper.

Experiment 1. Dried on the sand-bath at a temperature above the melting point of tin, 28·61 grains of nitrate of bismuth lost 9·29 grains, and retained 5·16 grains of volatile matter, or consisted of

		Experiment.	Subnitrate by theory.
Oxide of bismuth.	14·16	100·	100·
Volatile matter	5·16	36·44	34·24
	<hr/> 19·32	<hr/> 136·44	<hr/> 134·24

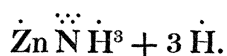
Experiment 2. A portion of nitrate dried in a stove at a temperature not exceeding 180° FAHR., till it ceased to lose weight, was thereafter found to consist of

Oxide of bismuth	21·24	100·
Volatile matter	7·57	35·64
	<hr/> 28·81	<hr/> 135·64

It appears from the second of these experiments that the subnitrate of bismuth may be produced at a temperature so low as 180° FAHR., and from the first experiment that the subnitrate may be exposed to a temperature of 500° FAHR. without decomposition.

Several experiments were made to produce another definite subnitrate, containing a greater proportion of oxide of bismuth, by the action of heat upon this subnitrate, but without success. The salt was partially decomposed at various temperatures under redness, but no definite compound resulted. Hence the subnitrate described is probably the only definite subnitrate of bismuth that can exist. The small pearly crystals obtained on throwing the neutral nitrate of bismuth into a moderate quantity of water, are of the same composition as the subnitrate obtained by heat.

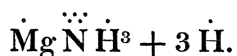
5. *Nitrate of Zinc.*



This salt is easily obtained by dissolving zinc in nitric acid. It is very soluble in water, and moderately deliquescent.

Experiment. 29·17 grains of the crystals ignited, left 7·86 grains oxide of zinc. In this experiment we have 0·2694 oxide from one salt, which is very near 0·2713 oxide, the proportion which should be left, supposing the salt to contain six atoms of water. By efflorescence at 212° one part of this salt loses 0·18 water, which is one half of the whole water which the salt is assumed to contain, namely, 0·3639 water. It loses no acid at 212°. Hence this salt is of the same constitution as the nitrate of copper, but is not decomposed at so low a temperature. The proportion of water, however, cannot be reduced below three atoms without a loss of acid, and there appears to be a subnitrate of zinc resembling the subnitrate of copper.

6. *Nitrate of Magnesia.*



Experiment. 27·12 grains of crystals of nitrate of magnesia, when calcined, left 4·3 grains caustic magnesia; a result which indicates 6·17 atomic proportions of water in the salt, or the salt contains six atoms of water.

The nitrate of magnesia stands exposure to a heat which would melt lead without losing acid. At that high temperature the proportion of water is reduced to one atom, which cannot be expelled without loss of acid. The salt remains in a fused state and transparent, and dissolves afterwards completely in water.

Experiment. 18·40 grains of the crystals, containing 7·71 grains water, lost 6·60 grains by a strong sand-bath heat continued till the salt ceased to lose weight. This is a loss of exactly five sixths of the water contained in the salt.

Experiment. 19·76 grains, containing 8·28 water, by similar treatment lost 6·77,

which approaches very closely to 6.90 grains, the number representing five atomic proportions of water.

This single atom of water retained by the nitrate of magnesia, is not displaced and expelled upon heating the salt, together with an atomic proportion of nitrate of potash to 600° or 700° FAHR., so that the retention of an atom of water does not indicate a disposition, upon the part of nitrate of magnesia, to form a double salt. It is probable that this peculiar and intimate combination of nitrate of magnesia with one atom water does not exist in the crystals or ordinary hydrate of nitrate of magnesia, but is the result of a new arrangement of the constituents of the salt at a high temperature. There are indications of the existence of a similar nitrate of water.

There does not appear to be a subnitrate of magnesia like the subnitrate of copper.

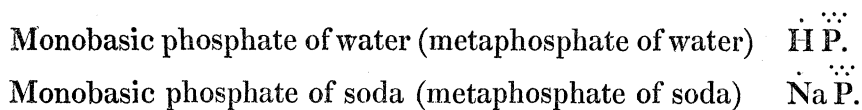
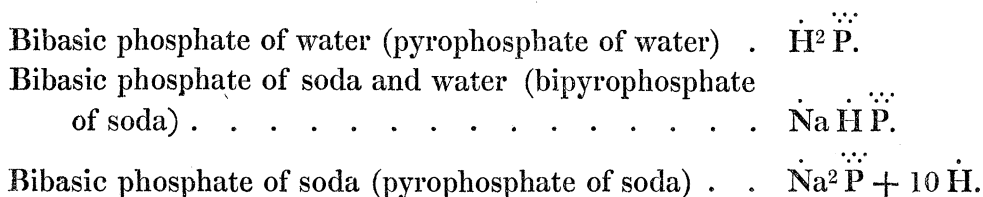
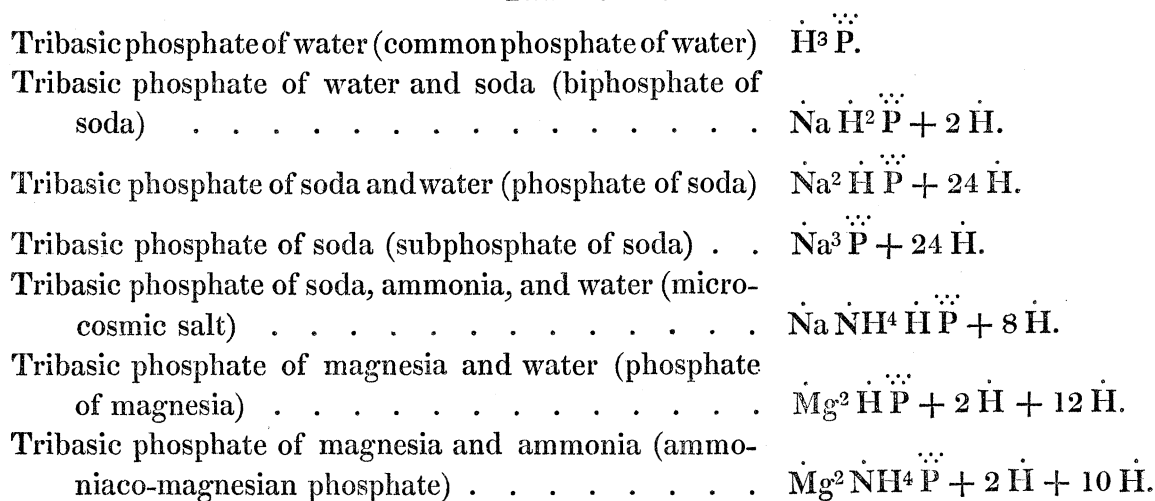
Supposed Double Nitrates and Supernitrates.

