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## Structure and Properties of the Condensed Phosphates. I. Some General Considerations about Phosphoric Acids<sup>1</sup>

BY JOHN R. VAN WAZER\* AND KARL A. HOLST

Although numerous articles concerning phosphate chemistry have regularly been appearing in the literature for the last one hundred years, there is as yet no consistent and universally accepted concept of the structure of many condensed phosphates. Until rather recently, in fact, the whole field of phosphate chemistry was in a chaotic state. For example, a given crystalline compound was variously known as the mono-, di- and trimetaphosphate. Now, however, the joint application of X-ray diffraction studies, careful microscopic techniques and systematic thermal analyses have led to a rather full concept of the constitution of many crystalline phosphates.<sup>2</sup> It can probably be stated safely that continued study along these lines will satisfactorily clarify the remaining problems concerning the crystalline phosphates.

On the other hand, many phosphate compositions exhibit a pronounced tendency to form glasses upon the cooling of their melts, and viscid or even fluid masses upon the addition of precipitating agents to their aqueous solutions. Although many of these amorphous materials have been found to have useful properties,<sup>3</sup> little progress has been made in the fundamental study and interpretations of their properties. It is the purpose of this series of papers to report data which can be used in conjunction with the informa-

tion already published to evolve theoretically sound structural representations of the various condensed phosphates, including the amorphous compositions, and to incorporate phosphate chemistry into the generally accepted picture of inorganic chemistry. In this paper published X-ray data and a pH titration study of various phosphoric acids are used to show that only certain of the many conceivable arrangements of phosphorus and oxygen are to be found in phosphate ions which are relatively stable in aqueous solution.

### Principles of Structure

Unfortunately, complete X-ray analysis of crystalline phosphates is very laborious, but there is enough information to enable us to set up a general hypothesis of phosphate structure. Studies of orthophosphates,<sup>4</sup> pyrophosphates,<sup>5</sup> aluminum tetrametaphosphate,<sup>6</sup> sodium trimetaphosphate,<sup>7</sup> and the alpha<sup>8</sup> and delta<sup>9</sup> forms of phosphorus pentoxide as well as its vapor<sup>10</sup> have been completed. In all cases the structures are shown to be built up of interlinked PO<sub>4</sub> groups composed of four oxygen atoms situated at the corners of a tetrahedron in the center of which is the phosphorus atom. The concept of phosphorus surrounded tetrahedrally by four oxygens is in accord with quantum theory and the combining of atomic dimensions.

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(1) A resumé of the information dealing with pH titrations of phosphates given in Papers I and IV of this series was presented by Van Wazer at the 111th Meeting of the American Chemical Society (Division of Physical Inorganic Chemistry) April, 1947.

(2) Quimby, *Chem. Rev.*, **40**, 141 (1947).

(3) Of 300 U. S. patents on condensed phosphates issued from 1900 to 1947, approximately 80% are primarily concerned with amorphous compositions.

(4) West, *Z. Krist.*, **74**, 306 (1930); Schulze, *Z. physik. Chem.*, **B24**, 215 (1934).

(5) Levi and Peyronel, *Z. Krist.*, **92**, 190 (1935); Peyronel, *ibid.*, **94**, 311 (1936).

(6) Pauling and Sherman, *ibid.*, **96**, 481 (1937).

(7) Caglioti, Giacomello and Bianchi, *Atti. accad. Italia. Rend.*, **3**, Sec. 7, 761 (1942).

(8) deDecker and McGillavry, *Rec. trav. chim.*, **60**, 153 (1941).

(9) deDecker, *ibid.*, **60**, 413 (1941).

(10) Hampson and Stosick, *THIS JOURNAL*, **60**, 1914 (1939).

In condensed phosphates, the  $\text{PO}_4$  tetrahedra are joined together by the sharing of oxygen atoms. Because of bond angle requirements, no more than two and probably only one oxygen atom can be shared between any two tetrahedra, as is depicted in Fig. 1. Since the sharing of two oxygens between a pair of tetrahedra entails the formation of a four membered ring and hence a pronounced distortion of the bond angles, the single connection of Fig. 1 is to be preferred. The double connection was only included because of a report<sup>11</sup> of the existence of dimetaphosphoric acid in the vapor state.

