XIII. *Researches on the Arseniates, Phosphates, and Modifications of Phosphoric Acid. By* Thomas Graham, *Esq. M.A. F.R.S.E. Professor of Chemistry in the Andersonian University of Glasgow. Communicated by* Edward Turner, *M.D. F.R.S. &c.*

I. *Of the Subsalts.*

No classes of salts have more liberally rewarded investigation than the arseniates and the phosphates. Witness the discovery of the extraordinary phosphates of lime by Berzelius; the observation of the identity of form of the corresponding arseniates and phosphates by Mitscherlich, and the doctrine of isomorphism to which that observation led; the discovery by the same chemist of two biphosphates of soda, agreeing in composition but differing in form; and lastly, the discovery of the pyrophosphates by my friend and townsman Mr. Clark. Much, however, still remains to be done to complete the history of these interesting salts.

1. *Subarseniate and Subphosphate of Soda.*

The extraordinary disposition of arsenic and phosphoric acids to form subsesquisalts—such as the brown arseniate and the yellow phosphate of silver, the common subarseniates of lime, lead, &c.—is well known. Corresponding alkaline salts exist, which merit the consideration of chemists.

To a strong solution of arseniate or phosphate of soda add a solution of caustic soda till the liquor feels soapy between the fingers. At least half as much soda as already in the salt must be added, but an excess of alkali is not injurious. Concentrate the liquor till a pellicle forms on its surface, and then allow the solution to cool. At the temperature of 150°, tufts of slender prismatic crystals appear in it; these rapidly increase in quantity, and finally fill the vessel. The crystals must be drained as well as possible, and the mother-liquor may be thrown away, as it contains little else than the excess of caustic soda and the soluble impurities of the salts. It is necessary, without loss of

time, to redissolve the crystals in twice their weight of hot water, to filter the solution through paper, and to recrystallize.

Both salts crystallize readily, as their solutions cool, in the form of six-sided prisms, which are generally slender. The prism is often terminated by a flat surface, which appears to be a right section. The angles of the crystals were not measured, but two of them are much more obtuse than the remaining four. The subarseniate may be procured in crystals of larger size than the subphosphate, but of the same form. These salts in the crystalline form are not altered by exposure to the air, but in solution they absorb carbonic acid; and when again crystallized, a portion of carbonate is found to adhere pertinaciously to the crystals. It is easy, however, to produce fine crystals by the process described, free from carbonic acid, and apparently pure.

A solution of the subarseniate is precipitated exactly neutral, by an excess of fused nitrate of silver, the brown subarseniate of silver falling down, which proves the alkaline subarseniate to be in the same state of neutrality as the metallic subarseniate, and consequently of a similar constitution. The subphosphate gives, with the same reagent, the yellow subphosphate of silver, and leaves a liquid either neutral or very faintly alkaline by the most sensible cudbear paper. The alkalinity, however, must be accidental, as it disappears on the addition of the smallest quantity of acetic acid. These salts, therefore, rank as subsesquisalts, containing one proportion and a half of base to one of acid[*]. They are interesting as the only known soluble salts of that constitution. The subphosphate had been previously crystallized by Dr. DALTON and recommended as a reagent[†]; but it was supposed to contain twice as much soda as the common phosphate. MITSCHERLICH also infers the existence of a subsesquiphosphate of soda, from the quantity of carbonic acid expelled, when phosphate of soda is calcined with carbonate of soda[‡]. The same salt appears likewise to have fallen into the hands of Dr. THOMSON, as an accidental product, but is described as a carbono-phosphate of soda, being probably impure[§].

In regard to the properties of these salts. They are strongly alkaline to the taste, and act upon chlorine and iodine like free alkalies. Indeed the excess

[*] Three atoms oxygen in the base for five atoms oxygen in the acid.

[†] Manchester Memoirs, N.S. vol. iii. p. 12.   [‡] Annales de Chimie et de Physique, tom. xix. p. 363.

[§] First Principles, &c. vol. ii. p. 451.

of their alkali is separated by the weakest acids, even by carbonic acid, and the common rhomboidal phosphate or arseniate afterwards appears on crystallizing. When the pure crystals are thrown into neutral nitrate of ammonia, the volatile alkali is disengaged. At 60° FAHR. 100 parts water dissolve 28 crystallized subarseniate of soda; and the crystals by themselves melt at 186°.

At 60°, 100 parts water dissolve 19·6 crystallized subphosphate of soda, and the crystals melt at 170°. Hence, although more fusible, they are less soluble than the crystals of subarseniate.

It is a fact of extraordinary interest, that the acid of this subphosphate is not convertible into pyrophosphoric acid by the action of heat upon the salt, like the acid of the common phosphate of soda. Indeed, when the pyrophosphate of soda itself is calcined with an excess of carbonate of soda, carbonic acid is expelled, and the former salt passes entirely into subphosphate of soda, which crystallizes in the usual form, and contains not pyrophosphoric but phosphoric acid. This change takes place equally well although both the carbonate and pyrophosphate be made anhydrous before being calcined; and we can obtain consequently an anhydrous subphosphate of soda. A solution of pyrophosphate of soda, to which sufficient caustic soda or carbonate of soda has been added, cannot be evaporated to dryness without becoming subphosphate. But pyrophosphate of soda may be boiled with caustic soda for hours without sensible alteration, provided the solution is not evaporated to dryness; and it crystallizes afterwards in its original form, exhibiting no disposition whatever to form a subpyrophosphate.

I may premise thus early, that the preceding facts, and many others to be afterwards enumerated, appear to be most easily explained on the hypothesis that phosphoric acid, in contradistinction to pyrophosphoric, is characterized by a disposition to unite with three atoms of base;—that common phosphate of soda, for instance, is a phosphate of soda and of water, and that its symbol is $\overset{..}{N}a^2\overset{...}{H}\overset{...}{P}$. Now for this basic water an atom of any of the usual bases may be substituted; an atom of soda, for instance, as in our subphosphate, of which the symbol is $\overset{..}{N}a^3\overset{...}{P}$; an atom of oxide of silver, as in the yellow subphosphate of silver; and so in the other subphosphates. We have here a clue also to the disposition of phosphoric acid to form such subsesquisalts; for the common phosphate of soda which we use as a precipitant

exchanges its basic water for a fixed base. Hence, although a phosphate of neutral composition, such as the common phosphate of soda, cannot be made anhydrous without becoming pyrophosphate, the subphosphates, having an excess of fixed base, may be anhydrous, as was observed by STROMEYER; and indeed they are not convertible into pyrosalts.

The pyrophosphoric acid of CLARK, which exists in the pyrophosphate of soda, appears to unite with only two atoms of base.

Phosphoric acid, produced in white flakes on burning phosphorus in air or oxygen gas, or the acid heated to redness by itself, constitutes, we shall afterwards find, a third modification of phosphoric acid. This third variety is characterized by alone coagulating albumen; by producing precipitates, even when free, in muriate of barytes, lime, &c.

Much time and attention were devoted to the determination of the water of combination of the foregoing subsalts. Both salts, when dried by heat, act upon glass with as much violence as the caustic alkalies, absorb carbonic acid with avidity, and retain a small but notable quantity of water under the most intense heat. The problem is therefore environed by difficulties.

(1.) Excellent hard crystals of subarseniate of soda lost nothing when reduced to powder and exposed to a dry atmosphere. Dried most cautiously in a platinum flask, on a sand-bath,

Water.