As double nitrates are said to exist, I have repeatedly attempted to form them; but when nitrate of magnesia, nitrate of zinc, or nitrate of copper was mixed with nitrate of potash or with nitrate of ammonia, the salts uniformly separated again in crystallizing. There is no proof of the existence of a single supernitrate.

Most of the nitrates of oxides not belonging to the magnesian class are anhydrous salts, such as the nitrates of potash, soda, barytes, strontian, lead, &c., and do not suggest any new subject matter of inquiry.

III. *Of Phosphates.*

In the present state of our knowledge phosphoric acid is quite peculiar in being capable of combining with bases in three different proportions, forming, besides the usual class of salts containing one atom of acid to one atom of protoxide as base, two other anormal classes of salts, in which two and three atoms of base are united to one atom of acid, namely, the pyrophosphates and the common phosphates. Arsenic acid forms only one class of salts, but that class is anormal, every member of it containing three atoms of base to one atom of acid, like the common phosphates. These anormal classes of phosphates and arseniates, with perhaps the phosphites, are, I believe, the only known salts to which the ordinary idea of a subsalt is truly applicable; or in the formulæ of these salts only, ought more than one atom of any protoxide to appear in a basic relation to one atom of acid. All other reputed subsalts are probably neutral in composition, as I have endeavoured to show in the case of the subnitrate of copper; for to this salt they all bear an analogy in their small solubility and other properties, while they exhibit little resemblance to those classes of phosphates and arseniates which really possess more than one atom of base. The following Table contains the formulæ of the most important phosphates, with a new nomenclature of these salts, which I offer for consideration.

First Class.*Second Class.**Third Class.*

It is my object to get rid of the trivial names pyrophosphates, metaphosphates, and common phosphates, which have tended to keep up an erroneous impression that the phosphoric acid is of a different nature in these classes of salts, or is modified in some way unknown. This notion has arisen from the pertinacity with which phosphoric acid continues combined with a constant number of atoms of base, whether it be one, two, or three, although the base itself be repeatedly changed by decomposing the original combination. But this is an occurrence quite analogous to the formation of different sets of sulphurets or of chlorides, when we decompose two or more different oxides of the same metal, such as the oxide and suboxide of mercury, by sulphuretted hydrogen or by muriatic acid. The metal continues in the same relative state of saturation throughout a series of such decompositions; and so does the phosphoric acid, because in both cases the decomposition is effected by an equivalent substitution.

A difficulty occurs in naming two members of the tribasic class, so as to distinguish them from each other, namely, the biphosphate of soda and phosphate of soda, both of which contain soda and water as base. But this difficulty is obviated by placing

first in the name that base of which two atoms are present. Thus the biphosphate of soda is "the phosphate of water and soda," and the phosphate of soda is the phosphate of soda and water, both being at the same time characterized as "tribasic."

What I have to add at present in regard to the phosphates relates chiefly to the last three salts, of which formulæ are given in the preceding Table, which belong to classes of tribasic phosphates that were not examined in my former paper upon the phosphates*. But I may premise a few observations, which are more strictly supplementary to the results of that paper.

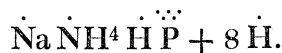
1. The bibasic phosphate of water (pyrophosphate of water) is possessed of very considerable stability. Both weak and concentrated solutions of this salt have been kept for five or six months without any sensible change or production of the tribasic phosphate of water.

2. It appears to be impossible to crystallize any bibasic phosphate (pyrophosphate) of potash. Such salts can exist in solution, but not in the dry state. The same observation applies to the bibasic phosphates of ammonia, or we have no pyrophosphates of ammonia except in solution. Indeed, the solution of the bibasic phosphate of water and ammonia assumes another atom of basic water when the evaporation is carried far, and crystallizes as the tribasic phosphate of water and ammonia (biphosphate of ammonia).

3. In the case of tribasic phosphates containing potash, I have succeeded in crystallizing the tribasic phosphate of potash, and the tribasic phosphate of water and potash, but not the tribasic phosphate of potash and water, or what would be considered on the old view as the neutral phosphate of potash.

4. Both the bibasic and tribasic phosphates of water may be treated with an excess of caustic potash in solution without the formation of any precipitate or sparingly soluble combination. It is only in the monobasic phosphate of water that a sparingly soluble combination is formed by potash, such as that which is described by Dr. THOMSON under the name of diphosphate of potash.

I. *Tribasic Phosphate of Soda, Ammonia, and Water.* (*Phosphate of Soda and Ammonia: Microcosmic Salt.*)



I have repeated more than once the analysis of this salt, and obtained the same result as M. MITSCHERLICH. It appeared to contain 0.5094 of volatile matter: and there may be derived from an atom of this salt one atom of phosphoric acid, of soda and of ammonia respectively, and ten atoms of water. It has hitherto been viewed as a double phosphate or combination of phosphate of soda with phosphate of ammonia; but no reason can be assigned why these particular salts should combine together, and combinations of salts of soda and ammonia are exceedingly unusual.

