XLVIII.—*The Phosphoric Acids.*

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THE molecular constitution of ortho-, pyro-, and meta-phosphoric acids and the conversion of one into another have been the subjects of many investigations and differences of opinion.

Graham (*Phil. Trans.*, 1833, **52**, 253) by qualitative tests showed the existence of the three varieties of phosphoric acid, and concluded that "the other modifications (meta- and pyro-) pass directly into the condition of this acid (ortho-) on keeping their aqueous solutions for some days or more rapidly on boiling."

Sabatier (*Compt. rend.*, 1888, **106**, 63), by titrating solutions of the meta-acid of different strengths at regular intervals and using various indicators, concluded that the meta- passes directly into the ortho-variety without the formation of pyro-acid, or at least with the formation of only a trace of it at first, the rate of change being accelerated by concentration and by heat. In further communications (*ibid.*, 1889, **108**, 738, 804), he assumes, with Fleitmann and Henneberg, the existence of complex molecules of the meta-acid, and finds that the rate of change is accelerated by the addition of sulphuric and hydrochloric acids, whilst it is retarded by acetic acid.

Blake (*Amer. Chem. J.*, 1902, **27**, 68), by measurements of the rate of change of the refractive index, concluded that a 10*N*-solution of the meta-acid was completely hydrated in four days.

The results of the investigations of Berthelot and André (*Compt. rend.*, 1896, **123**, 776; 1897, **124**, 265), Giran (*Ann. Chim. Phys.*, 1903, [vii], **30**, 203), and Tanatar (*J. Russ. Phys. Chem. Soc.*, 1898, **30**, 99) have been summarised in a paper by Balareff (*Zeitsch. anorg. Chem.*, 1910, **68**, 288), wherein he concludes that their experimental methods, and consequently their conclusion (that pyro-acid is formed as an intermediate substance) are open to criticism. In this paper, Balareff, by an analytical method based on the formation of cadmium or copper pyrophosphate, concludes that the meta-acid passes by hydration directly into the ortho-variety. In a previous paper (*Zeitsch. anorg. Chem.*, 1910, **67**, 234) he showed that whilst at moderate temperatures the dehydration of the ortho-acid produces pyro- and then meta-, at very high temperatures the change from ortho- to meta- should be direct. He did not, however, realise the latter condition experimentally.

Tilden and Barnett (Trans., 1896, **69**, 158) have shown by vapour-density determinations that the molecule of metaphosphoric acid when in the state of vapour is not simple, but is a bimolecular complex, which at a very high temperature shows signs of dissociation. The experiments described at the end of the present communication confirm their observations on the complexity of the molecule.

It appears from the results of the above-mentioned authors that the question of the intermediate formation of pyrophosphoric acid during the hydration of the meta-variety is still unsettled, and, further, that there is uncertainty as to the molecular condition of the three varieties of phosphoric acid in solution.

Our experiments were first directed towards a study of the changes in the depression of the freezing point which a solution of the meta-acid undergoes on keeping, and also the direct estimation of the amount of meta-acid present in such a solution from time to time. Two solutions, the strengths of which were approximately

N- and 2*N*-metaphosphoric acid, were used. The following table gives the depression at varying intervals of time:

TABLE I.

Time (in days).	Depression of f. p.	
	N-Solution.	2*N*-Solution.
0	0·697	1·452
2	0·900	1·900
5	1·100	2·465
7	1·203	2·685
10	1·305	2·895
12	1·425	3·150

It will be seen from the above values that the depressions recorded for the 2*N*-solution are slightly more than double those for the *N*-solution, so that it follows, that whatever the nature of the change which is taking place may be, increasing the strength of the solution from *N* to 2*N* does not materially affect the velocity.