In Exp. 1.   42·42 grs. crystallized salt lost 21·13 .... 49·81 per cent.
——— 2.   26·04 ——————————— 12·94 .... 49·69 ———
——— 3.   41·   ——————————— 20·40 .... 49·76 ———

Mean ... 49·75

These results exhibit the entire quantity of water which the salt abandons by the action of heat alone; for an adopter being applied to the flask and made tight by luting, the salt was in each case subsequently heated for a few minutes to full redness, without any further loss of weight. No sensible absorption of carbonic acid occurred when the experiment was conducted in this manner. The salt was not fused; indeed it is not fused by a strong white heat.

But the calcined salt still contains water, as may be shown by fusing it with any body capable of combining with the excess of alkali. A quantity of bichro-

mate of potash in a glass tube may easily be kept in a state of fusion by the flame of a lamp. On throwing the calcined subarseniate into that fused and anhydrous salt, a notable quantity of water was given off, which condensed in the upper part of the tube.

Exp. 1. About 50 grains of the fused bichromate of potash, as it falls to pieces in the progress of cooling, but still warm, were introduced into the platinum flask containing 13·1 grains of calcined salt of Experiment 2nd above, and the whole maintained in a state of fusion for a considerable time at a low red heat, by means of a spirit-lamp. The salt lost 0·16 grain additional, and no green oxide of chromium was formed. This is an additional loss of 0·62 per cent. on the crystallized salt, and makes the entire water amount to 50·31 per cent.

Exp. 2. 25·57 grains of crystallized subarseniate were introduced, with a little water, into a crucible containing already 20 grains of pure anhydrous arsenic acid, calcined immediately before by a spirit-lamp heat which does not decompose it. The whole was cautiously dried, and finally fused by a red heat. The loss amounted to 12·8 grains, or 50·06 per cent.

Exp. 3. To 25·11 grains of binarseniate of soda previously fused in a crucible, 45·5 grains of subarseniate of soda were added, with water sufficient to dissolve the whole. Cautiously evaporated to dryness in a crucible partially covered by a watch-glass, as usual, and finally heated to redness, the subarseniate lost 22·88 grains, or 50·29 per cent. This last is certainly the preferable mode of determining the problem.

The mean of the three experiments detailed gives the entire water in the subarseniate of soda 50·22 per cent., while the proportion expelled by heat alone amounts to 49·75 per cent. Hence the quantity retained amounts to 0·47 per cent.

When the calcined salt retaining this small quantity of water is reduced to an impalpable powder, and heated afresh on the sand-bath, the whole water is expelled, with the exception of a mere trace.

Although small, the quantity of water retained in the calcined salt could not be passed over without investigation, as it may afford indication of some internal change which the subarseniate undergoes. Calcined in the open fire, this salt absorbs carbonic acid gas, and afterwards effervesces briskly with an

acid. The salt becomes at the same time anhydrous. This may arise from the hydrate of soda becoming carbonate of soda.

A portion of subarseniate of soda, dried by the spirit-lamp, was reduced to powder, and calcined anew with a mass of carbonate of ammonia in the same crucible, so that the maximum absorption of carbonic acid (as it was imagined,) might take place. The salt was kept uncovered for some time, at a low red heat, after all the volatile carbonate had escaped. It was found that the quantity of carbonic acid absorbed, might be determined most exactly by disengaging the gas over mercury by means of a small quantity of muriatic acid slightly diluted.

Eleven grains of calcined salt afforded 0·49 cubic inch of carbonic acid gas, at 60°; of which the weight is 0·23 grain, and which is equivalent to 0·56 grain of carbonate of soda. Hence, by calculation, 100 parts of the calcined salt contain 2·1 carbonic acid, or 5·1 carbonate of soda; 2·1 carbonic acid are equivalent to 0·9 water; but 50 calcined salt, it was previously shown, retain 0·47 water, and therefore 100 calcined salt retain 0·94. It would thus appear that the carbonic acid is just in quantity sufficient to occupy the place of the water. The carbonic acid is not expelled by an intense white heat.

The supposition is quite inadmissible that our salt contains the notable quantity of soda which becomes carbonate, as a casual impurity, and not essential to its composition; for the salt employed in all these experiments was in large, clear and perfect crystals. Such a supposition is also opposed by the analytic determination of the soda.

The quantity of water in the salt, namely, 50·22 per cent., is not easily reconciled with our best data for atomic weights. Adopting the atomic weight of arsenic acid, given by BERZELIUS, which I had an opportunity of verifying, a salt of

> *24 atomic proportions of water correspond with 50·82 per cent.
> 23½ ——————————————————— 50·29 ———
> 23 ——————————————————— 49·75 ———

Our experimental result agrees closely with the middle number, and is perhaps

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* We are obliged to adopt the double atom of arsenic acid here ($\ddot{\text{As}}$ = 1440·1); and consider these subsalts as consisting of one proportion of arsenic acid (containing five proportions oxygen,) and three proportions of base (containing three of oxygen).

compatible with either 23 or 24 atoms of water. Chemists will probably agree with me that the last supposition is the most likely. If so, it is curious that the subarseniate differs only from the neutral arseniate, by the substitution of an atom of soda for an atom of water, for the last salt contains 25 atoms of water.

It is well known that the analytic determination of the acid in the arseniates and phosphates is attended with considerable difficulty, chiefly from unsteadiness in the proportions of the precipitates.

41·87 grains of crystallized subarseniate of soda, precipitated by an excess of pure acetate of lead, gave a neutral mother-liquor, and a quantity of subarseniate of lead, which successfully washed by decantation, without the use of a filter, and heated to redness, weighed 46·41 grains; 35·17 grains of this subarseniate of lead, freshly calcined, were dissolved entirely in water, acidulated with nitric acid; and, precipitated by sulphate of soda, gave 35·86 grains of sulphate of lead, which contain 26·38 oxide of lead. In such calculations the atomic numbers of BERZELIUS are adopted in this paper. Hence the portion of subarseniate of lead analysed contains 8·79 arsenic acid; and the whole 46·41 grains subarseniate of lead contain 11·62 arsenic acid, which is therefore the quantity of arsenic acid in the portion of subarseniate of soda submitted to analysis. Hence crystallized subarseniate of soda contains 27·76 per cent. arsenic acid.

The soda of the salt was determined in the usual way. The arsenic acid being precipitated by acetate of lead, and received on a filter, the excess of lead was removed by carbonate of ammonia added to the hot liquor. The solution of acetate of soda resulting, was then filtered, concentrated, and transferred into a platinum crucible, in which it was evaporated on the sand-bath to dryness with the greatest caution; partially covered by a watch-glass; and eventually decomposed by a full red heat gradually applied to the crucible still covered by the watch-glass, as from the effervesence during the decomposition of the acetates, small particles are thrown up with considerable force, and would otherwise be lost. The solution of carbonate was then filtered, evaporated to dryness in a crucible, and raised to a strong red heat. The following results were obtained after a knowledge of all the necessary precautions had been acquired.

Exp. 1. 39·98 grains of crystallized subarseniate of soda yielded 15·61 carbonate of soda, equivalent to 9·14 soda; or the salt contains 22·87 per cent.

soda. Now 22·87 soda contain 5·85 oxygen, and 50·22 water contain 45·74 oxygen; or the oxygen in the water is 7·819 times that in the base. But as there are three atoms of oxygen in the base, there are 7·819 × 3, or 23·457 atomic proportions of oxygen in the water.

Exp. 2. 40·3 grains of crystallized subarseniate of soda yielded 15·73 carbonate of soda, equivalent to 9·21 soda; or the salt contains 22·85 per cent. soda.

Exp. 3. 21·62 grains of crystallized salt gave 8·41 carbonate of soda, equivalent to 4·93 soda; or 100 grains of crystallized salt contain 22·8 soda.

