

XXX.—*On the Tetraphosphoric Amides.*

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

IN previous communications I have described a series of acid amides which may be viewed as pyrophosphoric acid, in which one, two, or three molecules of HO have been replaced by NH_2 . The formulæ of these bodies, of course, contains P_2 . I have now to describe another series of acid amides which require formulæ containing P_4 , and may, therefore, be termed tetraphosphoric.

So far as is known at present, these compounds are produced only by the action of water on the amidated oxychlorides of phosphorus.

If the oxychloride PCl_3O be saturated with dry ammoniacal gas, either at a low or a moderate temperature, the resulting white mass will dissolve in water, with the exception, perhaps, of a little pyrophosphotriamic acid. The solution is sure to contain pyro-diamic acid, but, generally speaking, on the addition of alcohol a precipitate appears. It is not, however, uniform in character, sometimes being a viscid liquid, at other times a light solid, and more frequently a sticky flocculent precipitate, very suggestive of the idea that it is a mixture of the two. The ultimate analysis of different preparations confirmed this idea, or rather led to the belief that there were more than two compounds precipitable by alcohol from the aqueous solution. Notwithstanding the ingenuity and perseverance of my assistant, Mr. Tribe, it was found impossible to determine the conditions under which one or other of these acids was formed, or to separate them in a perfectly satisfactory manner; still I believe that I am in a position to assign formulæ to the liquid and the light solid compounds.

AMIDES INSOLUBLE IN ALCOHOL.

Liquid Compound.—Two different preparations gave very limpid liquids. They were purified by washing with alcohol, or by solution in water and reprecipitation with spirit. They were dried over sulphuric acid in vacuo, but were found to be very hygroscopic, and very difficult to free from the last traces

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of water. The analysis was effected by boiling with hydrochloric acid, which resolves all these compounds after a while into orthophosphoric acid and ammonia.

I. 0.197 grm. of the first preparation gave 0.556 grm. of the ammonio-chloride of platinum.

II. 0.271 grm. gave 0.307 of pyrophosphate of magnesium.

III. 0.0955 grm. of the second preparation gave 0.108 grm. of pyrophosphate of magnesium.

IV. 0.2115 grm. gave 0.595 grm. of ammonio-platinum salt.

V. 0.2565 grm. gave 0.291 grm. of pyrophosphate of magnesium.

These numbers, reduced to a percentage, give—

	First preparation.		Second preparation.		
	I.	II.	III.	IV.	V.
Phosphorus	—	31.63	31.58	—	31.68
Nitrogen	17.70	—	—	17.65	—

These numbers show that the equivalents of P and N are in the ratio of 4 to 5, and they approach to what is required by the formula $P_4N_5H_{17}O_{11}$:—

Phosphorus	32.04
Nitrogen	18.09
Hydrogen	4.39
Oxygen	45.48
	100.00

This body combines with ammonia to form a liquid compound less soluble in water, and insoluble in alcohol, from which, however, unlike the acid, it does not readily separate in drops. On treating this ammonium compound with a weak acid, the original liquid is restored.

An aqueous solution of this body gives solid precipitates with many metallic salts, but its composition seems generally to be altered by union with the metal. Indeed, those salts which have been analysed always contained less than five atoms of nitrogen; and when any of them were decomposed by an acid, the liquid body was not reproduced, or, at any rate, was mixed with the solid tetraphosphoric amides, and with pyro-compounds. Nitrate of silver, for instance, gives, in a slightly acid solution, a white flocculent precipitate, which seems to be

somewhat soluble in water; in an ammoniacal solution, a very heavy yellow compound, which increases in weight and in depth of colour on standing for some days with the ammonio-silver salt. Neither of these gave uniform results on analysis, and neither of them contained nitrogen in a larger proportion than three atoms to four of phosphorus; indeed, the yellow compound contains the smaller amount, and seems to consist, in a great measure, of orthophosphate of silver.

It would appear, therefore, that the elements of ammonia are easily separable from this liquid. It will stand a heat of 100°C . without decomposition, but a cold solution of hydrate of potassium makes it give forth an ammoniacal odour. It may be regarded as an acid ammonium-salt, and for theoretical reasons, to be explained presently, I am disposed to call it *terammoniated tetraphospho-diamic acid*, $\text{P}_4(\text{NH}_2)_2(\text{NH}_4)_3\text{HO}_{11}$.