* Philosophical Transactions, 1833.

The view expressed above in the formula is much more likely to be true, namely, that this salt is simply a tribasic phosphate, of which the three atoms of base are all different: they are soda, oxide of ammonium, and water; and the salt possesses eight atoms of water of crystallization. By a graduated heat it is possible to expel the water of crystallization of this salt, and likewise the ammonia of its oxide of ammonium; and the water of the last remaining as base, the salt $\text{Na H}^2\ddot{\text{P}}$ is produced.

M. MITSCHERLICH now admits that there is no tribasic phosphate corresponding with this, but containing potash instead of oxide of ammonium, a conclusion of which I have ascertained the accuracy.

I endeavoured to form a tribasic phosphate to contain two atoms soda and one atom of oxide of ammonium, but such a salt appears to have no existence. For when ammoniacal gas was passed into a strong and hot solution of the common phosphate of soda, a slight deposition of the tribasic phosphate of soda took place, followed by the rhomboidal crystals of the common phosphate unchanged.

It likewise appears that when the bibasic phosphate of soda and the bibasic phosphate of potash (pyrophosphates) are mixed together, no new salt is produced; but the former may be crystallized out, and the latter remains uncrystallizable.

II. *Tribasic Phosphates containing Oxides of the Magnesian Class.*

1. *Tribasic Phosphate of Zinc and Water. (Phosphate of Zinc.)*



This salt, which is nearly insoluble, is obtained in minute silvery plates, by mixing three ounces of sulphate of magnesia with four ounces of phosphate of soda, each dissolved in two pounds of cold water. These crystalline plates consist of

		Theory of $\text{Zn H}\ddot{\text{P}} + 2\text{H}.$
Anhydrous salt . . .	100	100
Water	19.63	17.77
	<hr/>	<hr/>
	119.63	117.77

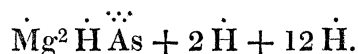
Dried above the melting point of tin the crystals still retained a glistening appearance, but had lost two thirds of their water; for they now consisted of

		Theory of $\text{Zn H}\ddot{\text{P}}.$
Anhydrous salt . . .	100	100
Water	6.08	5.92
	<hr/>	<hr/>
	106.08	105.92

The two atoms of water which are expelled in the above experiment are, notwithstanding, pretty strongly attached to the salt, being retained at the boiling point of water. Indeed these two atoms of water are highly constitutional, and are found in all the phosphates of this class.

This phosphate fuses at a red heat, after it becomes anhydrous, but it continues soluble in dilute acids.

2. *Tribasic Arseniate of Magnesia and Water.* (*Arseniate of Magnesia.*)



This salt precipitated on mixing dilute solutions of 500 grains of arseniate of soda and 300 grains of sulphate of magnesia. It consisted of

		Theory of $\text{Mg}^2 \ddot{\text{H}} \ddot{\text{As}} + 14 \ddot{\text{H}}.$
Anhydrous salt . . .	100·	100·
Water	86·58	86·25
	<hr/> 186·58	<hr/> 186·25

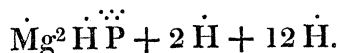
This salt contains in all fifteen atoms of water, of which three are retained and twelve expelled at the boiling point of water. Dried at 212° it consisted of

		Theory of $\text{Mg}^2 \ddot{\text{H}} \ddot{\text{As}} + 2 \ddot{\text{H}}.$
Anhydrous salt . . .	100·	100·
Water	17·17	17·25
	<hr/> 117·17	<hr/> 117·25

It therefore retains pretty strongly two atoms of water besides its basic atom, resembling the preceding salt in this respect.

This arseniate and the corresponding phosphate are rendered insoluble in dilute acids by the effect of a strong red heat.

3. *Tribasic Phosphate of Magnesia and Water.* (*Phosphate of Magnesia.*)

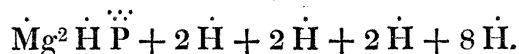


This salt appears in distinct prismatic crystals in the course of twenty-four hours, upon mixing two ounces of sulphate of magnesia with three ounces phosphate of soda, each dissolved in two pounds of water. Cold water is capable of dissolving about one thousandth part of its weight of these crystals. They have been stated erroneously to be much more soluble. The proportion of water which they contain has hitherto been stated at fourteen atoms instead of fifteen, which is the truth. By analysis the crystals were found to consist of

		Theory of $\text{Mg}^2 \ddot{\text{H}} \ddot{\text{P}} + 14 \ddot{\text{H}}.$
Anhydrous salt . . .	100·	100·
Water	121·7	119·76
	<hr/> 221·7	<hr/> 219·76

I find that the proportion of water retained by this salt is readily reduced at 212°, from fifteen atoms to seven, by the escape of eight atoms of water. Of the seven atoms retained one is basic, and therefore expelled with difficulty; but from a variety

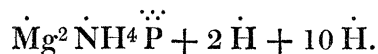
of experiments which I have performed it appears probable (although I have never attained very precise results) that the other six atoms go off in pairs at different temperatures between 212° and 350° FAHR. But even at 410° the quantity of water retained by this salt was sensibly above one atomic proportion. We may with considerable probability represent the consecutive combinations of this salt with water by such a formula as the following :



Besides the preceding salt there is a tribasic phosphate of magnesia, which is obtained as an insoluble precipitate on mixing tribasic phosphate of soda with sulphate of magnesia. Of this salt the whole three atoms of base are magnesia, as its name implies. Dried at 212° it retains five atoms of water. At a red heat it glows, but it continues soluble in acids even after exposure to a white heat. But I did not succeed in forming the other tribasic salt, containing two atoms of water and one atom of magnesia as bases, which is wanted to complete the series. Such a salt does not appear to exist.