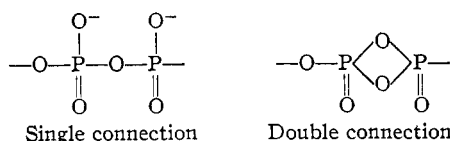


Fig. 1.—The way that  $\text{PO}_4$  groups can be connected together to form condensed phosphates.

Although a purely ionic treatment has been accorded the simple polyatomic anions such as  $\text{PO}_4^{3-}$ , it is now fairly obvious that such groupings are held together by chemical bonds exhibiting a large amount of covalency. Stabilization of the group is effected by resonance between the numerous possible structures involving single and multiple covalent bonds as well as ionic bonds. According to Pauling,<sup>12</sup> double bonds make a large contribution to the over-all structure; and resonance between the four formal valence-bond

structures, such as  $\text{O}=\text{P}(\text{O})_2-\text{O}$ , is not an appreciable factor in stabilizing the group.

When the oxygen atoms of a  $\text{SiO}_4$  group are shared with adjacent  $\text{SiO}_4$  tetrahedra, the silicon-oxygen bond length is virtually unaffected, even in the extreme case of silica, in which all four oxygens are shared.<sup>12</sup> Therefore, it would seem reasonable to assert that chemical reactions of the silicates in which the breaking of a silicon-oxygen bond plays a major role would not be tremendously affected by the degree of condensation of the silicate.

From the rather meager X-ray data<sup>13</sup> on bond lengths in ortho- ( $\text{P}-\text{O} = 1.56 \text{ \AA}$ ), pyro- ( $\text{P}-\text{O} = 1.56 \text{ \AA}$  for the bond to the shared oxygen and  $1.52 \text{ \AA}$  for the others) and metaphosphate (several per cent. greater than  $1.51 \text{ \AA}$  for  $\text{Al}_4(\text{P}_4\text{O}_{12})_3$ ), this generalization would also seem to apply to phosphates in which condensation had not proceeded beyond the sharing of two oxygens per tetrahedron. However, the observed bond lengths in phosphorus pentoxide ( $\text{P}-\text{O} = 1.65 \text{ \AA}$  for the bonds to the three shared oxygens and  $1.40$

$\text{ \AA}$ . for the bond to the single unshared oxygen per  $\text{PO}_4$ ) indicate that the resonance which stabilizes the less condensed forms is appreciably absent in  $\text{PO}_4$  groups in which three oxygen atoms are shared. One would expect the increase in energy due to the lack of resonance to show up in the activation energies of the more obvious degradation mechanisms as well as in the corresponding free energy. Therefore, in any environment in which reactions involving the degradation of condensed phosphates are possible, it is to be expected that assemblies in which three of the four oxygens of a  $\text{PO}_4$  tetrahedron are shared with other  $\text{PO}_4$  tetrahedra will be exceedingly unstable and will degrade much more rapidly as compared to those in which one or two oxygens are shared. Such an environment is found, for example, in aqueous solution.

Since hydrogen and phosphorus exhibit the same electronegativity,<sup>14</sup> the effect of the covalent bonding of hydrogen atoms on the resonance energy of a  $\text{PO}_4$  group should be quite similar to the effect of the sharing of oxygen atoms with other tetrahedra. Thus, in aqueous solution, only those phosphates should be detectable in which the combination of essentially covalent bonds linking a single  $\text{PO}_4$  group to either pentavalent phosphorus or hydrogen is less than three. It is obvious that a  $\text{PO}_4$  group with a total of three bonds to hydrogen and pentavalent phosphorus will immediately ionize in water to produce a completely dissociated hydrogen ion, since the activation energy for ionization in water is undoubtedly negligibly small as compared to the activation energy of the complicated hydrolysis process involved in breaking a  $\text{P}-\text{O}-\text{P}$  linkage.