A portion of this liquid acid remained perhaps a year covered with alcohol. Crystals grew about it, and eventually it seemed almost wholly converted into crystals. A solution of the best of them in water gave indications of their being the ammonium-salt of some unknown acid, which yielded a white silver-salt, but no ferric compound, either at the ordinary temperature or on boiling. The mass was dissolved in water, and evaporated in vacuo; but the substance, after crystallisation, was found to have changed into ordinary phosphoric acid and ammonia.

Solid Acid.—It has already been stated that when the liquid compound is treated with a metallic salt, and the resulting precipitate is decomposed by an acid, more or less of the solid acid is obtained; but this is a very destructive process, and another method of preparing the substance seemed practically to give better results. It was found that the sticky flocculent precipitate often thrown down when alcohol was added to the solution of mixed acids, contained between 4 and 5 atoms of nitrogen to 4 of phosphorus; but it was also found that by the action of strong acids upon it a change took place in its physical properties, and the percentage of phosphorus was gradually raised. This was easily effected by dissolving the mixed acids in water adding a very large quantity of some mineral acid, reprecipitating by alcohol, and repeating the process until the flocculent substance became rather sparingly soluble in water, and quite friable when dry. This also was a destructive process, but while imperfect preparations showed that this solid acid contained less

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amidogen and less oxygen than the liquid acid already described, two specimens, the one prepared by hydrochloric, the other by sulphuric acid, gave numbers agreeing well with the formula, $P_4N_4H_{10}O_9$.

0.170 grm. of acid gave 0.225 grm. of pyrophosphate of magnesium.

0.085 grm. gave 0.227 grm. of ammonio-chloride of platinum.

	I.	II.
That is,— Phosphorus ..	36.96	—
Nitrogen	—	16.75

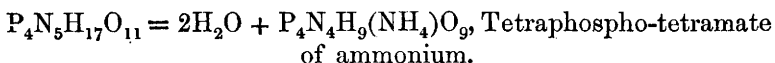
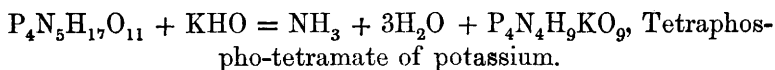
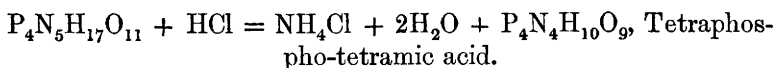
almost identical with tetraphospho-tetramic acid $P_4(NH_2)_4H_2O_9$.

Phosphorus	37.12
Nitrogen	16.76
Hydrogen.....	3.00
Oxygen.....	43.12
	100.00

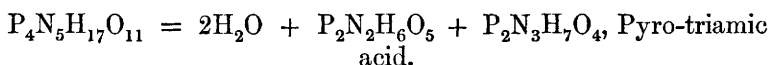
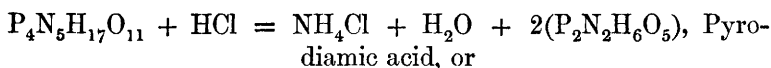
The symmetrical formula given above assumes that none of the nitrogen exists as ammonium, and this is justified by the fact that a solution of the compound gives no immediate precipitate with bichloride of platinum.

This solid acid can be produced equally well by the action of acids or alkalis on the liquid compound; for instance, of cold strong solutions of nitric acid, or of carbonate or hydrate of potassium, or by boiling it for an hour or two with pure water. Pyrophospho-diamic acid, and other compounds are generally produced at the same time, while in two or three instances there was a little white solid formed, which was practically insoluble in water, and gave the ordinary reactions of pyrophospho-triamic acid.

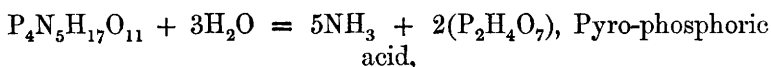
A comparison of the formulæ will show that these decompositions may be simple enough:



In practice there is always more or less of a further breaking down, such as,



The final result of the continuous breaking down of this liquid compound is probably in every case—



which, in its turn, assuming the elements of more water, becomes 4 molecules of PH_3O_4 , Orthophosphoric acid.

This solid -tetramic acid combines with bases, and may be separated from its salts apparently unchanged.

The ammonium compound is solid, like the acid itself, and is also precipitable by alcohol from its aqueous solution. It seems to give up all its ammonia when dried in vacuo, but a specimen dried in the air gave 19·3 per cent. of nitrogen. The formula $\text{P}_4(\text{NH}_2)_4 \text{H}(\text{NH}_4)\text{O}_9$ requires 19·9 per cent. This seems also to have been very nearly the composition of one specimen of the solid white precipitate obtained by alcohol, though it had been dried for 4 or 5 days over sulphuric acid in vacuo. Ammonia added to a strong solution of the acid, produced at first a crystalline precipitate, which was re-dissolved on adding more of the alkali, from which it may be inferred that there are two ammonium compounds.