It may be mentioned here in reference to the monobasic phosphate of magnesia (metaphosphate of magnesia), that although this salt does not present itself on mixing the monobasic phosphate of soda with the sulphate of magnesia, yet it is readily precipitated in the form of a soft viscid body, on using the acetate of magnesia instead of the sulphate.

4. *Tribasic Phosphate of Magnesia and Ammonia. (Ammoniaco-magnesian Phosphate.)*



This salt is the well-known granular precipitate formed on adding a salt of magnesia to any soluble tribasic phosphate with which ammonia or a salt of ammonia has been mixed. I was much interested in ascertaining the true constitution of this salt, and have carefully analysed seven or eight different specimens of it, prepared with and without free ammonia in the liquors. The result is that only one tribasic salt of these constituents exists, although two have often been admitted ; while in this compound there exists only one atom of ammonia instead of two, as M. RIFFAULT has supposed. I subjoin the preparation and analysis of one specimen of this salt. 350 grains of crystallized phosphate of soda, 100 grains of chloride of ammonium, and 200 grains of *aqua ammoniæ* were dissolved together in four pounds of cold water, and 200 grains of crystallized sulphate of magnesia were added to that mixture. The precipitation was gradual, and the liquor remained alkaline. The precipitate was slightly washed with cold water, and afterwards dried in the air for ten days, the thermometer being 65° FAHR., without artificial heat. The true proportions of water, which this and many other precipitates affect, have often been mistaken, and definite hydrates not obtained, from using hot solutions in their preparation. Of this preci-

pitrate 26·8 grains lost by ignition 14·5 grains, or one part of the precipitate contains 0·541 volatile matter. For the ammonia, the volatile matter from 9·65 grains of the precipitate was sent over quicklime contained in a tube, so as to arrest the water. The loss, or the ammonia, amounted to 0·67 grain, or to 0·0695 of the precipitate. Hence this precipitate consists of

		Theory of $\text{Mg}^2\text{N}^1\text{H}^4\text{P} + 2\text{H} + 10\text{H}_2\text{O}$
Anhydrous salt . . .	45·90	45·85
Ammonia . . .	6·95	6·98
Water . . .	47·15	47·17
	<hr/> 100·	<hr/> 100·

From the manner in which this specimen of the salt was prepared, it should contain the maximum proportion of ammonia of which the salt admits, and yet that proportion is one atom only, and not two, as it was estimated by RIFFAULT. A salt of the same composition was obtained from the same materials, omitting the caustic ammonia. In that case the product was not so abundant, and the mother liquor remained acid from the production of tribasic phosphate of water and soda, which has an acid reaction. When this salt, contained in a little retort, is heated in a very gradual manner to 212° by means of a water-bath, it is possible to distil over ten atomic proportions of the water without any ammonia whatever. Of the three atoms of water which remain, (the whole quantity originally present in the salt being thirteen atoms,) one appears to be combined with the ammonia in the formation of oxide of ammonium, while the other two are the constitutional water of the tribasic phosphate of magnesia and water.

It appears, then, that this salt is not a double phosphate, or combination of two phosphates, but that it is formed from the tribasic phosphate of magnesia and water, by the substitution of oxide of ammonium for the basic water of that salt; and it is a tribasic phosphate of magnesia and oxide of ammonium. The oxygen in the magnesia is double that in the oxide of ammonium.

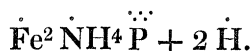
This salt is the type of a class of tribasic phosphates, in which the magnesia is replaced by the other oxides, which are isomorphous with that base. Two of these salts were discovered and carefully examined by Dr. OTTO of Brunswick*.

Dr. OTTO's analysis of what we may call the tribasic arseniate of manganese and ammonia corresponds exactly with the analysis given above of the magnesian salt, except that he derives only twelve instead of thirteen atoms of water from his salt. The deficiency in the proportion of water found by him, I attribute to the use which he made of hot water in washing his salt.

His analysis of the tribasic phosphate of the protoxide of iron and ammonia is particularly interesting, as it proves that this salt is precipitated, containing no more than three atoms of water, or exactly of the composition of the magnesian salt dried

* Journal für Praktische Chemie von ERDMAN und SCHWEIGGER-SEIDEL, 1834, p. 409.

at 212°, as we have described. The constitution of this salt of iron I would therefore represent by the formula



In the same paper Dr. OTTO describes another extraordinary phosphate, under the name of paraphosphate of soda, ammonia, and oxide of manganese, which does not belong to any class of phosphates that I have examined, but may possibly be a combination of two bibasic phosphates. Its constituents are $2 \ddot{\text{P}}$, 2Mn , NH^4 and 6H . It is prepared from bibasic phosphates, and would be said in the old language to contain pyrophosphoric acid.

IV. Of Sulphates.

In a former paper upon water as a constituent of sulphates*, I examined particularly the constitution of hydrated sulphuric acid and of the sulphates of the magnesian class of oxides. All these salts contain one atom of constitutional water, which is displaced in the formation of the double sulphates by an atom of an alkaline sulphate. This view is illustrated by the following formulæ:

Sulphate of water (acid of sp. gr. 1.78) $\text{H} \ddot{\text{S}} \text{H}$

Sulphate of magnesia $\text{Mg} \ddot{\text{S}} \text{H} + 6 \text{H}$

Sulphate of magnesia and potash $\text{Mg} \ddot{\text{S}} (\text{K} \ddot{\text{S}}) + 6 \text{H}$

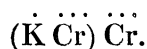
Sulphate of water and potash (bisulphate of potash) . . $\text{H} \ddot{\text{S}} (\text{K} \ddot{\text{S}}).$

It will be found upon experiment that the salts sulphate of magnesia and sulphate of zinc become anhydrous at much lower temperatures when mixed with sulphate of potash than by themselves, the sulphate of potash displacing the constitutional water of the other salt at a very moderate heat, although the salts are mixed in the state of dry powders.

