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 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 PO_4 groups and the electrostatic effect of successive ionizations.[22] 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 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 PO_4 tetrahedra are present, it is concluded that only unbranched chains and rings composed of interlinked 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 PO_4 groups in which three oxygen atoms are shared.

RUMFORD, R. I. RECEIVED AUGUST 14, 1948

[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[1]

BY JOHN R. VAN WAZER*

By quickly chilling melts in the $Na_2O-P_2O_5$ 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 $2Na_2O\cdot P_2O_5$. 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 $Na_2O\cdot P_2O_5$, was discovered over a century ago[2] and has been a subject of interest ever since. This material is called Graham's salt, or less advisedly, sodium hexametaphosphate. Vitreous P_2O_5 also has been studied,[3] but not as extensively.

During recent years these glasses have found widespread industrial application[4] 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 $Na_2O\cdot P_2O_5$ and $5Na_2O\cdot 3P_2O_5$ which have the most desirable combination of properties for commercial purposes. The glasses between P_2O_5 and $Na_2O\cdot P_2O_5$ 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.[3] The idea of polyphosphates,[5] 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.[6] The molecular complexity of the phosphate glasses also has been expressed[7] 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

---

* Present address: Great Lakes Carbon Corporation, Morton Grove, Illinois.

[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).

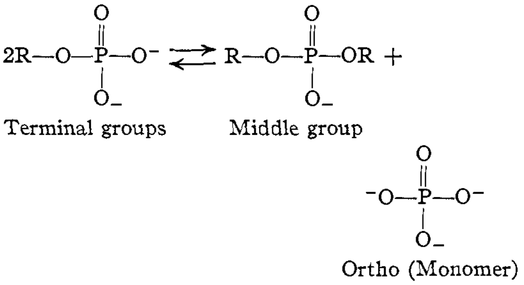
and that there is always at least one classification which contains only vitreous material. The best known of these classifications has been called "hexametaphosphate," and has been so defined that the glass having the composition $Na_2O \cdot P_2O_5$ falls completely within its bounds. It should be noted here that no one has demonstrated that glass of this composition is not as complex a mixture of condensed phosphates as the glasses having a mole ratio of $Na_2O/P_2O_5 > 1$. In fact, measurements with the ultracentrifuge[8] show that solutions of Graham's salt (glasses for which $1.01 > Na_2O/P_2O_5 \geqslant$ unity) contain an appreciable proportion of high molecular weight material. A study[9] of the rate of diffusion of the glass in aqueous solution also indicates a large average molecular weight. In addition, Samuelson[10] has shown that the diffusion and ultracentrifuge measurements can be correlated with the amount of titratable weak acid in Graham's salt solutions by assuming a polyphosphate model having many atoms in a straight chain.

Thus we find one member of a continuous series of glasses being studied as a unique and unusual compound, while other members of the same series are summarily classed as mixtures of crystalline salts containing more or less of the unique glass.[11] It is the purpose of this paper to view the Na_2O–P_2O_5 glasses as a group and to present a first approximation theory of structure which is applicable to glasses throughout the entire range of composition.

Theory

According to modern views[12] concerning the constitution of glasses, the silicate and phosphate glasses consist of a network of interlinked SiO_4 or PO_4 tetrahedra, in the interstices of which are interspersed cations such as sodium. Presumably the melts from which the glasses were made exhibit the same general sort of structure, except that there is much more freedom of motion for the individual cation or tetrahedron. In the first paper of this series it was demonstrated that, in any environment in which reactions involving the degradation of condensed phosphates can occur, molecular arrangements in which three of the oxygens of a PO_4 tetrahedron are shared with other tetrahedra will be exceedingly unstable with respect to those in which one or two oxygens are shared. Since rearrangement and interchange of tetrahedra undoubtedly take place in sodium phosphate melts, there will be no PO_4 groups sharing three oxygens in the melts as long as there is at least one sodium to each phosphorus atom. This means that the sodium phosphate glasses can profitably be divided into two groups: Case I for which the Na_2O/P_2O_5 mole ratio is equal to or greater than unity, and Case II for the range between pure P_2O_5 and $Na_2O \cdot P_2O_5$. In Case I there are no branching points and hence the PO_4 groups must be interlinked into chains or rings. At the $Na_2O \cdot P_2O_5$ composition there can be only singly charged PO_4 groups (middle groups) forming rings and/or infinite chains; and at the $2Na_2O \cdot P_2O_5$ composition there can be only doubly charged PO_4 groups (terminal groups) forming two-membered chains, *i. e.*, pyrophosphate ions, according to the idea presented in the next paragraph. In the intermediate range the fraction of the PO_4 groups in the terminal position is equal to Na_2O–P_2O_5/P_2O_5. Undoubtedly there is a continuous dynamic equilibrium in the melt so that a given PO_4 group can change roles and will alternate between being a terminal and a middle member of the unbranched structures. In Case II there are no terminal groups and branching is found, with the fraction of the total number of PO_4 groups at which branching occurs equal to $(P_2O_5$–$Na_2O)/P_2O_5$.