There certainly are two silver salts. If the aqueous solution be treated with nitrate of silver, a white or nearly white precipitate falls; if it be treated with the ammonio-nitrate, the precipitate is of a dirty yellow colour, very easily affected by light, and readily distinguishable from the bright yellow precipitate obtained from the liquid acid. These two salts were prepared from a small specimen of this acid, which was considered pure.

0·078 grm. of the dirty yellow salt gave 0·068 grm. of chloride of silver, and 0·073 grm. of ammonio-chloride of platinum.

This gives the following numbers:—

Nitrogen	5.90
Silver	65.63

showing that nearly 6 atoms of silver had combined with the acid, and indicating the composition $P_4N_4H_4Ag_6O_9$, a very likely formula, as the silver has replaced all the hydrogen which is theoretically possible in this kind of compound.

Phosphorus	12.70
Nitrogen	5.74
Hydrogen	0.41
Silver	66.40
Oxygen	14.75
		<hr/>
		100.00

Two specimens of the lower silver-salt gave discordant results, but led to the belief that the white salt is the bibasic tetramate $P_4(NH_2)_4Ag_2O_9$, mixed with a small quantity of the higher compound.

AMIDE INSOLUBLE IN WATER.

If oxychloride of phosphorus be rapidly saturated with ammonia gas the temperature becomes very high, and on the addition of water, a white body remains, which is not pyrophosphotriamic acid, for it does not give a yellow compound when treated with ammoniacal nitrate of silver. In order to prepare this substance in a pure state, the compound of PCl_3O and $4NH_3$, produced without regard to temperature, should be heated for a while at rather above $200^\circ C.$, indeed at any temperature between that and what is required to volatilize the chloride of ammonium. Some molecular change is thus effected in the amidated oxychloride, and on the addition of water, little or none of the phosphorus finds its way into solution in any form, while there is produced a new insoluble acid.

The ultimate composition of this body was determined by the usual method of analysis.

I. 0.384 grm. gave 1.405 grm. of ammonio-chloride of platinum.

II. 0.059 grm., of another preparation, gave 0.208 grm. of ammonio-chloride of platinum.

III. 0.203 grm. of a third preparation, gave 0.280 grm. of pyrophosphate of magnesium.

IV. 0.261 grm. of a portion which had been washed with strong HCl before drying and weighing, gave 0.359 grm. of pyrophosphate of magnesium.

V. 0.249 grm. of the same, gave 0.871 grm. of ammoniochloride of platinum.

VI. 0.218 grm. dried at 100° C., gave 0.810 grm. of ammoniochloride of platinum.

VII. 0.218 grm. of the same, gave 0.303 grm. of pyrophosphate of magnesium.

These numbers give:—

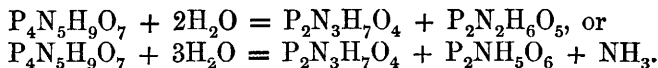
	I.	II.	III.	IV.	V.	VI.	VII.
Phosphorus	—	—	38.52	38.41	—	—	38.80
Nitrogen ..	22.4	22.12	—	—	21.95	23.29	—

These numbers indicate 5 atoms of nitrogen to 4 of phosphorus, and agree best with the formula $P_4N_5H_9O_7$.

Phosphorus	39.36
Nitrogen	22.22
Hydrogen.....	2.86
Oxygen.....	35.56
	100.00

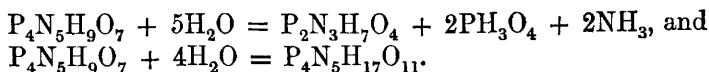
As this formula does not admit of each atom of nitrogen being satisfied with two atoms of hydrogen, we cannot look on the substance as a complete amide. I suggest as its name, simply, tetraphospho-pentazotic acid.

The body, however, though insoluble in water, is liable to be decomposed by it. When boiled with water, it is at once resolved into pyrophosphoric compounds, and without change of appearance, for the -triamic acid produced is white and insoluble, like the original compound, while -diamic and -amic acids enter into solution.



