from two to infinity leads to a distribution function

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

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.

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

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

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

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

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.

large amount of literature on glasses of this approximate composition, these glasses will be treated as a group and called Graham's salt. This classification, however, is not meant to imply that Graham's salt differs from the other sodium phosphate glasses except in degree. As the properties of the glasses vary most greatly as the $(Na_2O + H_2O)/P_2O_5$ ratio decreases and approaches closely to unity, some samples of monosodium orthophosphate were recrystallized several times and dehydrated by heating at 500° for periods of time as long as a month.

The glasses in the composition range between pure P_2O_5 and Graham's salt were made by combining these two materials. By stirring phosphorus pentoxide into a melt of Graham's salt in a platinum dish a relatively small amount of phosphorus pentoxide could be added to the melt. However, because of the extreme volatility of phosphorus pentoxide it did not seem practicable to lower the Na_2O/P_2O_5 ratio below 0.8 by this procedure. Melts containing more phosphorus pentoxide were prepared by heating well-mixed combinations of phosphorus pentoxide and finely ground Graham's salt in a sealed tube of Pyrex or Vycor glass. In order to avoid silicate contamination the melting and cooling processes were carried out rapidly and the outer layer of the resulting phosphate glass, where it was in contact with the silicate glass, was discarded. Qualitative tests disclosed no silicate in the portions of the melts retained for study. Sodium phosphate melts containing more than one mole of phosphorus pentoxide to sodium oxide easily supercool to a glass so that moderately rapid cooling is sufficient to give a completely vitreous product. When commercial C. P. phosphorus pentoxide was used in their preparation, the glasses were brownish colored. This color might possibly be attributed[1] to the interaction between the phosphorus pentoxide and lower oxides of phosphorus, as a glass made from phosphorus pentoxide that had been purified by repeated sublimation in oxygen was not found to be colored.

Analysis.—The gravimetric method[2] of the Association of Official Agricultural Chemists was used in analyzing the glasses for P_2O_5 content. Although duplicate determinations were found to check to within 1 part in 1000, the absolute values are probably only correct to about 1 part in 500. The phosphorus pentoxide content of the glasses was also determined by an electrometric titration between the first and second neutralization points of the ortho–pyro mixture formed by acid hydrolysis of an aqueous solution of the glass. This second method yielded results to about 1 part in 200 and the values obtained with it were found to check with the gravimetric results to within this precision.

According to the first paper in this series, the number of end-groups in a phosphate glass can also be easily and unequivocally obtained by analytical methods, since for each mole of end-groups there is one equivalent of titratable weak acid. The determination of the amount of titratable weak acid function was performed by weighing out a sample of the glass containing about 5×10^{-3} equivalent of weak acid function, and dissolving it in about 200 ml. of water with continuous stirring. As soon as solution was complete, C. P. hydrochloric acid was added to the sample to reduce the *p*H below 3, and the solution was immediately back titrated with 0.1 *N* sodium hydroxide using a glass electrode *p*H meter to obtain data for a titration curve. The first and last neutralization points in such curves were always sufficiently sharp so that the measurement could be made to 1 part in 200.

In the early part of this work analysis for bound water content of the glasses for which $Na_2O/P_2O_5 \geqslant 1$ was made by measuring weight loss upon heating. However, this method was discarded in favor of a titration suggested by Quimby,[3] which gives results that can easily be duplicated to within 1 part in 50. In this procedure a sufficient amount of glass is weighed out and dissolved in water so that from 10 to 20 ml. of 0.1 *N* base will be used in titrating to the weak acid endpoint. A *p*H curve is plotted for each titration and the end-point is obtained from the graph. If some orthophosphate is present in the glass, the titratable water of constitution will probably be less than the total water of constitution, since for each mole of orthophosphate there can be up to one mole of hydrogen too weak to titrate.

Since the glasses for which $Na_2O/P_2O_5 \geqslant 1$ had been extensively dehydrated while being made, the titratable water of constitution was always found to be less than 0.2% of the total weight. Although no method for the analysis of bound water exists for glasses in which $Na_2O/P_2O_5 < 1$, these glasses must also have been rather free from bound water since the phosphorus pentoxide and Graham's salt from which they were made were quite anhydrous.