These experiments agree very closely among themselves; but I am doubtful whether this method gives the alkali with perfect precision in the case of the arseniates, but somewhat in excess. The general result of the analyses may be stated as follows:

<div align="center">Subarseniate of soda.</div>

	Experiment.	Theory of 23 atoms water.
Arsenic acid	27·76 . . .	27·69
Soda	22·85 . . .	22·55
Water	50·22 . . .	49·75
	100·83	100·

(2.) The crystals of subphosphate of soda submitted to analysis were smaller than the crystals of subarseniate, but well formed and remarkably pure, containing not a trace of sulphuric, muriatic, or carbonic acid.

Exp. 1. A quantity of the salt had been reduced to powder and exposed to a dry atmosphere, in which it lost a little weight; of the salt so dried, 29·12 grains lost by red heat in a platinum retort, as described in the case of the subarseniate, 16·07 grains; which is 55·19 per cent. water.

Exp. 2. 21·83 grains of crystallized salt heated in the platinum retort on the sand-bath lost 12·05 grains, or 55·2 per cent. Being heated thereafter to redness by the lamp, the loss appeared to be only 12·01 grains; but the calcined salt had acquired a little carbonic acid, notwithstanding the precautions, and now effervesced with acids. These two experiments give, therefore, the same result.

The salt still retained a little water, about twice as much as the subarseniate in the same circumstances. But when the calcined subphosphate was

reduced to an impalpable powder, and heated anew, the greater portion of the water which had been retained was readily expelled.

Exp. 3. Fused with recently ignited protoxide of lead, 19·36 grains of crystallized salt lost 10·84 grains, or 55·99 per cent., which is the entire water in the salt.

Exp. 4. To 17 grains of biphosphate of soda recently fused in a crucible, 35·54 grains of crystallized subphosphate of soda were added, with a quantity of water, in which the salts were dissolved together by digestion. Evaporated to dryness, and calcined by a red heat without fusing, the salts sustained a loss of 19·92 grains. Hence 100 crystallized salt have abandoned 56·05 water.

Calcined with access of carbonic acid, the subphosphate, like the subarseniate, absorbs that gas, becoming at the same time anhydrous; but redissolved in water and evaporated, it affords crystals of the original form and composition, which retain a trace of carbonic acid.

A quantity of the subphosphate ignited in an open crucible was found to consist of

> Subphosphate of soda 100
>
> Carbonic acid . . . .   2·3

Another portion, calcined with a mass of dry carbonate of ammonia in the same crucible, consisted of

> Subphosphate of soda 100
>
> Carbonic acid . . . .   2·25

A quantity of subphosphate of soda dissolved in a solution of carbonate of ammonia, was thereby purposely contaminated by a large quantity of carbonic acid, and calcined three times in succession with alternate pulverization. It finally consisted of

> Subphosphate of soda 100
>
> Carbonic acid . . . .   1·7

Or of

> Subphosphate of soda 100
>
> Carbonate of soda . . . .   4·3

It seemed to follow from the last experiment, that, by pulverizing the salt

and recalcining it, the quantity of carbonic acid may be diminished, as in the case of water in the hydrate of the same salt.

The calcined salt did not fuse at a strong white heat, but acquired a beautiful blue tint where in contact with platinum.

By the mean of two experiments detailed above, 100 crystallized subphosphate of soda contain 56·03 water. Twenty-three atoms would be 55·61 per cent. only, and twenty-four atoms water would be 56·66 per cent.*

The soda of the subphosphate was determined directly, in the same manner as the soda of the subarseniate.

Exp. 1. 41·23 grains of crystallized salt gave 17·27 carbonate of soda, equivalent to 10·12 soda. Hence 100 of crystallized salt contain 24·54 soda.

Exp. 2. 40 grains of the crystallized salt gave 16·97 carbonate of soda, equivalent to 7·03 soda, or 24·87 per cent. soda.

It was also attempted to determine the phosphoric acid directly, by precipitating with nitrate of silver, which leaves a mother-liquor either exactly neutral or feebly alkaline. The result was 18·6 per cent. phosphoric acid, which certainly approaches the truth. But the subphosphate of silver was discovered to carry down with it a portion of nitrate of silver, which comes away gradually, but which no continuance of washing is sufficient entirely to remove. The subarseniate of silver has the same property. Thus to precipitate 27·5 grains of crystallized subphosphate of soda, 38·1 grains of fused nitrate of silver were found necessary, which is more than one grain above the theoretical quantity: 25 grains of crystallized subarseniate of soda required 31·08 grains of nitrate of silver for complete precipitation, which is an equally excessive proportion of the precipitant. From these precipitates fumes of nitrous acid were evolved, on the application of heat. When nitrate of ammonia, exactly neutral, was first mixed with the solution of subarseniate of soda, a less quantity of nitrate of silver sufficed; 30·05 grains of nitrate of silver left still an excess of arsenic acid, when added to 25 grains of subarseniate of soda; but on introducing 0·06 grain of nitrate of silver additional, the liquid contained an excess of silver: but the nitrate of ammonia retains in solution a trace of subarseniate of silver. It is curious that the pure subarseniate of silver, precipitated in the way last mentioned, withdraws nothing from a solu-

* Assuming the double atom of phosphoric acid (P̈) = 892·3.

tion of nitrate of silver. This shows that the subarseniate of silver carries down the soluble nitrate only at the moment of precipitation, and by the agency of some chemical affinity very different from the attraction of animal charcoal for many bodies in solution.

The addition of a little acetic acid to a solution of subarseniate of soda, occasioned a notable deficiency in the amount of the precipitate by nitrate of silver.

It may be safely concluded from the quantity of soda which it contains, that the salt under examination is a subsesquiphosphate. The crystals consist of

Subsesquiphosphate of soda . . . . 43·97
Water . . . . 56·03
—————
100·

2. *Subphosphates and Subarseniate of Potash.*

The corresponding salts of potash were formed, but I did not succeed in obtaining them in a state of purity.

When caustic potash is added in excess to phosphoric acid, the solution becomes muddy although dilute, and a precipitate partly flaky and partly in a gritty powder shows itself. This precipitate in both conditions is a diphosphate of potash according to Dr. THOMSON, who examined it *. When arsenic acid was treated in the same way, with excess of caustic potash, no insoluble salt fell; but on concentrating the solution it crystallized almost entirely in the form of minute needles. These crystals I could not free from carbonate; and either of themselves, or rather from the presence of free potash, they were deliquescent in the extreme. There is every reason to believe that they constitute a subsalt corresponding with the subsalt of soda.

A crystallized subphosphate of potash, however, may be formed by fusing together phosphoric acid and an excess of carbonate of potash (bicarbonate was employed). A strong solution crystallizes in small needles, like the preceding subsalts. These crystals were exceedingly soluble, and retained a little carbonate of potash, but were not at all deliquescent. They precipitated the yellow subphosphate from nitrate of silver in excess, and left a neutral or slightly alkaline mother-liquor.

* Inorganic Chemistry, vol. ii.

The soluble subarseniate and subphosphate of soda present a favourable opportunity of forming the corresponding insoluble earthy and metallic subsalts. Salts of this formula, it is well known, generally present themselves, even when the alkaline salts of arsenic and phosphoric acid, which are neutral in composition, are employed as precipitants. But the consequent and unavoidable acidity of the mother-liquor is apt to prevent complete precipitation, the phosphates, with few exceptions, being soluble in an excess of acid.