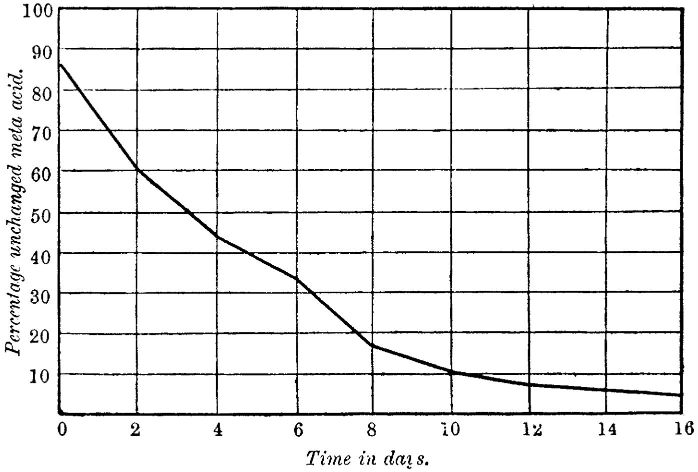
In order to determine the rate at which the hydration took place, the amount of unchanged meta-acid in the solution was estimated from day to day by precipitation with barium chloride. This method was adopted only after numerous trials with other reagents, but preliminary experiments led us to conclude that it was quite trustworthy. When barium chloride is added in large excess to a solution containing ortho-, pyro-, and meta-phosphoric acids, a precipitate is obtained, which, when washed and dried at 100°, was found to have a composition represented by the empirical formula $Ba(PO_3)_2$. A large number of samples of this precipitate were prepared and analysed by decomposition with nitric acid, the barium being subsequently estimated as sulphate, and they were found to have a practically constant composition. To test the method still further, a solution of the meta-acid, which had been kept for some time, was precipitated with largely varying amounts of barium chloride, the smallest amount being a slight excess. When the same volumes of the acid solution were taken, the weight of the precipitate obtained did not materially vary. A solution of meta-acid of about normal strength was prepared, and a portion of it precipitated with barium chloride from time to time. The amount of unchanged meta-acid could therefore be calculated, and the values in the following table were obtained:

TABLE II.

Time (hours).	Unchanged meta-acid, per cent.	Unchanged meta-acid in gram-mols.	Water in gram-mols.	K_1.	K_2.
0	84·92	0·829	55·53	—	—
46	60·80	0·518	55·22	0·0045	0·0043
99	44·35	0·378	55·08	0·0053	0·0035
142	31·87	0·270	54·97	0·0036	0·0034
190	17·63	0·150	54·85	0·0053	0·0053
238	10·28	0·088	54·79	0·0048	0·0048
287	6·61	0·056	54·76	0·0039	0·0040
382	4·55	0·039	54·74	0·0017	0·0016

The fresh solution contained 0·852 gram-molecule of metaphosphoric acid, but 15 per cent. of it had changed before the measurements were begun.

An examination of the above table shows, in the first place, that the values for the percentage of unchanged meta-acid in the solution do not fall on a regular curve, the rate of decrease becoming markedly accelerated after the solution has been kept for about 140 hours. These values are shown for the sake of clearness on the annexed curve. Further, from the values of K_1 and K_2, which represent the velocities of the reaction calculated for a unimolecular and bimolecular change respectively, it is evident that the hydration of the meta-acid does not take place according to any simple scheme.



As further evidence on this point, the freezing points of a solution of the same strength as that employed for the determination of the meta-acid by precipitation with barium chloride were determined, and the theoretical values were calculated on the assumption that the acid changed directly into the ortho-variety, dissociation being of a negligible amount. (The latter conclusion is justified by conductivity measurements.)

TABLE III.

Time (hours).	Unchanged HPO_3 in 100 c.c. solution.	Converted HPO_3 calc. as H_3PO_4 in 100 c.c. solution.	A. Depression due to unchanged HPO_3 calc. for simple mols.	B. Depression due to unchanged HPO_3 calc. for double mols.	C. Depression due to unchanged HPO_3 calc. for triple mols.	D. Depression due to changed HPO_3 calc. as H_3PO_4.	A + D.	B + D.	C + D.	Observed depression.
0	6·64	0·21	1·544	0·772	0·515	0·039	1·583	0·811	0·554	0·697
46	4·14	3·26	0·963	0·481	0·321	0·619	1·582	1·100	0·940	0·900
99	3·02	4·64	0·702	0·351	0·234	0·880	1·582	1·231	1·214	1·040
142	2·17	5·69	0·504	0·252	0·168	1·080	1·584	1·332	1·248	1·170
190	1·20	6·87	0·279	0·139	0·099	1·305	1·584	1·444	1·404	1·240
238	0·70	7·48	0·163	0·081	0·054	1·420	1·583	1·501	1·474	1·305
287	0·45	7·79	0·105	0·052	0·035	1·479	1·584	1·531	1·514	1·420
382	0·31	7·96	0·072	0·036	0·024	1·511	1·583	1·547	1·535	1·500