The fraction of the phosphorus present in the glasses as orthophosphate was found by a modification of the method of Wurzschmitt and Schuhknecht.[4] According to these authors orthophosphate can be determined in a mixture of phosphates by forming the yellow orthophosphomolybdic complex in aqueous solution and extracting it with ethyl acetate. In the modification of the method used here, the concentration of orthophosphate was obtained from colorimetric measurements on the ethyl acetate extract. The glasses for which $Na_2O/P_2O_5 \geqslant 1$ were found to have less than 0.1% of the total phosphorus present as orthophosphate.

---

(1) Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

(2) "Methods of Analysis," Assocn. of Official Agri. Chemists, Washington, D. C., fifth ed., 1940, pp. 21–22.

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

(4) Wurzschmitt and Schuhknecht, *Angew. Chem.*, **52**, 711 (1939).

The Bell method[5] for the determination of pyrophosphate in mixtures of various phosphates has also been applied, using somewhat larger samples than recommended to increase the sensitivity to small amounts of pyrophosphate, to the glasses for which $Na_2O/P_2O_5 \geqslant 1$. The values for the percentage of total phosphorus present as pyrophosphate obtained by use of this method are compared in Table I with the values calculated from equations 4 and 6 of Paper II of this series with $\bar{n}$ set equal to two. It is seen that the equation for the Poisson distribution gives values which agree quite closely with the analytical results whereas the amounts of pyrophosphate calculated from the exponential distribution corresponding to random reorganization are too large. Because neither the analytical method nor the theory are claimed to yield highly precise results by their authors, the values in Table I are only given to 1%.

TABLE I

PYROPHOSPHATE IN SODIUM PHOSPHATE GLASSES

Glass composition		Percentage of phosphorus as pyrophosphate		
Na_2O/P_2O_5	$\bar{n}$	Bell analysis	Poisson distribution	Random reorganization
1.01	141	<0.3	0	0
1.05	37.0	<0.3	0	0
1.17	11.9	<0.3	0	1
1.43	4.61	3	3	12
1.53	3.74	6	9	19
1.62	3.20	16	18	29
1.68	2.93	25	27	35

Chain Length Determination.—If a pure anhydrous sodium phosphate glass for which $Na_2O/P_2O_5 \geqslant 1$ consists of only chain phosphates with no rings or orthophosphate present, the number average chain length, $\bar{n}$, can be obtained from either of the two equations

$$Na_2O/P_2O_5 = (\bar{n} + 2)/\bar{n} \qquad (2)$$

or

$$\bar{n} = \frac{2(\text{Equivalents of strong acid function})}{\text{Equivalents of titratable weak acid function}} \qquad (3)$$

As the titration method for bound water indicates, a small amount of water of constitution can be considered to enter into the molecular structure interchangeably with the sodium oxide. Therefore, equation 2 can be modified by substituting the term $(Na_2O + H_2O)$ for Na_2O when $Na_2O \gg H_2O$. The presence of rings (*e. g.*, trimeta) can be corrected for by multiplying the P_2O_5 or strong acid by the fraction of the total phosphorus not found in ring structures. A similar correction can be carried out for orthophosphate. For most of the glasses studied here these corrections were very small; however, for the Graham's salts the approximate amount of rings was found from the fractionation data (see Fig. 3) and the value of $\bar{n}$ was appropriately corrected. Slight corrections for bound water and a trace of orthophosphate were also used to obtain the chain length reported for the glass of Fig. 5.

Solubility Fractionation

Description of Experiments.—Application of the standard procedures of analytical chemistry to the study of solutions of sodium phosphate glasses has demonstrated unquestionably that these solutions contain complex mixtures of condensed phosphate molecule-ions.[5,6] There is, of course, another standard procedure for the solubility classification of complex mixtures, which was introduced in the study of organic high polymers. This procedure, known as fractionation, consists of successive additions of a poor solvent to a solution in amounts sufficient to precipitate only a small fraction of the mixture. These fractions are not so arranged as to contain all of a given molecular species; rather they are graduated molecular mixtures of less complexity than the original mixture. According to Cragg and Hammerschlag[7] "the precipitated phase is either a swollen gel or a very viscous liquid, and contains a high proportion of polymer. The material of higher molecular weight tends to concentrate in the precipitated phase, that of lower molecular weight in the supernatant liquid."

Application of the principles of solubility fractionation to the separation of constituents in solutions of sodium phosphate glasses in the composition range between $Na_2O{\cdot}P_2O_5$ and $5Na_2O{\cdot}3P_2O_5$ gave interesting results. A preliminary investigation of the process led to the conclusion that the stepwise addition of any organic solvent miscible with water would cause precipitation of concentrated, viscous liquids exhibiting successively smaller ratios of titratable strong to weak acid functions. Thus, if we assume that the ratio of strong to weak acid is a measure of the molecular weight of the condensed phosphate structures, the sodium phosphate glasses present a classical case of the application of solubility fractionation.