3. *Subarseniate and Subphosphate of Barytes.*

To a solution of subarseniate of soda, chloride of barium was gradually added till in slight excess. The precipitate first appeared gelatinous, consisting of little pellucid masses; but on the application of heat to the liquor, the precipitate immediately became small-flaky and heavy, and subsided. The mother-liquor proved strongly alkaline, and the precipitate, it was found, had taken down with it a quantity of subarseniate of soda, of which protracted washing did not entirely divest it. BERZELIUS has remarked that barytes is most disposed to combine with phosphoric acid in the proportion of a neutral salt, which is true also of arsenic acid, and accounts for the above derangement of precipitation, a little of the neutral salt being probably formed. The process was reversed, and into a large quantity of neutral solution of chloride of barium, a solution of 50 grains of subarseniate of soda was gradually poured with stirring. A pulverulent heavy precipitate fell easily. The filtered mother-liquor did not fully restore the blue colour of reddened litmus paper in some hours, but acted at once as an alkali on cudbear paper, although in a feeble manner. The precipitate, however, was easily washed. While still wet on the filter, it had acquired a sensible trace of carbonic acid; and when heated, it displayed, like the corresponding alkaline salts, considerable avidity for carbonic acid. 22·33 grains of this salt, heated to redness by the spirit-lamp, were found by one analysis to be composed of

Carbonic acid	0·18		
Arsenic acid	7·10	. . .	32·06
Barytes	15·05	. . .	67·94
	22·33		100

If we may trust a single analysis, the salt contains an excess of barytes; for by theory a subsesquiarseniate of barytes should be composed of ·

Arsenic acid	1440·1	. . .	33·4
Barytes	2870·6	. . .	66·6
	4310·7		100

When a solution of subphosphate of soda is added to chloride of barium, a corresponding subphosphate of barytes subsides as a heavy, small-flaky precipitate, leaving a mother-liquor neutral or nearly so.

4. *Subarseniate and Subphosphate of Lime.*

The subarseniate of lime, formed by pouring chloride of calcium into subarseniate of soda, is a bulky gelatinous body, and continues so although heated. It carries down subphosphate of soda, but to a less extent than the subarseniate of barytes prepared in the same way. Prepared by the converse process, the subarseniate precipitates in little gelatinous masses, as before; although the general aspect is flaky, particularly after the liquor has been heated. The mother-liquor from 50 grains of subarseniate of soda precipitated in this way, required several minutes to affect reddened litmus paper unequivocally, being slightly alkaline. The precipitate appears, therefore, to correspond closely with the subarseniate of soda. The properties of the subphosphate appeared to be similar. Such a phosphate occurs native, but hitherto had not been formed artificially.

BERZELIUS proves the existence of another subphosphate of lime, which has acquired the name of the Subphosphate of lime of bones,—a gelatinous body, formed when muriate of lime is poured into an excess of phosphate of soda; or when phosphate of lime, dissolved in muriatic acid, is precipitated by ammonia. The composition of this phosphate is singular and without parallel, consisting, on the simplest view which can be taken of it, of three proportions of phosphoric acid and four of lime. It is designated by GAY-LUSSAC the $\frac{3}{4}$ phosphate, while the preceding compound is called the $\frac{2}{3}$ phosphate. The anomaly may in some measure be removed by viewing this salt as a compound of one proportion of the neutral phosphate of lime and two proportions of the subsesquiphosphate. Its formula would be as follows:

$$\dot{C}a^2\ddot{P} + 2(\dot{C}a^3\ddot{P})$$
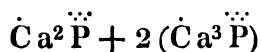
BERZELIUS finds the calcined bones of the ox to be composed of such a phosphate of lime with a small quantity of carbonate of lime. His analysis may be stated thus:

Phosphate of lime $\begin{cases} \text{Phosphoric acid . . } & 46\cdot45 \\ \text{Lime . . . . . } & 49\cdot7 \end{cases}$

Carbonate of lime $\begin{cases} \text{Lime . . . . . } & 2\cdot16 \\ \text{Carbonic acid . . } & 1\cdot69 \end{cases}$

$\left.\begin{array}{c} \\ \\ \end{array}\right\}51\cdot86$

$$\overline{100}$$

The only doubt we can entertain of this view arises from the circumstance, that the presence of carbonic acid in the calcined phosphate of the bones is no proof of the existence of carbonic acid in the same body previous to calcination. We know that the subphosphate of soda absorbs a variable quantity of carbonic acid when calcined. The quantity of carbonic acid which the earth of bones contains is variable. A specimen which had been calcined more than a year before, contained 1·2 per cent. As this was below the determination of BERZELIUS, I reduced a portion to fine powder, and kept it for some minutes in an atmosphere of carbonate of ammonia, at a heat scarcely amounting to redness. The earth, however, by this treatment, had lost carbonic acid, and now contained only 0·5 per cent. Another portion reduced to powder, and gently heated in the same way, but without the carbonate, retained 0·57 per cent. carbonic acid.

The earth of bones, although calcined at a high temperature, contains phosphoric acid and not pyrophosphoric acid, the excess of base preventing the transition. But eight ounces of earth of bones being mixed with two ounces of sulphuric acid, and calcined again, were found thereafter to contain a large proportion of an acid which precipitated silver white.

5. Subarseniate and Subphosphate of Lead.

When the subarseniate or subphosphate is poured into a solution of acetate of lead in excess, the salt which falls was found to contain an excess of base. I therefore had recourse to the converse process. To 50 grains of subarseniate of soda in solution, 50 grains of acetate of lead in solution were gradually added with stirring, which left an excess of the first in solution. The subarseniate of lead was washed by decantation, till the water digested upon it ceased to ac-

quire an alkaline reaction. Heated to low redness, this substance acquired a yellow tint, but became white again on cooling; it was found somewhat aggregated together by the heat, but not fused. 15·25 grains were dissolved in dilute nitric acid, and precipitated by sulphate of soda added in excess. The sulphate of lead amounted to 15·41 grains, equivalent to 11·336 oxide of lead. The washings became of a brown tint on the addition of sulphuretted hydrogen, but the quantity of lead which they contained was too small to be appreciated. This analysis affords a striking confirmation of the atomic weight of arsenic acid, deduced by BERZELIUS from his analysis of arsenious acid by sulphur. I place together the results of my analysis, and the composition of the same salt calculated by that accomplished analyst from his own data.

	Analysis.	Theory of BERZELIUS.
Arsenic acid	25·67	. . . 25·61
Oxide of lead	74·33	. . . 74·39

In another analysis, the quantity of lead which escaped precipitation by the sulphate of soda was even more notable, from the presence of too much nitric acid. The result was 74·18 per cent. oxide of lead. This salt I believe to be most suitable of all the arseniates for determining directly the combining proportion of arsenic acid.

II. *Of the neutral Phosphates and Pyrophosphates.*

It is well known that the phosphate of soda is a highly alkaline salt, although generally viewed as neutral in composition. MITSCHERLICH found that a solution of this salt required the addition of half as much acid as it already possesses, to deprive it of an alkaline reaction. This result I had an opportunity of confirming in a general way, although I could not ascertain the exact point of saturation, from the test-paper proving doubtful in its indications for a considerable distance on either side of the supposed point of neutrality.

Although Mr. CLARK's experiments afford strong evidence that the phosphate of soda of the usual form contains twenty-five atoms water, yet it was thought proper to settle the point by a careful experiment. Pure crystals were employed, which had been formed about six months before and were dry, but

possessed bright surfaces.   A portion for analysis was reduced to powder in a damp day, and pressed for twenty hours between folds of dry blotting paper. A crystal exposed to the air at the same time, beside the paper, remained perfectly bright.   Carefully dried and heated to redness, 35·44 grains of the salt lost 22·29 grains of water.   Hence the crystallized salt consists of

<div style="text-align:center">

Phosphate of soda . . . . 37·1
Water . . . . 62·9
———
100

</div>

Our result gives 25·22 atoms water, and therefore confirms the previous determination.