From the rather hypothetical discussion given above, we may conclude that in aqueous solutions of pure phosphoric acids there is one strongly ionized hydrogen for each phosphorus atom. This conclusion is in accord with a recent review<sup>15</sup> of phosphate chemistry which stated: "When any acid derivable from  $\text{P}_2\text{O}_5$  and water is titrated to  $\text{pH}$  4.3, one titratable hydrogen has been neutralized per atom of phosphorus." As the previously published experimental data<sup>16</sup> are not very extensive and only dealt with acids which could be prepared directly, a more comprehensive study has been made in this Laboratory and is reported below. In this work an attempt has been made to titrate the acid corresponding to at least one member of every known class of phosphates from which a titratable amount of acid could be produced.

### Experimental Information

**Preparation of Acids.**—Some of the condensed phosphoric acids were prepared by the various methods re-

(14) Pauling, ref. 12, pp. 58-75.

(15) Quimby, *Chem. Rev.*, **40**, 141 (1947).

(16) Gerber and Miles, *Ind. Eng. Chem., Anal. Ed.*, **10**, 519 (1938); Lum, Malowan and Durgin, *Chem. Met. Eng.*, **44**, 721 (1937).

(11) Tilden and Barnett, *J. Chem. Soc.*, **69**, 154 (1896).

(12) "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1945, pp. 239-250.

(13) See refs. 4-10.

ported for dehydrating orthophosphoric acid or hydrating phosphorus pentoxide. However, the majority of the acids studied were made from their salts by the use of an organic ion exchange resin, analytical grade Amberlite IR-100H.<sup>17</sup> A column was used to hold the resin when readily soluble phosphates were exchanged. This column was made of 30-mm. Pyrex tubing so arranged that solutions could be let into the top from a separatory funnel and removed from the bottom. There was also a provision for letting air into the top of the column and evacuating from the bottom. The column contained 2 kg. of ion exchange resin. In operating the column, a large excess of 2% C. p. hydrochloric acid was run through slowly, after which the column was evacuated. It was then flushed with several liters of distilled water, and with the water level even with the top surface of the resin in the column, several cc. of the phosphate solution was added. Then the water was allowed to drip slowly out of the column. Water from the bottom was replaced in the top of the column; and this recycling was continued until the layer of phosphate solution passing down the column approached the bottom. Then the column was drained and flushed several times with a few cc. of distilled water. According to this procedure the column acts as a multiple exchange apparatus. The amount of phosphate passed through the column per exchange was always less than 1 g. of salt. It should be noted that when most of the final wash-water was removed from the column by the application of suction to the receiver flask, over 99.6% of the phosphate put into the column could be recovered. This result is in accord with a recent publication<sup>18</sup> on the analysis of phosphate rock in which an ion exchange column was used.

When acids were to be made from quite insoluble or very slowly soluble phosphates, exchange was effected batchwise. In order to obtain complete exchange the finely powdered salt was stirred for several hours with a large volume of resin and enough water to cover the solids. Then the resulting solution was filtered off and passed through the column as usual. Insoluble salts are thus rendered somewhat soluble by removal of the metallic cation from solution.

C. p. reagents were used in the preparation of all phosphates studied.

**Hydrolysis and Exchange.**—For practical purposes, it was found that the ion-exchange column completely removed metallic ions from the phosphates studied. This conclusion was demonstrated for each sample by titrating a portion of the exchanged solution that had been boiled for a day to convert the condensed phosphoric acid to orthophosphoric acid containing some pyrophosphoric acid. As the second neutralization point of the ortho-pyrophosphoric acid mixture took twice as much base as the first neutralization point, exchange had been complete. If metal ions from the original phosphate were present, the acid would have appeared to have been partially neutralized and thus the second neutralization would have required more than twice as much base as compared to the first.

Since incomplete conversion to ortho- or pyrophosphate has an effect on the titrations opposite to incomplete exchange, a study was made of the effect on the titration curves of varying the length of time during which the samples were boiled. Under the conditions used, all of the condensed phosphates were shown to be completely hydrolyzed in less than four hours.