Table III contains these results. It will be noticed that the freezing point of the almost fresh solution gives a depression corresponding with a molecular weight for the meta-acid of between $(HPO_3)_2$ and $(HPO_3)_3$, and it has subsequently been shown that this abnormal value does not arise from ionisation, but is undoubtedly due to the presence of complex molecules. The depression has therefore been calculated for the unchanged meta-acid on the assumption that it is present (*a*) in simple molecules, (*b*) in double molecules, and (*c*) in triple molecules. The experimentally determined values in the last column show that the hydration of the meta-acid does not proceed according to the equation $HPO_3 + H_2O = H_3PO_4$, but that at the commencement of the reaction at any rate, the molecules of the meta-acid are complex. From these values it is neither possible to say whether pyro-acid is formed as an intermediate compound, nor whether the complex molecules of the meta-acid first break down and subsequently become hydrated.

Although it has not been found possible to estimate either the pyro- or ortho-acids quantitatively in a mixture of all three varieties, the presence of the pyro-acid has been shown qualitatively by the following method. A solution of the meta-acid which had been kept about a fortnight was neutralised with sodium hydroxide, using phenolphthalein as indicator, and the resulting liquid fractionally precipitated with silver nitrate. At first, the yellow precipitate of silver ortho-phosphate was obtained. This was filtered off, and more silver nitrate added. By repeating this process, a white precipitate formed, which gradually became yellow. By filtering it off immediately, it was found possible to obtain it absolutely colourless. If the neutralised solution be acidified by a small quantity of dilute nitric acid and then precipitated with silver nitrate, a colourless precipitate is obtained at once, owing to the differing solubility of the silver precipitates in nitric acid.

The white precipitate was washed and dissolved in nitric acid, and the silver precipitated with hydrochloric acid. The resulting acid solution did not coagulate albumen, although a trace of the meta-acid added to it at once brought about this change.

This process was frequently repeated with solutions of metaphosphoric acid which had been kept some time, and always with the same result, so that it must be concluded that the pyro-acid is formed by the action of water on the meta-variety. This confirms the views of Berthelot and André, but is not in accordance with the results of Sabatier and Balareff.

Since orthophosphoric acid on dehydration yields first pyro- and then meta-acid, it follows that on hydration the reverse change should occur. The results of Berthelot and André show that the change from meta- to pyro- proceeds more rapidly than that from pyro- to ortho-, and as the experimental method of Sabatier does not satisfactorily distinguish between pyro- and ortho-acids, the absence of pyro-acid recorded by various authors might arise from one change taking place too fast for observation.

The concentration of the solution will also have its effect. The more dilute it becomes, the faster one would expect the final state to be reached, unless the reaction is truly bimolecular, in which case the greatest velocity would be when the two reacting substances were present in equal concentration. It is therefore possible that the reason we have observed the presence of pyro-acid during the hydration is that our solutions were of a strength particularly favourable to its formation.

From the experiments already described, we were led to examine each of the phosphoric acids separately.

Pure crystalline ortho-acid, when dissolved in water, gave a depression of the freezing point concordant with a molecular weight of 93 (theory 98). Conductivity experiments showed the acid to be very slightly ionised, and it may therefore be concluded that the undissociated molecules in solution are represented by the formula H_3PO_4.

A few attempts were made to measure the vapour pressure of this acid during dehydration, but the results were inconclusive. Although the pyro- and meta-acids are readily formed from it, no sudden change in the vapour pressure was detected, such as one would expect when one compound changed into another. It would seem that molecular compounds are probably formed during the dehydration, a conclusion to which Balareff also inclines.