Mr. CLARK has the entire merit of discovering the change which takes place upon phosphate of soda by the action of heat, and his original description of the pyrophosphate of soda is very complete*.   He likewise remarked the connexion between the transition into pyrophosphate and the loss of the last atom of water of the phosphate of soda, which atom requires a much higher temperature to expel it than the other twenty-four; but he did not entertain the idea, broached in this paper, of the basic function of that atom of water in the constitution of the salt.

The phosphate of soda contains three atoms base; namely, two atoms soda and one atom water; and when added to the earthy or metallic salts, gives precipitates which uniformly contain three atoms base, namely, three atoms of the foreign oxide, as in the case of the subphosphate of silver, or one atom water and two atoms of the other oxide, as in the phosphate of barytes. These precipitations afford the strongest proof of the basic function of that atom of water which is essential to the phosphate of soda, as they can be accounted for, on the usual laws of double decomposition, on no other supposition. The pyrophosphate of soda, on the other hand, contains only two atoms' soda as base, and gives, accordingly, bibasic precipitates.

In his Traité de Chimie, DUMAS speaks in an incidental manner of a third phosphate of soda, differing from the two preceding, obtained by keeping for a long time a solution of the common phosphate at the boiling temperature; but I have been able to discover no description nor any other notice of this new

* Edinburgh Journal of Science, vol. vii. p. 298.

salt. To investigate the point, I boiled for several hours each day during three weeks, an ounce of phosphate and the same quantity of pyrophosphate of soda, in separate flasks, with several ounces of water. A considerable, heavy, flaky precipitate soon appeared in both, but was most abundant in the pyrophosphate. The flasks, on removing the liquors from them, were found strongly corroded. The solution of pyrophosphate, on being filtered and concentrated, yielded crystals of our subphosphate of soda to the last drop. It had evidently derived alkali from the glass, while a portion of its acid had also united with the oxide of lead of the glass, and formed a precipitate insoluble both in water and in acids. But the solution of the boiled phosphate of soda filtered, concentrated, and set aside in a cool place, became gradually filled with crystalline plates, which were the finest films and had a beautiful silky lustre. The mother-liquor being poured off, yielded a second, third, and fourth crop of crystals of the same singular appearance. The last drops of the liquor were still alkaline, but I thought not so strongly so as the phosphate of soda. The crystallization in these cases was gradual, and not hurried and confused. To look at these silky films, nobody would have guessed them to be phosphate of soda. But on examining them minutely, complete rhomboidal plates of the common form of phosphate of soda were distinguished; and the water of crystallization of the salt was found to be exactly the same as that of the rhomboidal phosphate. In a dry atmosphere, too, a portion of the silky plates, and an equal quantity of pounded crystals of the common phosphate lost their water pari passu. It is evident, therefore, that we have nearly obtained the phosphate of soda of an unusual appearance. I shall have occasion, in the sequel of the paper, to notice other circumstances in which the phosphate presents itself of this appearance. On dissolving and recrystallizing the silky plates, the usual solid rhomboids presented themselves. It was also determined by experiment, that neither the phosphate nor pyrophosphate of soda is altered by being boiled for a week in water contained in a silver capsule, in which no decomposition can take place. There can be no doubt, therefore, that these salts undergo no change at the boiling temperature, unless they react upon the material of the containing vessel. Even at the usual temperature a solution of these alkaline salts corrodes a glass phial and becomes turbid in the course of months.

III. *Of the Superphosphates.*

1. *Of the Biphosphate of Soda.*

This salt admits, as I shall immediately show, of so many changes in its constitution and properties, as to entitle it to be considered one of the most interesting of chemical substances. The facts which I have to communicate on this subject are certainly the most extraordinary of the paper, and were determined with care and considerable difficulty.

I had an opportunity of noticing the dimorphism of this salt, and confirmed the observation of MITSCHERLICH, that both forms of crystals possess the same chemical properties and the same proportion of water. Of the four atoms of water which the crystals contain, they lose, I find, two atoms at the temperature of 212°, and not a particle more till heated up to about 375°.

1st. Thus 4·96 grains of the crystals reduced to powder, when dried on the water-bath for several days, retained only 0·76 water, or consisted of

Biphosphate of soda	100
Water	18·09
	118·09

This is as nearly as possible one half of the entire water in the crystals, which by the mean of MITSCHERLICH's experiments consist of

Biphosphate of soda	100
Water	35·57
	135·57

2nd. 10·01 grains of the salt dried on the water-bath retained 1·53 water, which is 18·04 water to 100 dry salt, or the same result as in 1°.

3rd. 50 grains of the crystals lost 6·52 grains on the water-bath; their entire water being by theory 12·77.

There is every reason to believe that the two atoms of water retained are essential to the constitution of the biphosphate of soda, and that its composition is expressed by the following formula,

$$\dot{N}a \ddot{H}^2 \overset{\cdots}{\ddot{P}}$$
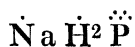
It contains three atoms base, namely, one atom soda and two atoms water, united to a double atom of phosphoric acid. The salt cannot sustain the loss of any portion of this water without assuming a new train of properties. There are accordingly three atoms oxygen in the base, (two in the water, and one in the base,) and five in the acid. When crystallized the salt contains, besides, two atoms water of crystallization.

The crystals of biphosphate of potash contain only the two essential atoms of water, and the lustre of their surfaces is not affected by a water-bath heat, nor by any degree of heat under 400° FAHR.

A solution of either of these alkaline biphosphates, when added to nitrate of silver, occasions a copious precipitation of the yellow subphosphate of silver; and if ammonia be cautiously added, so as merely to make up the excess of nitric acid disengaged, the whole phosphoric acid falls in that state. It is to be here remarked, that the three atoms base of the alkaline biphosphate are replaced in this precipitation by three atoms of oxide of silver.

2. *Second variety of Biphosphate of Soda, or Bipyrophosphate of Soda.*

When a quantity of the biphosphate of soda, previously dried on the water-bath, is afterwards gradually heated on a solder-bath, it begins to lose water at about 375°, and before it is raised to 400° it has lost exactly half the water which it possessed, or one atom. The dried salt may thereafter be heated up to 450°, and maintained for an hour or more at that temperature, without sustaining any further loss. When rapidly heated in a glass tube, the salt undergoes semifusion at some point near 400°, and the same quantity of water comes off in a state of ebullition.

1st. Thus 2·62 grains of the salt dried on the water-bath, when heated in a thin glass tube, lost at once 0·2 grain water on attaining 400°, which is one half of the water which it possessed, namely, 0·396 grain; while it was exposed again for four hours to a temperature between 450° and 470°, without losing 0·01 grain additional.

2nd. In one experiment, 18·45 grains of the crystallized biphosphate lost 3·68 grains by 400° FAHR. on the solder-bath. This is 27·04 of the 35·57 parts water, which are united to 100 dry salt in the crystals. The salt has lost 3·04 atoms of water.

3rd. A quantity of the salt, previously deprived of its two atoms water of crystallization, was kept for three hours at a temperature ranging between 400° and 460°. 11·19 grains of the salt so dried contained 0·9 water, or consisted of

Biphosphate of soda 100
Water . . . . 8·72
                                    ———
                                    108·72

The water retained amounts to 0·981 atom, which is a close approximation to 1 atom.

4th. A quantity of the salt which had been heated to 400° was dissolved in water, evaporated to dryness, and exposed again for some days on a solder-bath at a temperature not exceeding 400°. 13·94 grains of the salt so dried still retained 1·06 grain water, as was found by fusing the salt at a red heat; or it consisted of

Biphosphate of soda 100
Water . . . . 8·23
                                    ———
                                    108·23

This is less than one atomic proportion, which is 8·89 parts; but the temperature at which the salt loses its entire water is elevated no great number of degrees above that in which it loses the atom under consideration; and a protracted exposure to the air at 400° occasions the partial dissipation of the last atomic proportion of water, as in this experiment.