In that paper the opinion was supported, originally suggested I believe by M. MITSCHERLICH, that the bisulphate of potash is a double sulphate of water and potash, and therefore really neutral in composition. The only difficulty which stood in the way of generalizing this result, and maintaining that *all* the salts usually considered as bisalts are really neutral in composition, was the composition of the bichromate or red chromate of potash, a salt which unquestionably is anhydrous. Here, it might be said, is a true bisalt. But M. H. ROSE has lately published some observations in regard to anhydrous sulphuric acid, which, I think, afford a clue to the discovery of the true constitution of the red chromate of potash. It appears that the vapour of anhydrous sulphuric acid is absorbed by sulphate of potash and by chloride of potassium, without decomposition, and definite compounds formed; which, however, are destroyed by solution in water. Here we appear to have a class of

* Edinburgh Transactions, vol. xiii. p. 297; or London and Edinburgh Philosophical Magazine, 3rd series, vol. vi. pp. 327, 417.

combinations of sulphuric acid *with salts*. Chromic acid, which is isomorphous with sulphuric, forms combinations which I consider as analogous to these. With the neutral or yellow chromate of potash it forms the red chromate of potash, and with chloride of potassium it forms M. PELIGOT's salt; which differ only from M. ROSE's corresponding combinations of sulphuric acid, in being more permanent. The superior stability of these chromic acid combinations unquestionably depends upon the little affinity for water which their acid possesses, while the affinity of sulphuric acid for water is very great. Hence we may suppose that the red chromate of potash is not a direct combination of two atoms of chromic acid with one atom of potash, but a combination of one atom of chromic acid with one atom of yellow chromate of potash; and it may be represented as follows:



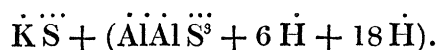
The red chromate of potash will thus belong to a new order of combinations, differing essentially from proper salts, which contain an oxide as base. This salt, therefore, cannot be adduced as militating against the law that "all salts are neutral in composition"; the only known exceptions to which law are, I believe, afforded by the anomalous classes of phosphates, phosphites, and arseniates.

I have devoted much time to the examination of *subsulphates* of the magnesian class of oxides, particularly of the subsulphate of zinc and the subsulphate of copper. These salts were generally formed by the partial precipitation of sulphate of zinc or sulphate of copper by means of caustic potash. They have both a disposition to carry down sulphate of potash, which is never entirely removed from them by washing; while one of them, the subsulphate of zinc, is itself decomposed by washing. When most successfully prepared, they were found to contain four atoms of metallic oxide to one atom of acid, (instead of three atoms oxide, as M. BERZELIUS supposed,) together with four atoms of water. I have not hitherto been able to form a distinct idea of their constitution, or to decide between different views which may be taken of it. But the force with which water is retained in these subsalts is very remarkable. The subsulphate of copper loses no portion of its four atoms of water at 212°, and I have not been able to reduce the quantity of water retained by this salt so low as one atomic proportion, even at the melting point of lead.

The constitution of the subsulphate of copper appears to be changed when it is made anhydrous by heat. In the progress of the desiccation of the salt, its colour passes from a dull blue to an olive green, and it finally becomes of a chocolate brown, and is then anhydrous. Water poured upon the brown matter comes off of a blue colour, dissolving out a considerable portion of the soluble sulphate of copper. It appears, therefore, that the water originally present in the subsulphate must discharge some important function in its constitution, the subsalt being obviously decomposed when made anhydrous.

The *Alums* form a most important class of the sulphates, but I have never had it in my power to compare their constitution with that of the sulphate of alumina itself,

which is not easily obtained in a crystallized state. This salt, however, is described as containing eighteen atoms of water, while the alums have twenty-four. At present I would merely throw out the conjecture, that in the alums we may have simply an alkaline sulphate with the sulphate of alumina attached, that salt carrying along with it its whole water of crystallization, and acquiring six atoms more. The quantity of water in potash alum may be reduced by efflorescence to six atoms in a stove of the temperature of 150° FAHR. Hence potash alum may perhaps be represented as follows :



I have shown by an analysis conducted in very favourable circumstances, that soda-alum contains, like potash-alum, twenty-four, and not twenty-six atoms of water.

V. Of Chlorides.

The affinity which the hydracids exhibit for water is weak. Of the lower hydrates of muriatic acid we know nothing, the volatility of the acid putting it out of our power to form and examine such hydrates ; but it is likely that they will correspond with the hydrates of the chloride of magnesium, &c., which can be examined.

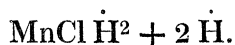
The law in the case of the chlorides of the magnesian class of metals appears to be, that they have two atoms of water pretty strongly attached to them, and which we may consider as constitutional. Thus chloride of copper crystallizes with two atoms of water, and with no lower proportion ; but several chlorides of this class have two or four atoms more, the proportion of water advancing by a multiple of two atoms.

1. Chloride of Copper.



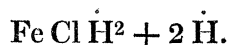
The blue prismatic crystals of chloride of copper become brown and lose the greater proportion of their water at a temperature not exceeding the boiling point of water. Fifteen grains of the crystals, exposed to a much higher temperature, lost 3.23 grains of water, leaving 11.77 grains of chloride of copper ; and when this quantity of chloride of copper was exposed to the atmosphere, it quickly recovered 3.16 grains of water, and resumed the blue colour of the crystallized salt. I believe this method of reabsorption, in the case of constitutional water, often to give hydrates of which the composition is even more exact than if they had been obtained from solution, owing to the absence of that water, which is often mechanically interposed between the plates of crystals. The hydrated chloride of copper obtained in this way consisted of

		Theory of $\text{CuCl}\dot{\text{H}}^2$.	
Chloride of copper . . .	11.77	100.	100.
Water	3.16	26.85	26.84
	<hr/> 14.93	<hr/> 126.85	<hr/> 126.84.