In Case I it is conceivable that some monomer, *i. e.*, orthophosphate ion, might be present in the glass. The formation of the monomer would proceed by the transfer of an electron from one terminal PO_4 group to another as shown in the equation.



$$2R{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O_-}{\overset{\|}{\underset{|}{P}}}}{-}O^- \rightleftarrows R{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O_-}{\overset{\|}{\underset{|}{P}}}}{-}OR + {}^-O{-}\overset{\displaystyle O}{\underset{\displaystyle O_-}{\overset{\|}{\underset{|}{P}}}}{-}O^- \quad (1)$$

The equilibrium represented by this equation will be very much in favor of the terminal groups and no orthophosphate should be detectable in completely anhydrous sodium phosphate melts because the orthophosphate ion represents a high concentration of negative charge. In other words, whether a given PO_4 tetrahedron is a monomer or a terminal or middle group depends on the spacial distribution of the surrounding sodium ions, which are assumed to be completely ionized. According to the standard fluctuation calculations[13] of statistical mechanics the probability of a high local concentration of sodium ions corresponding to the monomer will be vanishingly small.

If water of constitution is present in the melt, the situation is quite different since hydrogen has about the same electronegativity as phosphorus and can hence either form a covalent bond to one of the oxygen atoms in a PO_4 group or act as one of the positive ions demanded by each

---

(8) Lamm and Malgren, *Z. anorg. allgem. Chem.*, **245**, 103 (1940).

(9) Karbe and Jander, *Kolloid Beihefte*, **54**, 1 (1943).

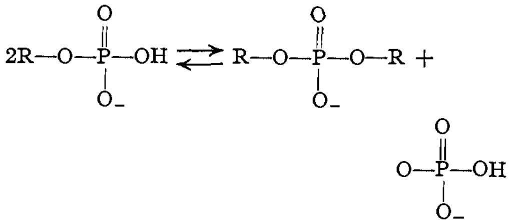
(10) Samuelson, *Svensk. Kem. Tid.*, **56**, 343 (1944).

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

(12) Zachariasen, THIS JOURNAL, **54**, 3841 (1932); also, for example, Stevels, *Philips Tech. Rev.*, **8**, 231 (1946).

(13) J. C. Slater, "Introduction to Chemical Physics," McGraw-Hill Book Co., Inc., New York, N. Y., 1939, Chapt. VII.

resonating PO_4 tetrahedron. The equation for the formation of monomer in the H_2O–P_2O_5 system is probably of the form



$$2R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}{-}OH \rightleftarrows R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}{-}O{-}R + O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}{-}OH \quad (2)$$

On the basis of charge distribution it is impossible to arrive at any conclusions about the equilibrium corresponding to equation (2). Undoubtedly there will be a significant amount of orthophosphate as is shown by the fact that, when crystalline pyrophosphoric acid is melted and cooled, a relatively stable liquid is formed which does not exhibit the characteristics of pyrophosphoric acid upon titration.[6,11] This liquid is a mixture of ortho-, pyro- and more condensed phosphoric acids.

According to Paper IV of this series, the dissociation constant of sodium from polyphosphatosodium complexes is *ca.* 10^{-3}; according to Paper I, the ionization constant of an end-group hydrogen is *ca.* 10^{-8}. Although these dissociation constants only apply to dilute aqueous solutions at room temperature, they reflect the influence of electronegativity and roughly indicate the relative amount of cation–anion association to be expected in the molten state.