In order to avoid hydrolysis, the fractionation procedure was carried out as rapidly as possible (within several hours) at room temperature. A clear solution containing several per cent. of the glass in a mixture of water and an amount of organic liquid insufficient to produce precipitation was made up by adding the organic liquid after the powdered glass had been dissolved with stirring. To this original solution enough organic liquid was added with stirring to cause it to appear cloudy. The cloudy suspension was stirred mechanically for ten minutes so that equilibrium between the phases might be obtained, and it was then centrifuged until a few drops of a clear viscid liquid could be found below the solution which

---

(5) Bell, *Ind. Eng. Chem., Anal. Ed.*, **19**, 97 (1947).

(6) L. T. Jones, *Ind. Eng. Chem., Anal. Ed.*, **14**, 536 (1942); R. N. Bell, *Ind. Eng. Chem.*, **39**, 136 (1947).

(7) Cragg and Hammerschlag, *Chem. Rev.*, **39**, 79 (1946).

TABLE II

TABULATION OF DATA FROM TWO TYPICAL FRACTIONATION EXPERIMENTS

Graham's Salt

200 g. of glass dissolved in 2000 ml. of water, then 200 ml. acetone added.

Fraction	Milliliters acetone added	Moles strong acid in fraction	Moles weak acid in fraction
1	45	0.278	0.00101
2	25	.264	.00138
3	35	.297	.00149
4	50	.325	.00202
5	70	.291	.00272
6	150	.232	.00413
7	1000	.078	.00451
8	(residue)	.178	.00318
Amt. recovered		1.943	.0204
Original amount		1.958	.0190
Percentage change		0.8% loss	7.4% gain

Quadrafos[a]

20 g. of glass dissolved in 500 ml. of water, then 100 ml. acetone added.

Fraction	Milliliters acetone added	Moles strong acid in fraction	Moles weak acid in fraction
1	60	0.0307	0.0101
2	5	.0088	.00295
3	12	.0158	.00553
4	20	.0220	.00822
5	35	.0236	.00962
6	45	.0212	.00965
7	60	.0153	.00735
8	90	.0115	.00647
9	150	.00860	.00545
10	300	.00645	.00473
11	(residue)	.00567	.0041
Amt. recovered		.1696	.0741
Original amount		.1742	.0750
Percentage change		2.9% loss	1.2% gain

[a] Reg. trade-mark Rumford Chemical Works. (The sample studied here had an average chain length of 4.63 and contained 0.5% of the total phosphorus in the form of orthophosphate).

had again become clear. After decantation the dense viscid phase was diluted with water to form a clear solution, portions of which were immediately treated with hydrochloric acid to lower the *p*H to *ca.* 2.5 and then titrated at once with 0.1 *N* sodium hydroxide. The remaining portions were acidulated with hydrochloric acid and boiled for a day to convert all the phosphate to the ortho form before titrating with 0.1 *N* base. Meanwhile the supernatant solution was again treated with the organic liquid and the process repeated. Although it was found that methyl, ethyl and isopropyl alcohols would adequately cause fractionation to occur, acetone proved to be the most satisfactory organic liquid. In an average experiment the ratio of acetone to water ranged from 0.2 for the first fractionation to 2 for the final fraction. Usually 10 to 15 fractions were taken and the amount of acetone used for each was gradually increased as fractionation proceeded. When further addition of acetone became impracticable, the organic liquid was removed from the residual solution by boiling *in vacuo* at room temperature, and the usual titrations were carried out on the remaining aqueous phase. It was generally found that 5 to 10% of the phosphorus present in the original sample remained in this residual fraction.

In some of the early experiments fractionation was carried out in a thermostat at 25°. However, it was felt that the advantages of this procedure were overweighed by the clumsiness of the set-up which appreciably extended the time of an experiment. Therefore the fractionations reported here were all done at room temperature (*ca.* 27°). Some preliminary studies were also made of the effect of *p*H on the fractionation procedure and it was found that the *p*H of the aqueous solution prepared for fractionation had no effect on the final results, within a *p*H range of 4 to 9. It was also generally found that the *p*H of aqueous solutions of all fractions obtained during a given run remained relatively constant from fraction to fraction. This means that equivalent amounts of anion and cation were driven out of solution together upon the addition of the organic liquid.