Several polarographic studies<sup>19</sup> on acids made from sodium phosphate glasses indicated that the sodium ion concentration was reduced about 1000-fold by passage through the exchange column. Samples of phosphoric acids from sodium salts have also been made by the exchange procedure so as to exhibit no yellow color in a visual flame test.

(17) Mfg. by the Resinous Products and Chemical Co., Philadelphia, Penna.

(18) Helrich and Rieman, *Ind. Eng. Chem., Anal. Ed.*, **19**, 651 (1947).

(19) See paper IV, *THIS JOURNAL*, **72**, 655 (1950).

In order to avoid the effects of hydrolysis the experimental work was carried out as quickly as possible. The approximate duration of each experiment is given in Table I, from which it can be seen that the period from the time the solid phosphate was added to the water to the time the titration was completed was never more than three hours and in some instances was only several minutes. As orthophosphoric acid is the final product formed in the hydrolysis of all condensed phosphoric acids, a measure of the rate of hydrolysis (other than that involved in reducing the number of shared oxygens per PO<sub>4</sub> group to less than three) can be found in the increase of titratable weak acid with time. In all of the cases reported here the increase in the amount of titratable weak acid was never more than 2% when the solution was allowed to stand, after the titration was concluded, for the same length of time that was needed to prepare it for the titration. In the case of sodium phosphate glasses for which Na<sub>2</sub>O/P<sub>2</sub>O<sub>5</sub> = 1.4 and 1.1, it was also found that the amount of 0.1 N base used to titrate the acid from the exchange column from one neutralization point to another was equal to the combined amount of 0.1 N base and 0.1 N acid used to titrate the original salt between the same neutralization points at the same phosphorus concentration.

**pH Titrations.**—The pH was measured in these titrations by a glass electrode and calomel half-cell, a model G Beckman pH meter being employed with shielded leads to the electrodes. Both carbonate-free 0.1 N sodium hydroxide and 0.1 N tetramethylammonium hydroxide were used as bases. The sodium hydroxide was made from a saturated solution and the tetramethylammonium hydroxide by treating tetramethylammonium bromide solution with carbonate-free silver hydroxide. The solutions of base were standardized against 0.1 N hydrochloric acid prepared from constant boiling acid.

The first neutralization point of most of the phosphoric acids studied could easily be determined by inspection of the titration curves since, with the exception of some glasses near the metaphosphate composition, the change of pH was very great in that region. It was estimated that in all cases the error in fixing the first neutralization point was less than 1%.

In titrating solutions of the pure acids with tetramethylammonium hydroxide it was found that the change in pH in the region of the neutralization points of the weakly acid hydrogens was often so slight as to make it difficult to precisely place the point of inflection (see Fig. 2 for example). This difficulty could be overcome, however, by the addition of an amount of a metallic salt of a strong acid insufficient to form a precipitate. The presence of the metal ion caused the weak acid function to become stronger. This phenomenon can be ascribed to complex ion formation<sup>19</sup> and the neutral salt effect. Carefully purified sodium chloride was generally used as the added metallic salt.

**Procedure.**—The solution of acid to be studied was divided into four equal portions, two of which were titrated immediately. The other two were boiled for five hours with intermittent addition of water to replace that which had evaporated. Then they were cooled and titrated.

### Results and Conclusions

**Strong Acid Function.**—Titration studies have been performed on more than a hundred different compositions representing all of the known classes of condensed phosphates that are made directly from the melt and can be dissolved without serious decomposition. These compositions are listed in Table I according to a general scheme of classification in which the glassy

materials are not given chemical names. Phosphates prepared by precipitation from solutions of these compositions were not studied since it appears quite certain that the precipitates will be composed of the same molecule-ions which were present in the solution before precipitation.