Dissolution in Water.—Experimental studies[14] on the hydrolysis of various phosphates indicate that the linkages between PO_4 tetrahedra, in which only one or two oxygen atoms are shared, are relatively stable in aqueous solution at room temperature. Since there is no reason to believe that the rate of hydrolysis would be unduly accelerated during the process of dissolution, a freshly prepared solution of a glass for which $Na_2O/P_2O_3 \geqslant 1$ (Case I) should contain essentially the same molecular structures that existed in the undissolved glass or the melt. This is not to be expected, however, for the glasses of Case II since the structures containing PO_4 groups in which three oxygen atoms are shared will be immediately degraded upon dissolution.

Several qualitative predictions can be made concerning the rate of dissolution of the glasses. The materials of Case I should dissolve readily, except for compositions having a Na_2O/P_2O_5 ratio very near unity, in which case the unbranched structures of interlinked PO_4 tetrahedra will be very long and will have difficulty in disentangling to go into solution. As the Na_2O/P_2O_5 ratio is decreased below unity, the rate of dissolution will become slower because of the increasing number of cross-linkages that act to hold the structure together. At first the rate-determining step in the dissolution process should consist of disentanglement; but, as the number of cross-linkages becomes greater with decreasing values of Na_2O/P_2O_5, the rate process will then be the breaking of P–O–P connections. For pure vitreous phosphorus pentoxide there is no untangling but only hydrolytic splitting of bonds upon dissolution, and this material dissolves in a reasonably rapid manner. This means that because of the effect of a small number of concealed cross linkages, there will be a minimum in the rate of dissolution in water in the composition range between Graham's salt and vitreous phosphorus pentoxide.

Distribution Functions.—Since the structures corresponding to Case II are destroyed when the glasses are dissolved in water, we shall confine our attention to Case I. The singly charged (or middle) PO_4 groups can either join together in metaphosphate rings or form the middle links in polyphosphate chains. Because of bond angle requirements the rings would not be made up of fewer than three PO_4 groups or six atoms. However, a solution of the appropriate Random Walk Problem[15] indicates that no appreciable amount of rings will be present. That is to say, if a number of random steps are taken in three-dimensional space so that the angle and length of each step have the values corresponding to the phosphorus–oxygen bond, the chance that this sequence of steps will lead back to the origin is vanishingly small. Although this conclusion was originally reached in a calculation of the amount of random coiling in hydrocarbon chains, it should be equally well applicable to fixing the distances between the ends of phosphate chains. In spite of the fact that these chains are continuously being built up and broken down in a dynamic equilibrium, there would appear to be nothing in this process which would affect the randomness of orientation of a chain at any instant unless special directive influences are operative. In phosphate melts at temperatures above which crystallization can occur, the only important directive influence is the negative charge on each PO_4 group. The mutual repulsion exerted by these charges seems to favor a stretched-out orientation and would not appear to increase the probability of ring formation.

We now have the problem of determining the distribution of polyphosphate chains corresponding to the vitreous compositions between $Na_2O \cdot P_2O_5$ and $2Na_2O \cdot P_2O_5$. If the effect of the charge on each PO_4 group is ignored, the same approach as used by Flory[16] in considering random reorganization in linear organic polymers can be applied. Using a derivation analogous to that of the Maxwell–Boltzman law and summing

---

[14] Watzel, *Die Chemie*, **55**, 357 (1942); Bell, *Ind. Eng. Chem.*, **39**, 135 (1947).

[15] H. Mark, "Physical Chemistry of High Polymers," Interscience Publishers, New York, N. Y., 1940, pp. 70–73.