Data and Interpretation.—Since *p*H titration is used as the analytical method in this work, the results are expressed in terms of strong and weak acid functions. As is illustrated in Table II, the amount of phosphorus recovered in all of the fractions was always greater than 97% of the phosphorus originally present, since the sum of the amounts of strong acid function recovered in the fractions was just slightly less than the amount of strong acid in the original glass. The amount of recovered weak acid was also found to be nearly equal to the amount originally used. This indicates that very little hydrolysis occurred during fractionation.

By substituting data such as are shown in Table II into equation 3 (with no corrections for rings or ortho) the chain length, n for each fraction can be obtained. In Figs. 1, 2, 3 and 4 such values of n are plotted as a function of the cumulative amount of phosphorus in the order in which the corresponding fractions were obtained in fractionation. These data are compared with theoretical plots of chain length *vs.* cumulative amounts of phosphorus calculated from equations 4 and 6 of paper II in this series. As can be seen in Fig. 1 the fractionation results fit the distribution derived for a random reorganization process when the average chain length is large. With decreasing $\bar{n}$ the random reorganization distribution is found to deviate more and more

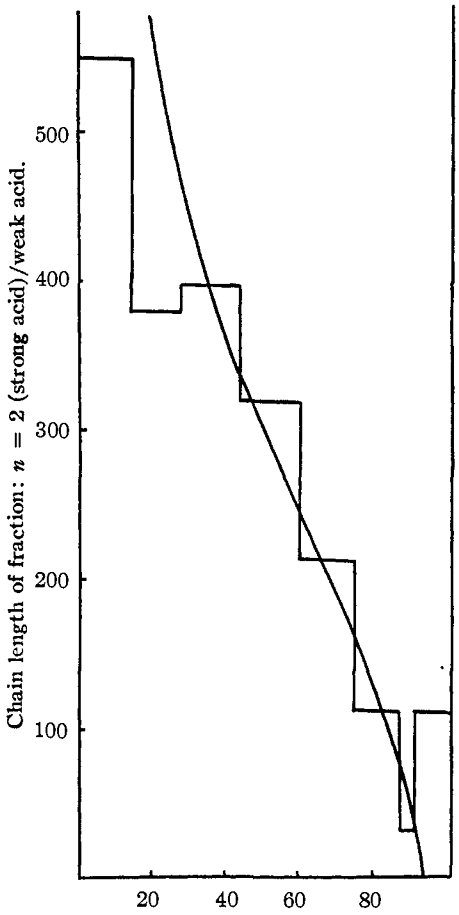

Fig. 1.—A comparison of the distribution corresponding to random reorganization with the data from a fractionation experiment for a sample of Graham's salt having a number average chain length of 193 (corrected for meta rings).

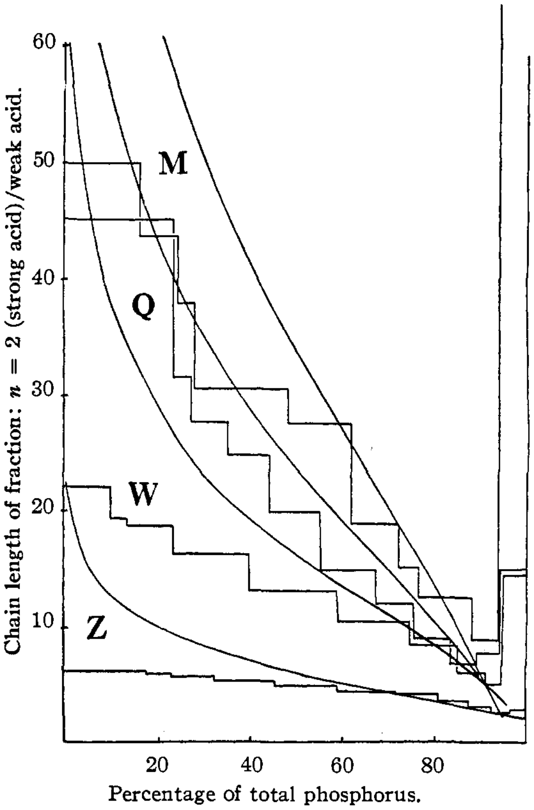

Fig. 2.—Distribution of polyphosphates in several sodium phosphate glasses. The smooth curves represent the theoretical distributions; the stepwise curves give fractionation data. Each curve is identified by the number average chain length of the original glass: M, $\bar{n}$ = 23.6; Q, $\bar{n}$ = 16.3; W, $\bar{n}$ = 11.3; Z, $\bar{n}$ = 4.6.

from the experimental data, as predicted in paper II. This is shown in Fig. 2. For the shortest average chain lengths physically obtainable the Poisson distribution function is a good approximation to the fractionation data. This fact can be seen in Fig. 3 in which the random reorganization process results in a very much broader distribution than that indicated by the fractionation or Poisson curves.