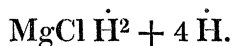
2. *Chloride of Manganese.*

Experiment.—Of the flesh-coloured crystals, 15·53 grains, precipitated by nitrate of silver, gave 22·57 grains of chloride of silver, equivalent to 5·56 chlorine, or to 9·92 chloride of manganese, which leaves 5·61 grains water in the salt, or 36·12 per cent. of water. Now a chloride of manganese with four atoms of water would contain 36·33 per cent. of water.

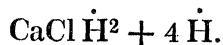
This salt readily lost half its water when dried at 212° in open air, or when dried over sulphuric acid in the vacuum of an air-pump at the ordinary temperature. But when the exposure of the salt in such circumstances was long protracted, a little of the constitutional water also was lost.

3. *Protochloride of Iron.*

In three experiments made upon different specimens of crystallized protochloride of iron, all newly and very carefully prepared, 13·69 grains chloride of silver were precipitated from 9·72 salt, 17·20 chloride of silver from 12·44 salt, and 15·75 chloride of silver from 11·21 salt. These experiments almost coincide in their results, which are, that 1 part of the salt contains 0·3466, 0·3463, and 0·3461 of chlorine. But such proportions of chlorine are decidedly under the proportion which a neutral salt with four atoms of water should contain, namely, 0·3593 chlorine. Indeed, the quantity of water in the salt is indicated by these experiments to be four and a half atomic proportions almost exactly. By crystallizing from an acid solution BONDORFF has lately obtained this salt in a state of purity, and containing four atoms of water.

4. *Chloride of Magnesium.*

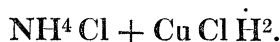
Of the crystals of this salt, which are decidedly deliquescent, 12·65 grains were found to contain 4·29 chlorine; or the salt contains 33·91 per cent. of chlorine, which approaches sufficiently near to the theoretical proportion 34·69 per cent., supposing the salt to contain six atoms of water.

5. *Chloride of Calcium.*

The crystals of this deliquescent salt, dried in vacuo till they began to effloresce, were found to contain six atoms of water, the proportion usually allotted to them; but it is remarkable, that, continued in vacuo over sulphuric acid for ten days during

the heat of summer, the crystals became opaque and of a talky lustre, without being disintegrated, and their proportion of water was reduced to two atoms.

6. *Double Chloride of Copper and Ammonium.*



Hydrated chloride of copper dissolved with chloride of ammonium, in the proportion of eleven of the first to seven of the last, readily affords a double salt, in which we appear to have an atom of chloride of ammonium with an atom of the hydrated chloride of copper attached. This double salt is less soluble than the chloride of copper itself, and retains more strongly the two constitutional atoms of water of that salt; illustrating in both of these points what appear to be two very general occurrences: namely, 1st, the reduced solubility of double salts; and, 2nd, the closer attachment which constitutional water exhibits for a salt when that salt itself enters into combination.

	Analysis.	Theory of $\text{NH}^4\text{Cl} + \text{Cu Cl H}^2$.
Chlorine	51·03	51·08
Copper	23·35	22·83
Ammonium (N H^4) . .	13·20	13·10
Water	12·09	12·99
	<hr/> 100·67	<hr/> 100·

The water cannot be entirely expelled without risking the sublimation of chloride of ammonium, and hence the quantity of water obtained is under the truth. The copper is above the truth, from having been precipitated by caustic potash in the state of oxide, which last when so obtained always retains a little potash.

There is a corresponding chloride of copper and potassium, but I did not succeed in forming analogous double salts with chloride of magnesium or with any other chloride of the class in the place of the chloride of copper.

The chlorides have probably their analogues in the cyanides, but with the single cyanides of iron, copper, &c., we are less acquainted. It is worthy of remark, however, that the disposition of the protocyanide of iron and of the cyanide of copper to combine with two atoms of cyanide of potassium may depend upon the cyanides of iron and of copper possessing two atoms of constitutional water, (like the corresponding chlorides,) which are displaced by two atoms of the alkaline cyanide in the formation of the double cyanides. In “ferrocyanic acid” we have the protocyanide of iron combined with two atoms of hydrocyanic acid, in the place of the same two atoms of water.

PLYMOUTH 1834.

July
P.M. A.M.

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24

High Water

13

D.I. of H.W. at N. Tr.
Theoretical D.I.

Theoretical D.I.

D.I. of H.W. at S. Tr.

Mean Level

July

A.M. A.M.