In titrating the acids corresponding to the phosphates listed in Table I, it was found that the same amount of base was needed to reach the

TABLE I  
A LIST OF CONDENSED PHOSPHATES WHOSE ACIDS HAVE ONE STRONGLY IONIZED HYDROGEN FOR EACH PHOSPHORUS ATOM IN AQUEOUS SOLUTION

Phosphates	Remarks about experiment
$\alpha, \beta, \gamma$ and $\delta$ $P_2O_5$ . For a description of these modifications see Yost and Russell "Systematic Inorganic Chemistry," Prentice-Hall, New York, N. Y., 1946, p. 180.	$P_2O_5$ added as fine powder to chopped ice and water; filtered to remove undissolved and gelatinous masses; then titrated while still cold. Duration of entire experiment = 10 min. for $\alpha$ and $\beta$ , 20 min. for $\gamma$ , fifteen minutes for $\delta$ $P_2O_5$ . Portion also titrated after boiling.
Acid formed by treating a suspension of commercial phosphorus pentoxide in mineral oil with moist ether.	1 g. $P_2O_5$ mixed with oil in homogenizer (Waring Blender) then added to 1 l. ethyl ether saturated with water; ice and water finally added to mixture. Aqueous phase removed and titrated immediately. Time from mixing to completion of titration, fifteen minutes. Portion titrated after boiling.
Glassy acids with the mole ratio $P_2O_5/H_2O = 20, 10, 8, 5, 3, 1.0, 0.8,$ and $0.5$ . (This includes the previously reported "meta" and "poly"-phosphoric acids. Also "ultraphosphoric acids.")	Prepared by heating mixtures of $P_2O_5$ and $H_2O$ in sealed tubes to ca. $300^\circ$ for one-half hour to produce homogeneous products which were cooled by pouring on a cold plate. Titration carried out immediately after filtration to remove the larger undissolved particles. Entire time in solution about 20 min.
Glassy acids with $H_2O/P_2O_5 = 1.0, 1.2, 1.4, 1.6, 1.8,$ and $2.0$ . (This includes the various "poly" and "meta"-phosphoric acids and pyrophosphoric acid.)	Prepared by dehydrating orthophosphoric acid in a Pt dish at various elevated temperatures. Quickly cooled. Titrations carried out as above.
Acids formed by the hydration of commercial phosphorus pentoxide in moist atmospheres.	See Balareff, <i>Z. anorg. Chem.</i> , <b>69</b> , 215 (1910), for details of preparation. Titrated in five minutes.
Sodium phosphate glasses with $Na_2O/P_2O_5 = 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.8, 0.6, 0.4,$ and $0.2$ . (This includes Graham's salt or "hexametaphosphate" and the various "polyphosphates" and "ultraphosphates.")	In the range of $Na_2O/P_2O_5$ from 1.0 to 1.7, samples were prepared by dehydrating mixtures of $Na_2HPO_4$ and $NaH_2PO_4$ in a Pt dish at $1200^\circ$ for three hours. Samples with $Na_2O/P_2O_5 < 1.0$ were prepared by mixing the $Na_2O \cdot P_2O_5$ glass with various amounts of $P_2O_5$ and fusing in a sealed tube. All samples were quenched between two cold copper slabs. Solutions passed through exchange column for $Na_2O/P_2O_5 \geq 1.0$ . Other glasses finely powdered and mixed with exchange resin. Entire experiment completed in thirty to sixty minutes.
Potassium phosphate glasses with $K_2O/P_2O_5 = 1.4, 1.2, 1.0$ and $0.8$ .	Prepared in the same manner as the sodium phosphate glasses. Small amount of crystalline material present. Titrations carried out as with sodium glasses.
Various phosphate glasses consisting of $P_2O_5$ and one or more of the following:	See examples in the following U. S. Patents for method of preparation:
$H_2O$ $CuO$ $B_2O_3$ $P_2S_5$	2,025,503      2,315,995
$Na_2O$ $Ag_2O$ $SiO_2$	2,156,173      2,324,124
$CaO$ $PbO$ $SO_3$	2,291,958      2,395,126
	2,307,472      2,405,884
Crystalline $H_4P_2O_7$	also Swedish Patent 104,755
Crystalline $Na_4P_2O_7$ and $Na_5P_3O_{10}$	For references to this compound see Quimby, <i>Chem. Rev.</i> , <b>40</b> , 141 (1947). Titration carried out in same manner as shown for sodium phosphate glasses for which $Na_2O/P_2O_5 > 1.0$ .
Crystalline $NaPO_3$ I (trimeta)	<i>Ibid.</i>
Crystalline $NaPO_3$ (tetrameta?) from $CuPO_3$	<i>Ibid.</i>
Sodium and potassium Kurrol's salts dissolved in solutions of Graham's salt.	Bonnemann, <i>Compt. rend.</i> , <b>204</b> , 865 (1937). See Pascal, <i>Compt. rend.</i> , <b>178</b> , 1541 (1924), for preparation. Passed through exchange column and titrated at once. Entire time in solution, ca. one hour.