The heated salt which retains one atom water, is still very soluble and possesses an acid reaction, but it is altered essentially in properties. Added to nitrate of silver, it produces a sparing chalky white, pulverulent precipitate, and a very acid liquor. By the cautious addition of ammonia so as merely to take up the excess of nitric acid, the entire phosphoric acid is precipitated in the same state. The precipitate proved, on analysis, to be the pyrophosphate of silver, containing two atoms oxide of silver to one double atom phosphoric acid.

Of this precipitate, heated to redness but not fused, 18·75 grains dissolved in nitric acid and precipitated by muriatic acid, afforded 17·82 grains chloride of silver, equivalent to 14·41 oxide of silver. The composition of this phosphate

and of the pyrophosphate of silver, with which it appears to correspond, is as follows:

	Experiment.	Theory.
Oxide of silver	76·85 . . .	76·49
Phosphoric acid	23·15 . . .	23·51
	100	100

Added to acetate of lead, this altered biphosphate likewise threw down the pyrophosphate of lead. The acid of this last salt was separated by sulphuretted hydrogen, and when afterwards neutralized by carbonate of soda, it afforded crystals of pyrophosphate of soda.

Now this variety of the biphosphate of soda, which may be called the bipyrophosphate, contains one atom of basic water, and its formula is,

$$\dot{N}a\,\ddot{H}\,\ddot{P};$$
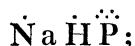
or it contains two atoms base like the salt of silver which it precipitates. This salt when treated with caustic soda affords the neutral pyrophosphate. It also occasions a precipitate in muriate of barytes, in which respect it differs from the proper biphosphate. I failed in all my attempts to obtain the bipyrophosphate of soda in a crystalline form. It uniformly dried up into the state of a friable white crust.

3. *Third variety of the Biphosphate of Soda.*

When the salt last described was exposed on the solder-bath for several days at a temperature between 400° and 470°, it lost weight; only 3·48 parts out of the entire 35·57 water were retained in one experiment, and 2·81 parts water in another. The whole water was expelled, with the exception of 0·38 to 100 dry salt, in other experiments in which the salt was heated on the sand-bath, probably at a temperature not much under 600°. The salt became in fact very nearly anhydrous. Now on pouring water upon the salt so dried, the greater part of it dissolved at once, but an inconstant quantity remained undissolved, varying from 6·57 to 18 parts in 100 salt, but increasing with the intensity of the heat to which the salt had been exposed. This insoluble matter is a fourth variety of the biphosphate, which shall immediately be noticed. As this insoluble salt may be proved to be of the same composition as the biphosphate, it follows that the soluble portion is unaltered in composition.

The insoluble portion appears a heavy dense powder; yet as a part of it remains in suspension in the liquid for a long time, it is necessary to filter to obtain the soluble salt in a state of purity.

The preceding two varieties of biphosphate of soda have a distinct acid reaction, but the solution of this salt is exactly neutral, as was determined by very careful experiments. This property is the best distinctive character of this variety that I can mention. When a solution of the salt is concentrated, it does not deposit any of the insoluble variety, but allows rings of dry salt to form round the margin of the fluid, which are soluble. I have not succeeded in crystallizing it in the vacuum of an air-pump, or by other means which were employed. The salt always dried up into a friable white crust, which on one occasion, when dried at 212°, contained 11·56 parts water to 100 anhydrous salt. This salt occasions a precipitate in muriate of barytes like the preceding. With nitrate of silver it gives a considerable white pulverulent precipitate, and the liquid becomes strongly acid. 8·38 grains of this precipitate dried and heated to redness without fusing, were found to consist of 6·58 oxide of silver and 1·8 phosphoric acid, or 77·32 oxide of silver and 22·68 phosphoric acid = 100; while the neutral pyrophosphate of silver, containing two atoms oxide of silver, consists of 76·49 oxide of silver, and 23·51 phosphoric acid. The correspondence is sufficiently close to prove that our silver precipitate is the same neutral phosphate which presents itself when the second variety of biphosphate of soda is precipitated in the same manner. Like that variety, also, this form of the biphosphate afforded crystals of the pyrophosphate of soda when treated with caustic soda.

In regard to the exact constitution of this variety I entertain considerable doubt. We are warranted to presume that the biphosphate of soda can exist in an anhydrous condition soluble in water, and neutral in its reaction on litmus. The formula of the salt may be,

$$\mathrm{N\,a\,\overset{...}{P}}$$

It must, however, be allowed that no confirmation of this view of the constitution of the salt can be drawn from the composition of the silver precipitate. But the precipitate that should fall by theory, is the biphosphate of silver. Now no such salt exists, the biphosphate of silver described by BERZELIUS containing the new modification of phosphoric acid.

4. *Fourth or insoluble variety of Biphosphate of Soda.*

When any of the preceding varieties of the biphosphate of soda is heated for a few minutes at a temperature approaching but not amounting to low redness, it becomes anhydrous, if not so before, and the whole of it becomes insoluble in water. We are apt to overheat the salt in a crucible if a lamp be employed. I found it the most convenient process to introduce a quantity of the crystallized biphosphate into a platinum crucible, to place this in sand contained in a Hessian crucible, and to place the whole in a situation in an open fire where it would not be heated with rapidity. The time was watched when the sand was red hot to within a small space of the platinum crucible, and the whole then withdrawn from the fire. The appearance of the heated salt depends entirely upon circumstances. If the heat be applied rapidly, the salt undergoes fusion on losing its two essential atoms of water, and is found of a slaggy appearance and hard. But if the heat be applied in a gradual manner, the water escapes without any fusion, the powder merely shrinks and aggregates slightly together. In both states the resulting salt is the same. It may be reduced with ease to the most impalpable powder, and in this condition is very slowly acted upon by continued digestion in a large quantity of boiling water. When it does dissolve, it appears to pass into the preceding variety. But it may be inferred analogically, that if a more intense heat could be applied to the salt under consideration without inducing another change (to be described), the salt would be rendered perfectly insoluble. The biphosphate of potash affords this analogy.

This last salt contains only the two essential atoms of water. When heated above 400°, it begins to undergo a semifusion, although the heat has been applied in a gradual manner; and becomes partially insoluble, without exhibiting the changes which precede this in the biphosphate of soda. A still higher temperature, approaching a red heat, renders the biphosphate of potash as insoluble as the biphosphate of soda. But the biphosphate of potash may be fused in a platinum crucible and heated to whiteness without undergoing any further change of state; and after being thus strongly heated, it may be reduced to powder and digested in boiling water for hours without dissolving to such an extent as to afford a solution capable of affecting nitrate of silver in a sensible manner. It may be inferred, therefore, that if the biphosphate of soda could

be sufficiently heated, water would be wholly incapable of acting upon it. Dilute acids have no action upon this insoluble variety of biphosphate of soda; but alkalies by long digestion withdraw a portion of the phosphoric acid. So far as we can judge, the acid appears not to be in a modified or altered condition.