A similar change also takes place, slowly, at the ordinary temperature. Specimens which had been set aside for a few days, were generally found to give a yellow compound, with ammoniacal nitrate of silver; and those which had been placed in bottles after having been dried only in the air, were found, after a few months, to be resolved mainly into pyro-triamic and

-diamic acids. In one case a large quantity of orthophosphate of ammonium was found; in another, some terammoniated tetraphospho-pentamic acid. The formation of these additional bodies is also easily explained:—



This substance resembles pyrophospho-triamic acid in combining readily with alkalis, and in decomposing metallic salts, forming, in every instance, insoluble, or nearly insoluble compounds. There were considerable difficulties attending the preparation of pure salts, besides the suspicion that the specimen of acid itself might not be always definite in composition. The following observations, however, may be worth recording:—

Ammonium Salt.—0.505 grm. of the acid, treated with strong aqueous ammonia, gave a solid compound, which, when dried at 100° C., showed an increase in weight of 0.028 grm., or 5.5 per cent. The formula $P_4N_5H_8(NH_4)O_7$, would give an increase of 5.1 per cent.

That the original substance is not an ammonium salt, in the ordinary sense of the term, is proved by the fact that it may be produced from the amidated oxychloride in the presence either of strong hydrochloric acid or of strong potash.

Potassium Salt.—If the acid be washed repeatedly with a solution of hydrate of potassium, a white insoluble compound is formed. A specimen was analysed:—

I. 0.203 grm. gave 0.253 grm. of pyrophosphate of magnesium.

II. 0.220 grm. gave 0.150 grm. of potassio-chloride of platinum, and 0.726 grm. of ammonio-chloride.

The numbers deduced from this are sufficiently close to those calculated from the formula $P_4N_5H_8KO_7$, to leave little doubt that this is the composition of the salt.

	Calculated.	Found.
Phosphorus	35.12	34.80
Nitrogen	19.82	20.69
Hydrogen	2.27	—
Potassium	11.07	10.89
Oxygen	31.72	—
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	100.00	

Copper Salt.—This acid decomposes chloride of copper dissolved in water, but a specimen so prepared was found to be imperfect; at least, it yielded on analysis 21·52 per cent. of nitrogen, and 6·12 per cent. of copper, whereas $P_4N_5H_8CuO_7$ would require 9·14 per cent. of the metal. When treated with an ammonio-copper salt, this first compound took up more copper, more in fact than one equivalent, for the new compound contained 11·49 per cent.

Lead Salt.—Three different specimens of this salt were prepared by the action of acetate of lead on the solid acid. They were found to contain respectively 30·3, 34·6, and 38·0 per cent. of metal, the last being associated with 11·86 per cent. of nitrogen. This also indicates more than one atom of lead, but the formula $P_4N_5H_7Pb_2O_7$ requires 39·8 per cent.

Silver compounds.—The action of silver salts on this acid appeared worthy of study, and has led to unexpected results.

If it be treated with ammoniacal nitrate of silver, it gives a heavy compound of a pale yellowish brown colour.

This analysed in the usual way gave:—

	First preparation.			Second preparation.	
Phosphorus	18·65	—	—	18·41	—
Nitrogen	—	11·32	11·05	—	10·05
Silver	54·59	54·19	54·18	54·20	54·48

These results do not agree with any formula.

If this acid be treated with neutral or slightly acidulated nitrate of silver, a heavy compound, also of a pale yellowish brown colour, is formed, but its composition is quite different from that of the preceding.

I. 0·352 grm., analysed in the usual way, gave 0·196 of chloride of silver.

I. 0·521 grm. of a second preparation gave 0·293 of chloride of silver, and 0·428 of pyrophosphate of magnesium.

III. 0·452 grm. of the same gave 0·257 of chloride of silver, and 0·367 of pyrophosphate of magnesium.

IV. 0·492 grm. of a third preparation gave 0·275 of chloride of silver, and 0·870 of ammonio-chloride of platinum.

V. 0·485 grm. of the same gave 0·272 of chloride of silver, and 0·424 of pyrophosphate of magnesium.

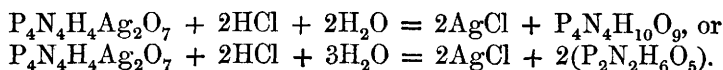
Which give the following percentages:—

	I.	II.	III.	IV.	V.
Phosphorus . . .	—	22·94	22·67	—	24·41
Nitrogen	—	—	—	11·09	—
Silver	41·91	42·33	42·80	41·98	42·21

This seems to show that the nitrate of silver had effected what the hydrochloric acid had failed to accomplish—the removal of a portion of the ammonia, and that the new compound was in fact $P_4N_4H_4Ag_2O_7$.