Now let us examine some details. It can be seen that the residual fraction in each fractionation experiment had a higher apparent chain length than the several fractions immediately preceding it. This anomaly can be explained by the results obtained in fractionating mixtures of sodium phosphate glasses with crystalline sodium trimetaphosphate. These results, such as the data given in Fig. 4, show that the trimetaphosphate, and presumably other ring phosphates, remain in the residue with the shortest chains. Therefore, an approximation can be made to the amount of ring phosphates present in the glass by attributing the excess magnitude of n for the residual fraction to the presence of rings. This approximation was used to set the low end of the theoretical curves which are compared with the experimental data in Figs. 1 and 2. When the experimentally determined amount of rings in the glasses is plotted in Fig. 5 as a function of the composition of the glass and compared with a theoretical curve for the amount of rings (Case II of the theory given in paper II) it would appear that the presence of phosphate rings is due to a rounding-off of the discontinuity predicted by the simple theory in going from Case I to Case II.

Several observations were also made of the character of the precipitated phase as a function of the chain length found for it. When samples of Graham's salt were fractionated, the precipitated phase corresponding to the first few fractions (n being very large) was extremely viscid with an estimated[8] viscosity between 50 and 100

---

[8] These estimations were carried out on the basis of visual appraisal and comparison with the appearance of a series of standard viscosity oils. Naturally they are only crude approximations.

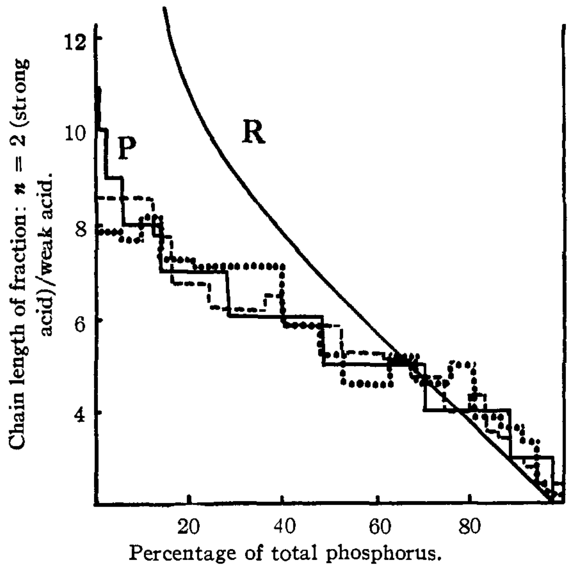

Fig. 3.—Comparison of the theoretical distribution curves (heavy solid lines) with data from two fractionation experiments for a sodium phosphate glass having a number average chain length of 5.0. This glass came from the regular production of Quadrafos (reg. trademark, Rumford Chemical Works): P, Poisson distribution; R, random reorganization distribution.

poises. As the value of n dropped, the precipitated phase became more fluid, until for values of n around 5 the precipitated phase from solutions of the appropriate glasses had an estimated viscosity of several tenths of a poise. For fractions with n near or below 3, the precipitated phase consisted in part of crystalline material. When mixtures of the glasses and crystalline phosphates were fractionated, the precipitated phase corresponding to the expected number of fractions was crystalline. These observations are qualitatively in accord with the theory of paper II.

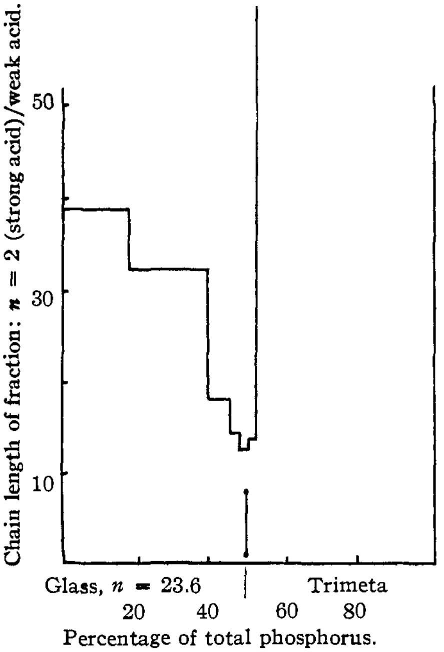

Fig. 4.—Fractionation of a 50–50 mixture of a sodium phosphate glass and sodium trimetaphosphate. The trimetaphosphate ring shows an infinite chain length as determined by end-group titrations.