5. Fifth variety of Biphosphate of Soda, or Metaphosphate of Soda.

When the preceding insoluble variety, or the biphosphate in any condition, is heated in a platinum crucible to low redness, it undergoes fusion, and on cooling presents itself as a transparent glass, which deliquesces in a damp atmosphere and is highly soluble in water. But the fused salt has undergone a most extraordinary and permanent change of properties. The solution has a very feeble acid reaction when compared with crystallized biphosphate. Indeed the addition of 4·3 anhydrous carbonate of soda to one hundred fused biphosphate of soda imparted to the latter a distinct alkaline reaction. When this salt is added to nitrate of silver, the phosphoric acid is nearly entirely thrown down in gelatinous flakes, which aggregate together as a soft solid when heated near 212°, and correspond in composition with the soda salt. This silver precipitate loses acid when washed. It agrees in properties with the biphosphate of silver described by BERZELIUS, which, when washed, appeared to pass into a sesquiphosphate. He formed it by adding phosphoric acid to nitrate of silver, but the phosphoric acid employed by him must have been the glacial acid recently dissolved*.

When the fused biphosphate of soda is added to muriate of barytes, nearly the whole of the phosphoric acid precipitates with the barytes as a flaky gelatinous precipitate, which contains only one atom barytes to the double atom phosphoric acid, like the soda salt. But all the new properties of this salt depend upon the acid having undergone an essential change in constitution. The acid may be separated in the usual way, namely, precipitating by acetate of lead, washing the phosphate of lead and decomposing it by a stream of sulphuretted hydrogen gas. After exposure for some hours to allow the escape of the sulphuretted hydrogen, the acid liquid, without being neutralized, uniformly produced an opal-white flaky precipitate in muriate of barytes, which appeared

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* Annales de Chimie et de Physique, tom. xlvi. p. 143.

immediately, unless the liquors were very dilute. This is also a character, I find, of phosphoric acid recently ignited per se. The acid of our salt possesses also the property of coagulating albumen. In fact, this acid appears to be the glacial phosphoric acid, which had been hastily assumed by recent writers upon this subject to be the pyrophosphoric acid, but is totally different. I shall take the liberty to designate provisionally the acid of the fused biphosphate of soda, the Metaphosphoric acid, from an hypothesis of its constitution to be immediately explained; and the fused salt itself, the Metaphosphate of soda.

The metaphosphate of soda is insoluble in alcohol. Its solution in water is not altered by time; at least no change could be perceived in a solution which had been kept for several months. When exposed to a temperature not exceeding 100° FAHR., the solution becomes viscid as it concentrates, and finally dries into a transparent brittle pellicle like gum. All my attempts to crystallize this salt by slow evaporation in the atmosphere, or by means of the air-pump, have failed. It never presented the slightest trace of crystallization. But many of the insoluble metaphosphates fall down in the state of hydrates, which have the fluid form; which may also be the form that the soda salt is disposed to assume.

The hydrated metaphosphate of soda dried over sulphuric acid in the vacuum of an air-pump, at the ordinary temperature of the atmosphere, was found to consist of

> Metaphosphate of soda 100
> Water . . . . 10·86,

by an experiment in which 11·64 grains of the hydrated salt lost 1·14 by fusion at a red heat. This is 1·22 atomic proportion of water.

When heated to 400°, the hydrated salt appears to retain 1 atom of water, and to pass into the bipyrophosphate of soda. 13·94 grains dried on the solder-bath at 400° for several days, retained 1·06 water; or the salt consisted of

> Biphosphate of soda 100
> Water . . . . 8·23
> ————
> 108·23

This is less than one proportion of water (8·89); but the additional loss of water

which the salt sustained is accounted for by the length of time that it was exposed to the heat, which had the effect of converting a small portion of it into the insoluble and anhydrous variety. The dried salt when dissolved in water gave with nitrate of silver a chalky, white, heavy precipitate, which evidently was not the usual metaphosphate of silver. A portion of the salt was therefore precipitated by acetate of lead, and the acid liberated in the usual manner. The acid did not disturb albumen, nor precipitate muriate of barytes; but when neutralized with caustic soda it gave excellent crystals of the pyrophosphate of soda. There can be no doubt, therefore, that the metaphosphoric acid has returned to the condition of pyrophosphoric acid. The question arises, Is this transition the consequence of merely exposing the metaphosphate of soda to a particular temperature (400°), or does the water interfere and the transition arise from the affinity of phosphoric acid for water, as a base, with soda? Now, upon trial, the anhydrous fused metaphosphate of soda, as it is first formed, was found to undergo no alteration when kept for several days between 400° and 600°. The change is therefore peculiar to the hydrated salt, and effected by the interference of the water.

A solution of the metaphosphate of soda may be treated with caustic soda, and even boiled with it, without any change in the nature of the acid; at least, the saline solution still precipitates silver white, and the acid when separated coagulates albumen. The solution may even be evaporated gently to dryness, without a change of acid; but if dried by a sharp sand-bath heat, and if the alkali be present in sufficient quantity, the common subphosphate of soda is formed.

The metaphosphate of soda forms a series of insoluble metaphosphates when added to solutions of the earthy and metallic salts.

Metaphosphate of Barytes.

The metaphosphate of barytes has already been alluded to. As this salt is soluble in an excess of the metaphosphate of soda, it is best prepared by adding that salt to muriate of barytes in excess. There is an abundant, white, flaky precipitate, and the mother-liquor remains acid. This precipitate washed and dried at 600° FAHR. formed brittle masses; these masses heated to redness give off water and undergo an imperfect fusion. 11·86 grains of the ignited salt

were dissolved with considerable difficulty by pure nitric acid, and then precipitated by sulphate of soda. The sulphate of barytes amounted to 9·69 grains, which is equivalent to 6·36 grains barytes. The composition of this metaphosphate, and of a biphosphate of barytes, is as follows:

	Metaphosphate of Barytes.	Biphosphate of Barytes.
Barytes	53·62	51·75
Phosphoric acid	46·38	48·25
	100·	100·

Our salt is therefore 1·87 per cent. deficient in phosphoric acid. I thought that muriate of barytes had perhaps been carried down by the precipitate, but on examining a portion I found it free of muriatic acid.

But another quantity of the metaphosphate of barytes was prepared, with the precaution of having a more decided excess of muriate of barytes, and the liquors less dilute. 6·61 grains of the ignited salt yielded 5·24 grains sulphate of barytes, which is equivalent to 3·44 grains barytes. This specimen therefore consisted of

Barytes	52·04
Metaphosphoric acid	47·96
	100

which will be found on comparison to correspond very closely with the biphosphate of barytes.

The metaphosphates in general precipitate with considerable difficulty from very dilute solutions, although when once precipitated they are highly insoluble. The last washings of the metaphosphate of barytes, hot water being employed, contained no sensible trace of barytes, for they had no effect upon a sulphate. Hence the metaphosphate of barytes is an insoluble salt.

The metaphosphate of barytes may be boiled in water for two hours without sensible change; but it then begins to dissolve, and the solution proceeds at an accelerated rate, till eventually the whole disappears. The resulting solution is strongly acid, and certainly contains biphosphate of barytes, for it precipitates silver yellow. We have here, therefore, an instance of an insoluble metaphosphate passing into a soluble phosphate.

Metaphosphate of Lime.

On adding metaphosphate of soda to muriate of lime in excess, a precipitate appears like what occurs on throwing into water a solution of an essential oil in alcohol. A transparent semi-fluid body of the consistency of pitch collects at the bottom, which is a hydrate of the metaphosphate of lime in the liquid form, but insoluble in water. This salt appears to have occurred to BERZELIUS, and is described in his paper on the phosphates*. He formed it by precipitating muriate of lime by metaphosphoric acid, but did not observe the circumstances necessary to insure the success of the process.

IV. Of the Modifications of Phosphoric Acid.

The distinctive character of phosphoric acid which exists in common phosphate of soda, as compared with the other modifications, is a disposition to form salts which contain three atoms of base to the double atom of acid. Of these salts the most remarkable is the yellow subphosphate of silver, which the soluble phosphates precipitate when added to nitrate of silver. This acid does not affect albumen; and the other modifications pass directly into the condition of this acid on keeping their aqueous solutions for some days, and more rapidly on boiling these solutions; or upon fusing the other modifications or their salts with at least three proportions of fixed base.