first neutralization point before and after hydrolysis, the titer values being in agreement to within 1%. This means that there is one strongly ionized hydrogen for every phosphorus atom and therefore only straight chain or unbranched ring phosphate molecule-ions can be found in aqueous solutions of phosphoric acids. The straight chains correspond to the polyphosphates of classical terminology and the rings to metaphosphates. It is interesting to note that any phosphate molecule containing one ring has the metaphosphate composition no matter how many straight or branched chains are connected to the ring. Also all chains, whether straight or branched, correspond to the polyphosphate composition. However, only simple rings or straight chains can exist in solution, since the other phosphate molecules would have  $\text{PO}_4$  groups in which three oxygen atoms were shared. In the case of solid phosphates which contain  $\text{PO}_4$  groups in which three oxygens are shared in order to satisfy valence requirements, these experiments show that the rate of the step in the hydrolysis whereby a P-O bond to a  $\text{PO}_4$  group sharing three oxygen atoms is broken is exceedingly rapid as compared to the subsequent hydrolysis steps.

From the shape of the titration curves it is apparent that the first ionization constants of all of these condensed phosphoric acids must lie in the range between  $10^{-1}$  and  $10^{-3}$ , according to the simple Arrhenius theory. This would indicate that the first acid hydrogens were completely dissociated. The careful study made by Nims<sup>20</sup> shows that a real ionization constant ( $K_1 = 0.752 \times 10^{-2}$ ) exists for the strong hydrogen of orthophosphoric acid. However, the factors stabilizing this slight association are apparently lacking in the simplest condensed phosphate, pyrophosphoric acid, which has<sup>21</sup> a first dissociation constant of  $1.4 \times 10^{-1}$  according to the Arrhenius theory.

In the next two papers of this series it is shown that the sodium phosphate glasses are predominantly made up of polyphosphates, the average number of phosphorus atoms in which increases to very large values as the  $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$  mole ratio approaches unity. As there is a negative charge on each phosphorus atom in a condensed phosphate, long chain polyphosphates bear a considerable charge and hence the electrostatic effects<sup>22</sup> involved in ionization will become greater with increasing chain length. Therefore, the strong acid function should become weaker as the  $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$  mole ratio approaches unity. This effect, which has also been observed by others,<sup>23</sup> is shown in Fig. 2. The titration curves are seen to rise less abruptly at the first neutralization point as the average chain length of the poly-

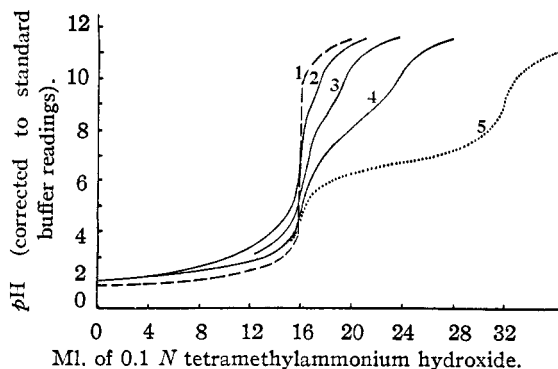


Fig. 2.—pH titration curves of fresh solutions of various condensed phosphoric acids. These acids were made from the following salts: curve 1, sodium trimetaphosphate; curves 2, 3 and 4, anhydrous sodium phosphate glasses for which  $\text{Na}_2\text{O}/\text{P}_2\text{O}_5 = 1.10, 1.23$  and  $1.50$ , respectively. Curve 5 corresponds to the orthophosphoric acid formed by complete hydrolysis of the condensed acids.