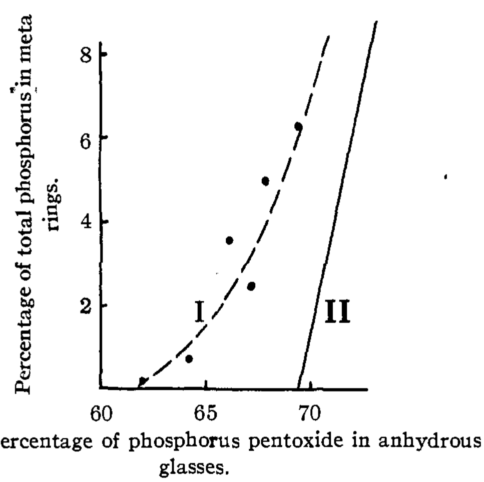

Fig. 5.—Approximate amount of metaphosphate rings in sodium phosphate glasses as determined from the excessively high values of n for the residual fractions: I, Case I; II, Case II.

One of the most interesting conclusions from this work is that the metaphosphate glass, commonly called Graham's salt, is not uniquely different from the rest of the phosphate glasses. As was pointed out by Samuelson,[9] Graham's salt consists of very long chain polyphosphates. Samuelson measured average chain lengths; and we have found the shape of the chain length distribution curves, *e. g.*, Fig. 1. In general, it can be said that a "hexametaphosphate" or Graham's salt is a mixture which consists primarily of long chain polyphosphates and thus is no different except in degree from the other sodium phosphate glasses for which the mole ratio Na_2O/P_2O_5 is greater than unity.

Rate of Solution and Solubility

Dissolution Rates.—When glasses for which the mole ratio $(Na_2O + H_2O)/P_2O_5$ lies between *ca.* 1.05 and 1.5 are ground up and sieved to definite particle sizes, it is found that the resulting powders dissolve in well-agitated water at approximately the same rate as do powdered, soluble crystalline salts. This is illustrated by Table III in which the results of a typical experiment are presented. It should be noted that as Na_2O/P_2O_5 decreases there is a slight reduction in the rate of solution. As $(Na_2O + H_2O)/P_2O_5$ approaches unity (*i. e.* $<$*ca.* 1.05), the glasses (Graham's salt) dissolve more slowly and in a less definable manner than do the glasses of higher

---

[9] Samuelson, *Svensk. Kem. Tid.*, **56**, 343 (1944).

ratio. These latter glasses dissolve with stirring, like crystalline salts, to give solutions that are immediately clear. On the other hand, particles of Graham's salt gradually hydrate to gelatinous masses which slowly become larger and more ill-defined and finally disappear into solution. This over-all process of dissolution is followed no matter how fast the solution is agitated and can be observed visually because of the difference in the index of refraction between the gelatinous masses and the homogeneous liquid. The rate at which the over-all process proceeds appears to be dependent on the exact composition of the glass, becoming less rapid as $(Na_2O + H_2O)/P_2O_5$ approches unity.

TABLE III

VELOCITY OF DISSOLUTION IN AGITATED WATER[a]

Solute	Relative time in which about 0.9 of the solid dissolved
Sodium chloride	0.9
$Na_3PO_4 \cdot 12H_2O$	1.1
Sodium phosphate glass with $Na_2O/P_2O_5 = 1.5$	1.0
Sodium phosphate glass with $Na_2O/P_2O_5 = 1.3$	1.0
Sodium phosphate glass with $Na_2O/P_2O_5 = 1.1$	1.2

[a] Ten grams of the material retained between 20- and 30-mesh Tyler standard sieves was added to 200 g. of distilled water mechanically stirred so as to produce a vortex. The time in which 95% of the solid dissolved was obtained conductometrically. All conditions were identical when the experiment was repeated with the various salts, and the temperature was kept at 25.0°.

As is well known in commercial practice, particles of any of the phosphate glasses having Na_2O/P_2O_5 greater than *ca.* 0.9 tend to congeal and stick together when added to water without agitation. This effect can be attributed to the ability of the glasses to form extremely viscid solutions[10] which bind the particles together into a mass that dissolves very slowly because of its small surface area. As this effect is dependent on the amount of agitation, it is not to be confused with the unusual type of dissolution observed when Graham's salt is added to well-stirred water.