[16] Flory, THIS JOURNAL, **64**, 2205 (1942).

from two to infinity leads to a distribution function

$$N_x = \frac{N}{(\bar{n}-2)}\left(\frac{\bar{n}-2}{\bar{n}-1}\right)^{x-1} \quad \text{for } x \geqslant 2;\ \bar{n} \geqslant 2 \qquad (3)$$

where N_x is the number of chains containing x PO_4 groups, N is the total number of chains, and $\bar{n}$ is the number average number of PO_4 groups per chain.[17] This equation can be put into a more useful form for comparison with experiment by solving for w_x, the fraction of the total number of PO_4 groups present in x-mers.

$$w_x = \frac{x}{\bar{n}(\bar{n}-2)}\left(\frac{\bar{n}-2}{\bar{n}-1}\right)^{x-1} \quad \text{for } x \geqslant 2;\ \bar{n} \geqslant 2 \qquad (4)$$

Equations (3) and (4) represent the distributions corresponding to a completely random process of chain making and breaking and should be a good approximation to the physical distributions to be found in the glasses for which $\bar{n}$ is large. However, the physical distributions corresponding to small values of $\bar{n}$ will be less broad than that given by equations (3) and (4) because of the necessity of having excessive local concentrations of sodium ions when a relatively large portion of the PO_4 tetrahedra involved in the reorganization process are terminal groups. In the next paper of this series it is shown that the experimental data on fractionation of glasses near the composition $5Na_2O{\cdot}3P_2O_5$ can be closely fitted to a distribution obtained by sorting middle PO_4 groups between pairs of terminal groups, assuming that the terminal groups are not involved in the reorganization process. This leads to a Poisson distribution of the middles as shown by the two equations

$$N_x = \frac{N(\bar{n}-2)^{x-2}}{(x-2)!}\,e^{-(\bar{n}-2)} \qquad (5)$$

$$w_x = \frac{x}{\bar{n}}\,\frac{(\bar{n}-2)^{x-2}}{(x-2)!}\,e^{-(\bar{n}-2)} \qquad (6)$$

where the symbols are the same as those used in equations (3) and (4) and both $\bar{n}$ and x are equal to or greater than two.

Acknowledgment.—I wish to thank Prof. James Krumhansl of the physics department at Cornell University for the many helpful discussions that we had concerning the subject matter of this paper.

Summary

A theory of the detailed structure of sodium phosphate glasses is presented. This theory treats the phosphate anions in the molten glass as condensation polymers with due regard being taken of the effect of ionic charge. In the composition range between pure vitreous phosphorus pentoxide and the glassy metaphosphate, the melts and hence the resulting glasses are shown to have a three-dimensional structure, which is destroyed when the glasses are dissolved. In the composition range corresponding to a Na_2O/P_2O_5 mole ratio equal to or greater than one, only straight chain polyphosphate anions are to be found, the size distribution of which depends on the Na_2O/P_2O_5 ratio. When the glasses are free of water of composition, no orthophosphate should be present.

RUMFORD, R. I. RECEIVED AUGUST 14, 1948

---

[17] Van Wazer, *Ind. Eng. Chem.*, **41**, 189 (1949).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF RUMFORD CHEMICAL WORKS]

Structure and Properties of the Condensed Phosphates. III. Solubility Fractionation and Other Solubility Studies

BY JOHN R. VAN WAZER*

According to the theory presented in the preceding paper of this series, sodium phosphate glasses lying in the composition range between $Na_2O{\cdot}P_2O_5$ and $2Na_2O{\cdot}P_2O_5$ consist primarily of a mixture of polyphosphate molecules. In this paper information pertinent to the validity of the theory will be discussed.

The Glasses

Preparation.—Although some of the glasses in the composition range for which the mole ratio $Na_2O/P_2O_5 \geqslant 1$ were made by quenching fused mixtures of appropriate quantities of mono- and disodium orthophosphates, it was usually found more convenient to fuse mixtures of anhydrous crystalline meta- and pyrophosphates. The crystalline sodium metaphosphate was prepared by heating C. P. monosodium orthophosphate for a week at 500° in platinum; and the anhydrous $Na_4P_2O_7$ was made by heating C. P. $Na_4P_2O_7{\cdot}10H_2O$ for several days at 300°. Several pounds of both anhydrous salts were kept on hand and when another phosphate glass was desired, the proper weights of the meta and pyro were combined and melted in platinum at temperatures near 1000°. The melts were quenched by pouring on a large copper slab and quickly pressing another copper slab on top. By this procedure completely clear glasses could be made from meta–pyro mixtures containing as much as 75% pyro.

In this study numerous preparations were made of glasses for which the Na_2O/P_2O_5 ratio was only slightly greater than unity. In view of the

---

* Present address: Great Lakes Carbon Corporation, Morton Grove, Illinois.