phosphates is increased. A comparison of the titration curve of trimetaphosphoric acid with that of acid from the metaphosphate glass of the same chemical composition shows that molecular size rather than chemical composition determines the exact strength of the strong acid function. We believe that measurement of the strength of the strong acid function might be developed as a method of determining the molecular weight of condensed phosphates in solution.

**Weak Acid Functions.**—Since only simple rings or unbranched chains of  $\text{PO}_4$  groups can exist in aqueous solutions of phosphates, weakly acid hydrogens must come from the ends of polyphosphate chains. This conclusion is borne out by the fact that the ratio of strong to weak titratable acid functions is 1:1 for pyrophosphoric acid and 3:2 for tripolyphosphoric acid and that solutions of carefully prepared crystalline trimetaphosphate ( $\text{NaPO}_3$  I) show only the slightest trace of weak acid. Examination of the ionization constants at  $25^\circ$  of the weak acid functions of the ortho-, pyro- and tripolyphosphoric acids gives added weight to this hypothesis. For orthophosphoric acid<sup>20,21</sup>  $K_2 = 0.6 \times 10^{-7}$  and  $K_3 = 3 \times 10^{-13}$ . For pyrophosphoric acid the ionization constants of the two weak hydrogens are close to  $2 \times 10^{-7}$  and  $4 \times 10^{-10}$  according to Kolthoff and Bosch.<sup>24</sup> Unfortunately, the dissociation constants of tripolyphosphoric acid have not been reported although preliminary studies in these Laboratories according to the method of Schwarzenbach, Kampitsch and Steiner<sup>25</sup> indicate that the constants are close to those of pyrophosphoric acid, with the weakest acid hydrogen being somewhat more dissociated. A careful determination of the ionization constants of both pyro- and tripolyphosphoric acids in the absence of metallic cations

(20) Nims, *THIS JOURNAL*, **56**, 1110 (1934).

(21) Abbott and Bray, *ibid.*, **31**, 729 (1909).

(22) Britton, "Hydrogen Ions," 3rd ed., Chapman and Hall, London, 1942, Vol. I, Chapt. XIII.

(23) Rudy and Schlosser, *Ber.*, **73B**, 484 (1940).

(24) Kolthoff and Bosch, *Rec. trav. chim.*, **47**, 826 (1928).

(25) Schwarzenbach, Kampitsch and Steiner, *Helv. Chim. Acta*, **28**, 828 (1945).

will be necessary in order to obtain correct values free from the confusing effects of complex ion formation.

The second ionization constant of orthophosphoric acid is nearly equal to the next to the last ionization constants of the pyro and tripoly acids. This is to be expected since the  $\text{PO}_4$  grouping from which these ionizations take place are subject to the same influences. The difference between the last two ionization constants of pyrophosphoric acid must be attributed to a combination of resonance coupling between adjacent  $\text{PO}_4$  groups and the electrostatic effect of successive ionizations.<sup>22</sup> Either effect will diminish with increasing chain length and so it would appear that the last two ionization constants of polyphosphoric acids should both approach a value near  $10^{-8}$  as the polyphosphate chain is lengthened.

**Acknowledgment.**—The authors wish to express their appreciation to Mr. Albert E. Marshall for his encouragement during this entire study and to Dr. Raymond L. Copson for his

kind advice. We also wish to thank Mr. Lynn Howick for running most of the titrations.

### Summary

1. Acids corresponding to many condensed phosphates were prepared. Titration of these acids in aqueous solution demonstrates that there is exactly one strongly ionized hydrogen for each phosphorus atom, and a single weakly dissociated hydrogen at each end of a chain of  $\text{PO}_4$  groups.