Phosphorus	24·22
Nitrogen	10·94
Hydrogen	00·78
Silver	42·19
Oxygen	21·87
	100·00

This may be regarded as the normal $P_4N_5H_8AgO_7$, in which one molecule of ammonium has been subsequently replaced by silver. But for the purposes of nomenclature, it may be better to view it as containing 4 molecules of NH, when it may be called *Tetraphospho-tetramate of Silver*. It is clear that the pentazotic acid cannot be regained from it by simply decomposing the salt with an acid. On trying the experiment both with hydrochloric and with nitric acid, it was found that no insoluble acid was produced, but that the solution contained tetraphospho-tetramic and pyrophospho-diamic acids. The formation of either of these is very natural.



As this new acid seemed to be deserving of further study, an attempt was made to prepare a large quantity of the silver salt from a new specimen of oxychloride of phosphorus; but the salt was lighter in colour and different in composition, though the silver and nitrogen proved to be in the same ratio. As the oxychloride was possibly not pure, it was re-distilled from an

additional quantity of boracic acid, but a similar result was obtained. The only known difference in the manner of preparation was that the amidated oxychloride had not been heated so long at a high temperature. A portion was therefore exposed to 230° C. for about ten hours, and a silver salt was prepared from it. The result was somewhat intermediate between those formerly obtained.

I. 0.380 grm. of silver salt gave 0.223 grm. of chloride of silver, and 0.720 grm. of ammonio-platinum salt.

II. 0.356 grm. gave 0.210 grm. of chloride of silver, and 0.311 of pyrophosphate of magnesium, which give:—

	I.	II.
Phosphorus ..	—	24.39
Nitrogen	11.88	—
Silver	44.17	44.40

The ratio of atoms of nitrogen and silver is still 2 : 1 or 4 : 2, but the salt cannot contain as much as seven atoms of oxygen. $P_4N_4H_2Ag_2O_6$ would require:

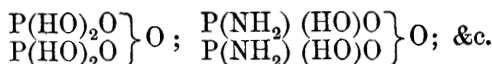
Phosphorus	25.71
Nitrogen	11.24
Hydrogen	00.41
Silver	43.37
Oxygen	19.27
	100.00

This silver compound also gave some tetraphosphodiamic acid, when decomposed by nitric acid.

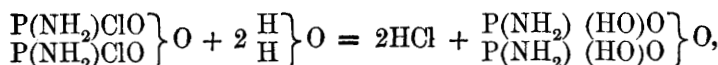
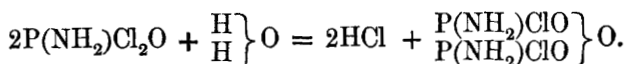
It is very evident that the investigation of these tetraphosphoric amides is still incomplete; but the difficulty of separating one from another, the apparent capriciousness of their formation, and the generally unsatisfactory character of compounds that will not crystallise, have induced me to leave the subject in its present condition. I think, however, that the existence of compounds analogous to the pyrophosphoric amides, but containing P_4 , is proved; but whether those containing P_4N_5 may not, after all, be mixtures, may be a matter of doubt. It will not be difficult to extend to these compounds the same method of reasoning by which I have previously endeavoured to explain the building up of the less complicated bodies.

Theoretical Constitution.

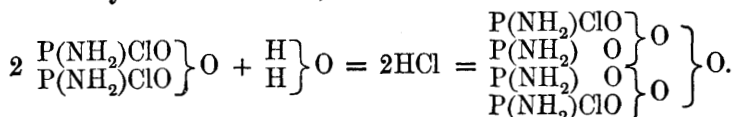
In previous communications I have regarded pyrophosphoric acid and its amide as bodies constituted on the water type, with the rational formulæ—



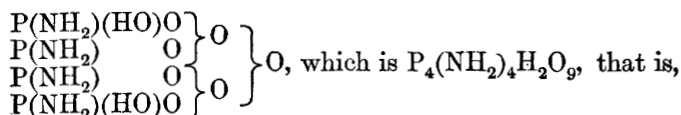
and the following was given as the probable process by which the -diamic acid is formed, when the amidated oxychloride of phosphorus attacks water:



the two reactions being perhaps simultaneous. But it does not follow that when two molecules of the amidated oxychloride have attacked one of water to form $\left. \begin{array}{l} \text{P}(\text{NH}_2)\text{ClO} \\ \text{P}(\text{NH}_2)\text{ClO} \end{array} \right\} \text{O}$, the remaining chlorine should be replaced by HO. The process of attacking both atoms of hydrogen in water may be repeated by the freshly formed chloride, thus—