Two varieties of pyrophosphoric acid have been examined. One was a viscid, syrupy liquid obtained by dehydrating the ortho-acid, and the other was obtained in aqueous solution by decomposing lead pyrophosphate by hydrogen sulphide. An approximately normal solution of the syrupy variety gave a depression of the freezing point, which indicated the presence of complex molecules of the acid of composition between $(H_4P_2O_7)_4$ and $(H_4P_2O_7)_5$, whereas in the solution obtained from the lead salt the molecules appeared to be simple. Conductivity measurements again showed little ionisation, so that it may be concluded that very complex molecules, whether associated or not with molecular compounds, are formed by dehydrating the ortho-acid.

The syrupy solution, on keeping for some time, became a mass of crystals, which gave qualitative tests for both ortho- and pyro-acids, so that in this condition the pyro-acid cannot be regarded as a stable substance.

Four varieties of metaphosphoric acid, differing either in physical characters or molecular condition in solution, have been examined. Very little ionisation is found to take place in dilute aqueous solutions, and the differences between them are almost certainly the result of polymerisation into molecules of varying complexity.

The first variety is obtained by heating to redness for a short time sticks of pure glacial phosphoric acid. As thus obtained, it is a vitreous solid, deliquescent in moist air, and readily soluble in water. Freezing-point determinations of its solution indicate the presence of molecules of composition $(HPO_3)_3$, the values not varying greatly for solutions of strength $2N$ or $N/10$.

When sodium metaphosphate glass is dissolved in water, a depression of the freezing point is obtained, which gives a molecular weight of 314, the theoretical value for $(NaPO_3)_3$ being 306. It appears therefore that not only the acid, but its alkaline salts, can exist in solution in termolecular complexes.

The second variety is obtained by heating the previous glassy solid to redness for several hours. It is a hard and brittle glass, having a sp. gr. of 2·488. It becomes sticky in moist air, but not so readily as the former variety. When a fragment of this glass is put into water a curious phenomenon, first recorded by Sabatier, takes place. Although a portion seems to dissolve directly, by far the larger amount of the substance is gradually shot off as minute particles into the surrounding water with a sharp, crackling sound, and the liquid becomes turbid through their presence, solution taking place slowly. When a fragment of this glass is placed in water and viewed microscopically, the particles are seen to be clear fragments with typical glassy fracture. They are expelled with considerable velocity, but as the solution in the immediate neighbourhood of the fragment becomes saturated with the acid, they are formed in constantly decreasing amount.

When this "crackling" variety of the meta-acid is heated for a long time (about twenty-four hours) at a dull red heat, its characters are found to be changed. Although still a hard and brittle glass, its specific gravity has somewhat diminished (2·216), and it is almost insoluble in water. A portion of this glass has been kept in the laboratory for many days without becoming sticky, and when ground to the finest powder takes several days to dissolve in water. No crackling is heard during solution, and no particles are shot off the mass of the glass. Freezing-point determinations show the presence of bimolecular complexes $(HPO_3)_2$.

When lead metaphosphate is decomposed with hydrogen sulphide, a solution of metaphosphoric acid is obtained, which apparently contains simple molecules of the acid (HPO_3), since freezing-point determinations give a molecular weight of 102 (theory 80), and the acid is slightly ionised.

These experiments on each of the phosphoric acids show that solutions containing simple molecules can be obtained by decomposing the lead salts, the acids prepared by the dehydration of the ortho-variety invariably containing more or less complex molecules.

The decomposition of a meta- or pyro-salt might be expected to yield simple molecules of the acids, whilst the dehydration of the ortho-acid, since it does not proceed strictly in two stages, would favour the formation of molecular complexes.

The following conclusions may be drawn from the experiments described in this paper:

1. Pyrophosphoric acid is formed as an intermediate compound during the hydration of metaphosphoric acid.
2. The rate of hydration does not accord with any simple order of reaction.
3. Meta- and pyro-phosphoric acids, when prepared by dehydrating the ortho-variety, give complex molecules in solution, but when prepared by decomposing the corresponding lead salts, simpler molecules result.

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