Crystallizable Material in Glasses.—The glasses described above appear to be completely miscible in water.[10] That is to say, there is a continuous range of composition between an infinitely dilute aqueous solution and rigid glasses containing a small percentage of water. Of course, when concentrated solutions of these glasses are allowed to age, precipitates of degradation products, such as the crystalline hydrates of the appropriate ortho- and pyrophosphates, are found to deposit. Thus, an aqueous solution containing 80% by weight of one of these glasses ($Na_2O/P_2O_5 = 1.45$) sets to a solid mass within several days. This behavior, however, is noticeably different from the action to be observed when glasses having Na_2O/P_2O_5 greater than *ca.* 1.5 are put into water. In this latter case the glasses deposit crystalline material as soon as they dissolve provided that the concentration is sufficiently high. The concentration at which a slight trace of crystalline material can be observed in the aqueous solution is given in Fig. 6 as a function of the composition of the glass. Although an extrapolation of the curve of Fig. 6 to the region of higher $\bar{n}$ would indicate that these glasses could give a solid phase in concentrated solution, the solutions when prepared are found to be clear. This behavior is attributable to the high viscosity of the concentrated solutions which inhibits the rate of formation of crystal nuclei.

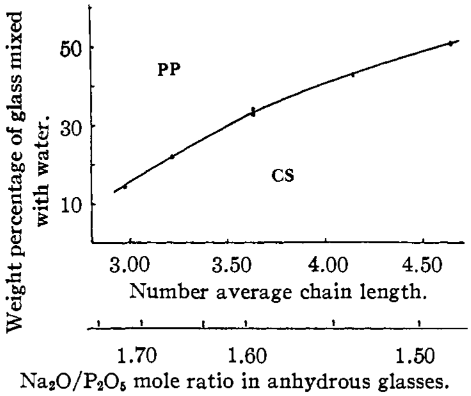

Fig. 6.—Region of composition and concentration in which the sodium phosphate glasses form a precipitate immediately when dissolved in water: PP, precipitate present; CS, clear solution.

The rapid formation of crystalline material from glasses near the tripolyphosphate composition can be readily observed by moistening a piece of the clear glass with a few drops of water. It is first noted that the surface of the glass becomes cloudy. Then, as the moisture permeates through the material, the depth of the cloudy layer increases until the entire piece is converted into a whitish mass. If a piece of glass that was originally hard, brittle and transparent, is allowed to sit for several hours in contact with a relatively small amount of water, the piece will still retain its gross shape although it will be found to be soft and plastic with an opaque white appearance. Microscopic examination reveals a mixture of fine crystalline particles (non-isotropic) in a viscid isotropic matrix.

In order to examine this phenomenon more thoroughly, powdered samples of various glasses in which Na_2O/P_2O_5 was greater than 1.5 were added to water in concentrations great enough to cause precipitate formation. These solutions were then stirred for three hours while in a thermostat kept at 25.38°. It was assumed that equilibrium between precipitate and solution would

---

(10) Van Wazer, *Ind. Eng. Chem.*, **41**, 189 (1949).

practically be obtained in that length of time without an undue amount of hydrolysis.

The solid phase was separated from the liquid by centrifuging followed by decantation. Then $\bar{n}$ and the fraction of the original phosphorus present were determined for each phase by titrations before and after hydrolysis. In all cases it was found that the total amount of strong or weak acid function present in the precipitate and supernatant liquid was equal, within experimental error, to the amount calculated from the composition of the original glass. Also $\bar{n}$ for the solid phase always lay between two and three. Since less than 1% of the total phosphorus in these glasses was found to be present as orthophosphate, titration data for the solid phase were interpreted in terms of a mixture of crystalline pyro- and tripolyphosphates. That is to say, the fraction of the phosphorus present in the precipitate as tripolyphosphate was set equal to $3(1-2/\bar{n})$. The results of these operations are presented in Fig. 7. Because of the high viscosity, the solid phase could not readily be separated from aqueous mixtures containing more than 50% glass. Therefore, the experimental data were restricted to a rather limited concentration range. The points given in Fig. 7 for 100% glass were calculated from the Poisson distribution by substituting $\bar{n} = 2$ and 3 respectively in equation 6 of paper II. As can be seen from the figure, the calculated values for the tripoly- and pyrophosphate content in the pure glasses is in good agreement with an extrapolation of the experimental curves. These data do not allow an unequivocable choice between the Poisson and random reorganization distribution functions since the two functions predict about the same total amount of phosphorus present as the tripoly- and pyrophosphates. However the random reorganization function requires approximately 10% more of the total phosphorus as pyrophosphate and this amount seems to be too large to fit the extrapolated curves.