8

Low Water

7

6

5

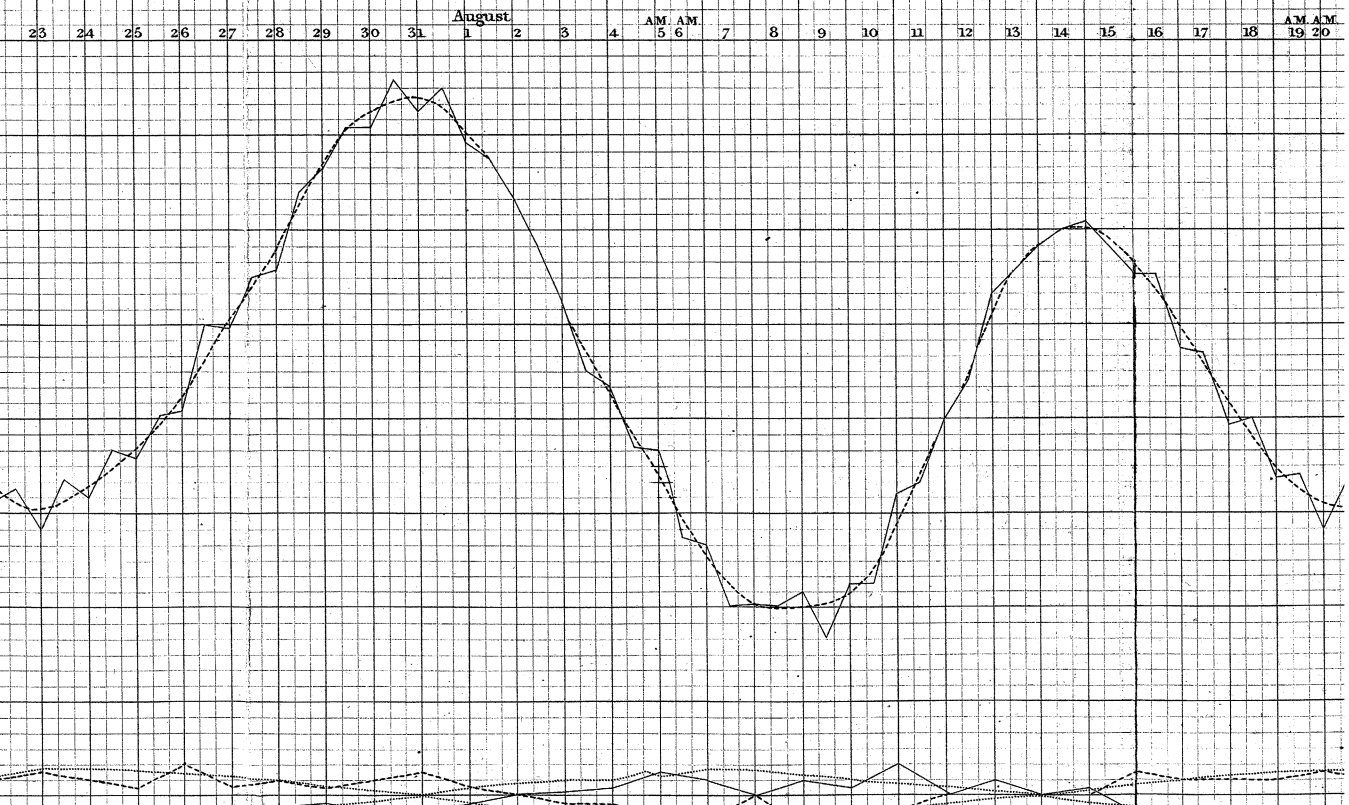
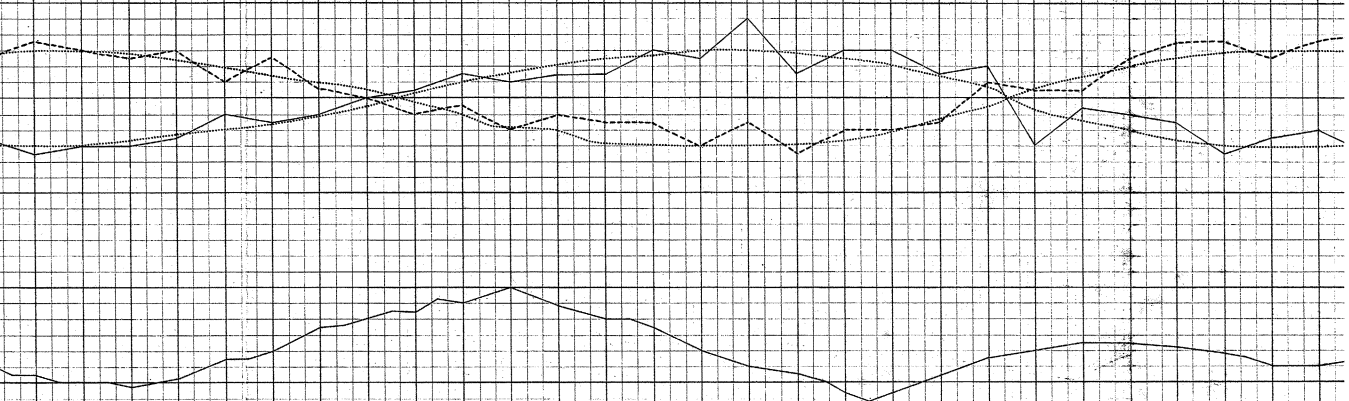
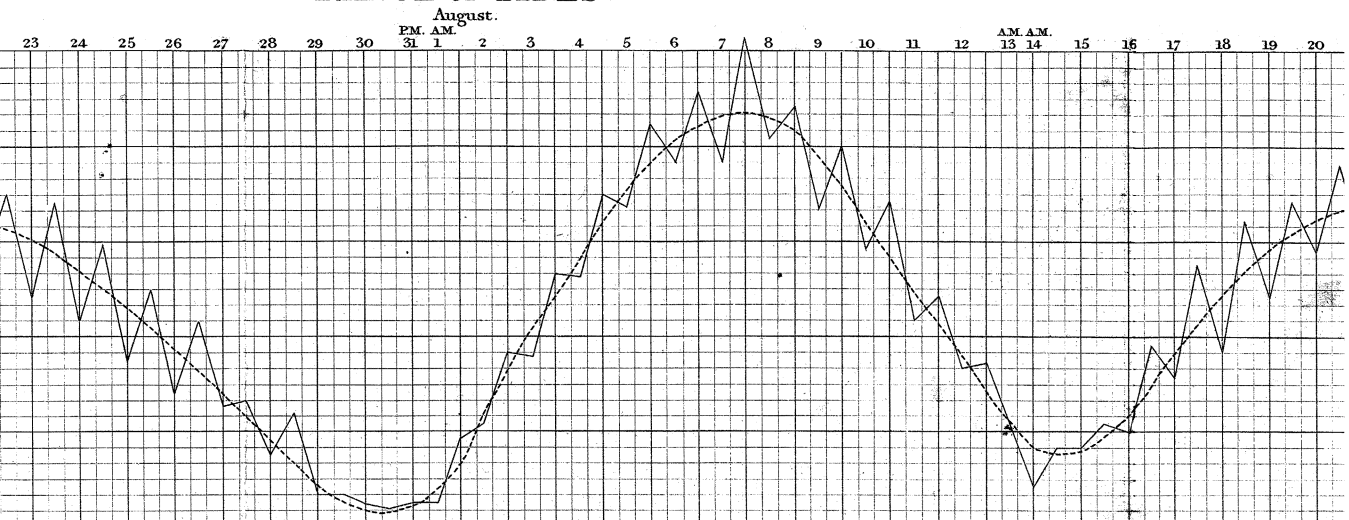
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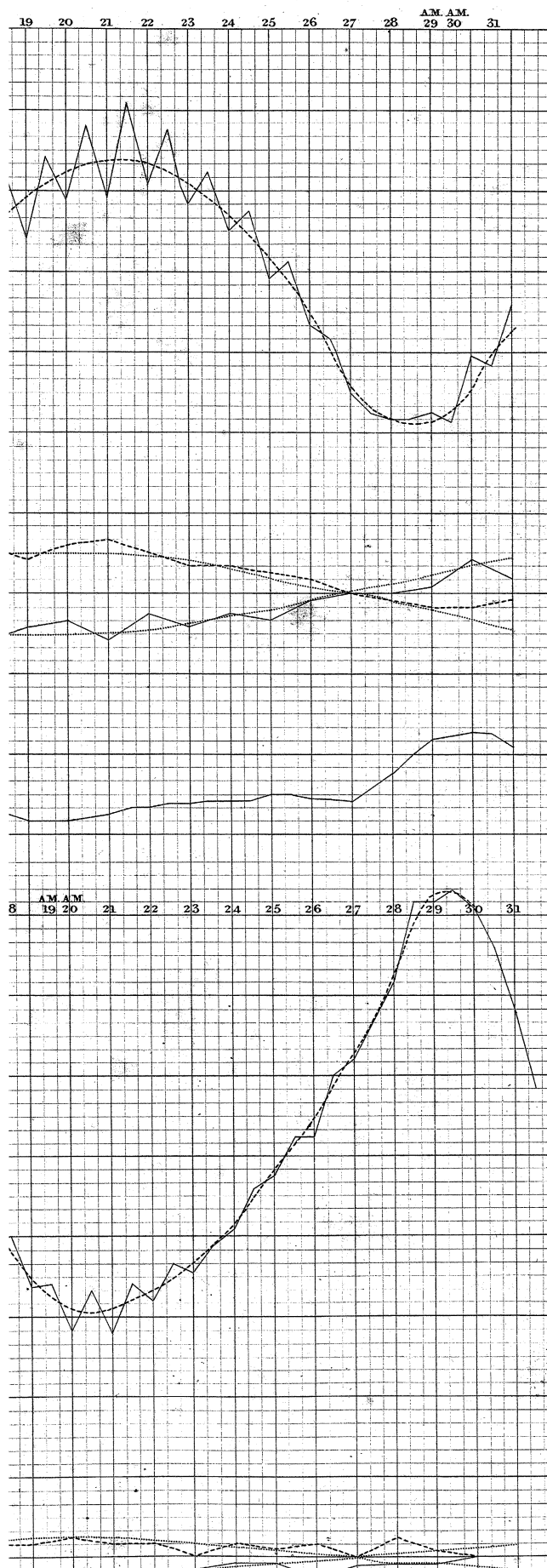
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