Pyrophosphoric acid, or the acid which exists in the fused phosphate of soda, is remarkably disposed to form salts having two atoms base, which is the constitution of the white pyrophosphate of silver, formed on testing the pyrophosphate of soda with a salt of silver. Such salts of the preceding acid as contain no more than two atoms of fixed base, pass into pyrophosphates when heated to redness. The acid under consideration, when free, does not disturb albumen, nor produce a precipitate in muriate of barytes.

The metaphosphoric acid is disposed to form salts which contain one atom of base to the double atom of acid. The other modifications pass into metaphosphoric acid when heated to redness per se, or when heated to redness in contact with no more than one atomic proportion of certain fixed bases, such

* Annales de Chimie et de Physique, tom. ii. p. 172.

as soda. This acid, when free, occasions precipitates in solutions of the salts of barytes and of most of the other earths and metallic oxides, and forms an insoluble compound with albumen. The glacial or metaphosphoric acid appears to be capable of dissolving in general only about four fifths of the quantity of carbonate of soda which it can decompose when converted into phosphoric acid. But a large quantity of the meta-acid passes into phosphoric acid on uniting with the alkali, and the solution deposits phosphate of soda in tufts composed of fine crystalline plates of a silky lustre. The salt presented itself of this appearance, it will be remembered, in the case of a solution of phosphate of soda which had been boiled for a long time in a glass vessel. The liquid about the crystals, in the present case, still contained metaphosphoric acid.

Now it is a matter of certainty that if we take one combining proportion of any modification of phosphoric acid, and fuse it with soda or its carbonate, we shall form a metaphosphate, a pyrophosphate, or a phosphate, according as we employ one, two, or three proportions of base. The acid when separated from the base will possess, and retain for some time, the characters of its peculiar modification. It would appear, therefore, that the acid is impressed with a disposition to form different classes of salts by the proportion of base to which it has been united, and that it retains this disposition even when liberated from the original compound. But I suspect that the modifications of phosphoric acid, when in what we would call a free state, are still in combination with their usual proportion of base, and that that base is water. Thus the three modifications of phosphoric acid may be composed as follows:

$$\text{Phosphoric acid} \quad \dotso \quad \overset{.}{H}{}^3\,\overset{\cdots}{P}$$

$$\text{Pyrophosphoric acid} \quad \dotso \quad \overset{.}{H}{}^2\,\overset{\cdots}{P}$$

$$\text{Metaphosphoric acid} \quad \dotso \quad \overset{.}{H}\,\overset{\cdots}{P};$$

or they are respectively a terphosphate, a biphosphate, and phosphate of water. Now, when one of these compounds is treated with a strong base, the whole or a part of the water is supplanted, *but the amount of base in combination with the acid remains unaltered.* There are thus three sets of phosphates, in which the oxygen in the acid being five, the oxygen in the base is three, two, and one. The constitution of the acids and of the salts of soda which they form, is exhibited in the following Table.

		Oxygen in		
		Soda.	Water.	Acid.
First Class.	Phosphoric acid	0 .	. 3 .	. 5
	Biphosphate of soda	1 .	. 2 .	. 5
	Phosphate of soda	2 .	. 1 .	. 5
	Subphosphate of soda	3 .	. 0 .	. 5
Second Class.	Pyrophosphoric acid	0 .	. 2 .	. 5
	Bipyrophosphate of soda . . .	1 .	. 1 .	. 5
	Pyrophosphate of soda	2 .	. 0 .	. 5
Third Class.	Metaphosphoric acid	0 .	. 1 .	. 5
	Metaphosphate of soda	1 .	. 0 .	. 5

The hypothetic composition of the acid hydrates may also be stated as follows:

	Acid.	Water.
Phosphoric acid	100 .	. 37·81 = 3 atoms.
Pyrophosphoric acid	100 .	. 25·21 = 2 ——
Metaphosphoric acid	100 .	. 12·61 = 1 atom.

By a heat of 300° a dilute solution of phosphoric acid in a platinum crucible concentrates readily till the water is reduced to the proportion of three atoms, at which stage the acid assumes a dark colour, and is of the consistence of treacle when cold, but much more fluid when hot. In this condition the acid gives an unmixed yellow precipitate with silver, and is entirely phosphoric acid. By exposure for seven days over sulphuric acid in the vacuum of an air-pump, the water was reduced to 43·5 parts, and almost the whole of the acid had crystallized in thin plates, which were deliquescent in the extreme, and which there is every reason to believe were the terhydrate. By a protracted exposure to 300° or 320°, the acid continues to lose water, but much more slowly. At 460° the water was quickly reduced to 34·4 parts, or little more than $2\frac{2}{3}$ atoms, in an experiment conducted in an open crucible, and the acid now precipitated silver white with a trace of yellow; but when neutralized by carbonate of soda, it afforded crystalline plates of phosphate of soda, among which no crystals of pyrophosphate existed. But it may be deemed possible from this result that a hydrate of phosphoric acid exists, containing $2\frac{2}{3}$ atoms water to 1 atom acid, which is 8 atoms base to 3 atoms acid, the proportion of base to acid in the salt termed by BERZELIUS, the phosphate of

lime of bones.   In another case in which the evaporation was conducted much more slowly in a platinum flask, the above compound was certainly not formed; but the evaporation at 415°, after advancing for several days, seemed to cease entirely when the water was reduced to 29·9 parts, which is very nearly $2\frac{1}{3}$ atoms of water.   Acid at this degree of concentration, neutralized as usual by ammonia, gave, with silver, a chalky white precipitate without a shade of yellow, which suggests the idea that an acid hydrate of $2\frac{1}{3}$ water may exist, having a corresponding silver salt.   Acid, so far concentrated, when neutralized by carbonate of soda, afforded a mixture of crystals of phosphate and pyrophosphate of soda, in which the latter predominated.   For the production of metaphosphoric acid, the concentration of a much higher temperature was requisite; but this acid was observed to appear before the proportion of water had fallen under 2 atoms, namely, when it amounted to 28·05 per cent. in one experiment.   By the greatest heat of the sand-bath, which was considerably above the melting point of lead, the proportion of water was reduced a little under 2 atoms, namely, to 22·99 parts; and the acid then contained abundance of metaphosphoric acid, as evinced by its power to coagulate albumen.   In the glacial phosphoric acid, DULONG found 100 acid united with 20·6 water, and ROSE 100 acid with only 10·42 water.   The latter determination falls short of 1 atom water, and would indicate that phosphoric acid may be rendered partially anhydrous by heat.   I do not enter upon the details of my experiments on the hydrates of phosphoric acid, as the subject is difficult, and requires a much more minute investigation than I have as yet had it in my power to give it.

   Although of opinion that there is only one phosphoric acid, and that the modifications are entirely due to the quantity of water combined with the acid, I have still retained the names which have come into use, and even proposed a third, *meta*phosphoric acid, implying merely that the acid to which this name is applied is phosphoric acid with something else, namely, with an atom of water.   As the classes of salts which the acid hydrates form are quite distinct, these trivial names are practically convenient, and may be adopted provisionally till chemists are prepared, by an extended knowledge of the salts, to innovate upon their nomenclature with more advantage than can be done at present.

I may be allowed to state, before concluding, that the binarseniate of soda does not appear to undergo the same remarkable changes as the biphosphate; at least, after being exposed to heat of various degrees of intensity, it continued to give the usual brown subarseniate, with nitrate of silver. But arsenic acid exhibits a weaker affinity for water than phosphoric acid, and is readily made anhydrous by heat.