2. Since there is one strong hydrogen for each phosphorus atom and since published X-ray analyses of crystalline phosphates have shown that only  $\text{PO}_4$  tetrahedra are present, it is concluded that only unbranched chains and rings composed of interlinked  $\text{PO}_4$  tetrahedra exist in solution.

3. This is in agreement with published data on atomic dimensions in phosphates which indicate that the resonance which stabilizes less condensed forms is appreciably absent in  $\text{PO}_4$  groups in which three oxygen atoms are shared.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF RUMFORD CHEMICAL WORKS]

## Structure and Properties of the Condensed Phosphates. II. A Theory of the Molecular Structure of Sodium Phosphate Glasses<sup>1</sup>

BY JOHN R. VAN WAZER\*

By quickly chilling melts in the  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$  system, it has been found possible to produce a continuous series of water soluble glasses in the composition range from pure phosphorus pentoxide to near  $2\text{Na}_2\text{O}\cdot\text{P}_2\text{O}_5$ . These glasses, or super-cooled melts, are all clear homogeneous substances showing only several diffuse diffraction rings when X-rayed, and conchoidal fracture and isotropism under the microscope. One of the glasses, corresponding to  $\text{Na}_2\text{O}\cdot\text{P}_2\text{O}_5$ , was discovered over a century ago<sup>2</sup> and has been a subject of interest ever since. This material is called Graham's salt, or less advisedly, sodium hexametaphosphate. Vitreous  $\text{P}_2\text{O}_5$  also has been studied,<sup>3</sup> but not as extensively.

During recent years these glasses have found widespread industrial application<sup>4</sup> because of their property of forming complex ions with alkaline earth metals and exhibiting pronounced colloidal activity in solutions. This has caused attention to be focused on the glasses between  $\text{Na}_2\text{O}\cdot\text{P}_2\text{O}_5$  and  $5\text{Na}_2\text{O}\cdot 3\text{P}_2\text{O}_5$  which have the most desirable combination of properties for commercial pur-

poses. The glasses between  $\text{P}_2\text{O}_5$  and  $\text{Na}_2\text{O}\cdot\text{P}_2\text{O}_5$  have not been described in the scientific or patent literature.

In the history of phosphate chemistry there have been several puissant ideas which have influenced the thought and interpretation of most of the workers in the field. The most important of these ideas is the concept of three phosphoric acids, ortho-, pyro- and meta-, originated by Thomas Graham.<sup>3</sup> The idea of polyphosphates,<sup>5</sup> which was suggested soon afterward, immediately became the subject of much criticism, and throughout the years the large majority of authors have interpreted their results in terms of ortho-, pyro- and metaphosphates. Naturally phosphate glasses have been described in these terms.<sup>6</sup> The molecular complexity of the phosphate glasses also has been expressed<sup>7</sup> in terms of the known crystalline phosphates. At the present time, crystalline forms have been discovered for ortho-, pyro-, tripoly- and several metaphosphates and solubility classifications have been so arranged that mixtures of these crystalline phosphates can be separated. This scheme is then applied to analysis of the glasses. However, it has been found that not all of the constituents of the glasses can be separated as crystalline phosphates

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(1) This theory, together with some of the fractionation data from the next paper in this series, was presented at the A. C. S. Symposium given at Syracuse University on June 29, 1948.

(2) Graham, *Phil. Trans. Roy. Soc.*, **123**, 253 (1933).

(3) Mellor, "Treatise on Inorg. and Theor. Chem.," Vol. VIII, Longmans and Co., London, 1931, p. 942.

(4) Schwartz and Munter, *Ind. Eng. Chem.*, **34**, 32 (1942).

(5) Fleitmann and Henneberg, *Ann.*, **65**, 304 (1938).

(6) Gerber and Miles, *Ind. Eng. Chem., Anal. Ed.*, **10**, 519 (1938); **13**, 406 (1941).

(7) Bell, *ibid.*, **19**, 97 (1947); Jones, *ibid.*, **14**, 536 (1942).