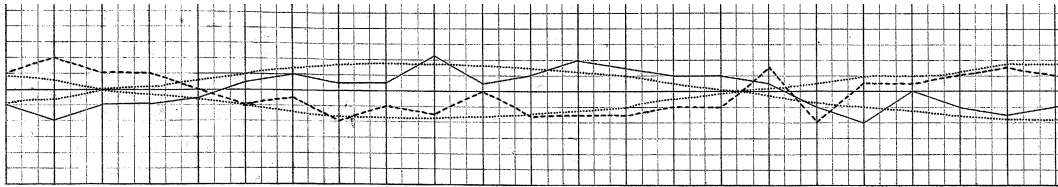
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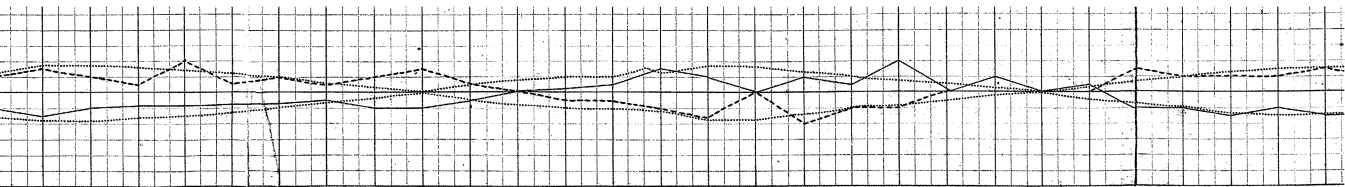
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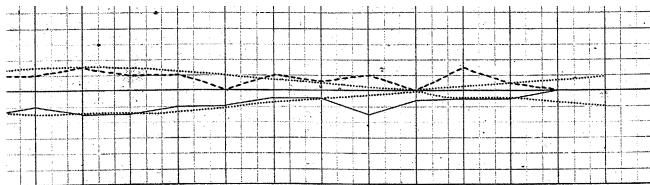
RANGE OF TIDES











Engraved by J. & C. Walker.