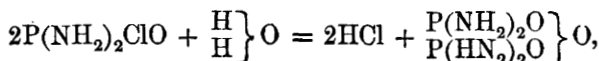


which, when acted upon by water in the usual way, gives 2HCl and

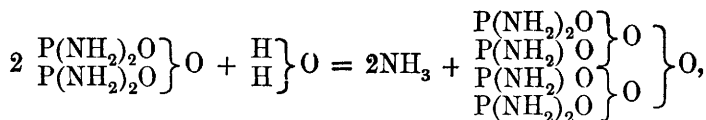


Tetraphospho-tetramic acid.

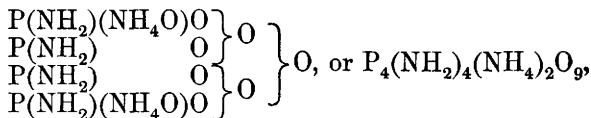
This acid may be prepared, like the pyro-diamic, from the higher amidated oxychloride $\text{P}(\text{NH}_2)_2\text{ClO}$. The first stage of the reaction, in both cases, will be—



and the second attack upon a molecule of water will give—



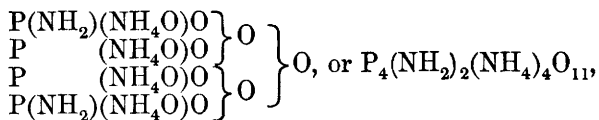
or *tetraphospho-hexamide*, a hypothetical body, to which I shall again refer, and which has simply to acquire the elements of $2\text{H}_2\text{O}$ to be converted into



Tetraphospho-tetramate of ammonium.

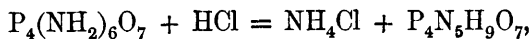
Now, this tetramic acid must be the fourth amide of a *tetraphosphoric acid* of the composition $\text{P}_4(\text{HO})_6\text{O}_7$; and this is no hypothetical substance, for it is known in its salts. It is in fact Fleitmann and Henneberg's phosphoric acid.

It is difficult to assign satisfactory rational formulæ to the two compounds containing P_4N_5 . The fact that the atoms of nitrogen are uneven in number, destroys the symmetry, and seems to point to their being products of decomposition of substances containing P_4N_6 . That they both belong to the tetraphosphoric series, is evidenced by their easily giving rise to tetraphospho-tetramic acid. The genesis of the liquid $\text{P}_4\text{N}_5\text{H}_{17}\text{O}_{11}$ from the hexamide, requires the assumption of H_2O by each phosphoric element, when it will be converted into



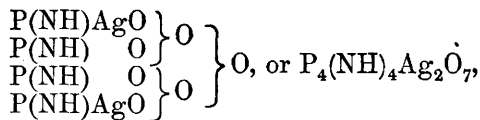
an *ammoniated tetraphospho-diamic acid*, which seems, I know not why, to part with one of its molecules of ammonia more readily than the other three.

The acid, $\text{P}_4\text{N}_5\text{H}_9\text{O}_7$, is easily derivable, theoretically speaking, by the action of free acid or hydrate of potassium on the hexamide



and this will account for its being monobasic. The action of

nitrate of silver on this pentazotic acid removes another molecule of NH_3 , and restores the symmetry, producing



Tetraphospho-tetrimate of silver.

If the view of the mutual action of water and the chlorides of phosphorus, given in this and preceding papers, be correct, we obtain the following rational formulæ for the four known phosphoric acids:—

Ortho-phosphoric acid $\text{P}(\text{HO})_3\text{O}$.

Meta-phosphoric acid $\text{P} \left\{ \begin{array}{l} \text{HO} \\ \text{O} \end{array} \right\} \text{O}$.

Pyro-phosphoric acid $\left\{ \begin{array}{l} \text{P}(\text{HO})_2\text{O} \\ \text{P}(\text{HO})_2\text{O} \end{array} \right\} \text{O}$.

Tetra-phosphoric acid (Fleitmann
and Henneberg's) $\left\{ \begin{array}{l} \text{P}(\text{HO})_2\text{O} \\ \text{P}(\text{HO}) \quad \text{O} \\ \text{P}(\text{HO}) \quad \text{O} \\ \text{P}(\text{HO})_2\text{O} \end{array} \right\} \text{O}$.