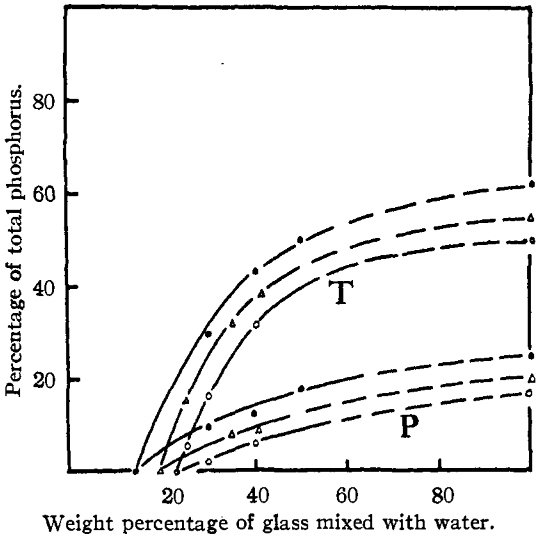

Fig. 7.—Curves giving the composition and amount of precipitate formed immediately on dissolving three sodium phosphate glasses in various amounts of water. Data for the three glasses having the following average chain lengths are denoted by these symbols; ●, $\bar{n}$ = 2.98; △, n = 3.13; ○, $\bar{n}$ = 3.23; top section, solution or glass (higher polyphosphates); T, tripolyphosphate; P, pyrophosphate.

Slowly Soluble Glasses.—In the range of composition between pure glassy P_2O_5 and the $Na_2O \cdot P_2O_5$ glass, the rate of solution is extremely slow as is shown in Table IV. At a mole ratio of Na_2O/P_2O_5 equal to *ca.* 0.5 the relative dissolution velocity reaches a minimum. Since the rate of solution in this composition range is of the same order of magnitude as the observed rates of hydrolysis of condensed phosphates, the molecular structures present in these glasses undergo substantial degradation during the process of escaping from the solid. Particles of these glasses do not stick together when placed in quiet water. This behavior can be explained by this degradation and the fact that the ever-present effects of diffusion and convection are sufficient to equitably distribute the dissolved matter as quickly as it goes into solution.

TABLE IV

VELOCITY OF DISSOLUTION OF SODIUM PHOSPHATE GLASSES[a]

Mole ratio of Na_2O to P_2O_5 in glass	Time necessary for 0.9 of the glass to dissolve
1.3	8 min.
1.1	8 min.
1.04	20 min.
0.88	2 hr.
.65	65 hr.
.59	100 hr.
.57	100 hr.
.15	2 hr.
.00 (γ-P_2O_5)	25 min.

[a] 1.5 g. of −20 + 30-mesh particles of the glass was added to 15 ml. of water contained in a 20-ml. vial at 25°. Stirring was effected by the rotation of a wheel to the circumference of which the vials were attached radially. The amount of undissolved salt was determined visually.

Discussion.—According to expectations, the polyphosphate mixtures corresponding to Case I of the theory are found to dissolve at a rate which is relatively independent of average molecular size until this average becomes very large. Then the rate determining step in the dissolution process consists of untangling and freeing the chains. As was predicted under Case II of the preceding paper, a minimum was found in the rate of solution for vitreous compositions between $Na_2O \cdot P_2O_5$ and P_2O_5.

Now let us consider the phenomenon of the immediate formation of crystalline precipitates in solutions of glasses near $5Na_2O \cdot 3P_2O_5$. When the amount of easily crystallizable polyphosphate (n = 2 or 3) in a mixture of various polyphosphates exceeds its solubility limit, a crystalline precipitate will quickly form. According to the equations of paper II, the relative amounts of chains having two or three phosphorus atoms apiece becomes quite large in glasses near $5Na_2O \cdot 3P_2O_5$. When this calculated composition is compared in Fig. 7 with the solubility data, it can be seen that a smooth curve connects the fraction of pyro- and tripolyphosphates theoretically present in the glass with the amounts of these phosphates precipitated from solution. In addition some study was made of the effect of phosphate glasses on the solubility of the crystalline phosphates. Although this work was abandoned because of its complexity, it also indicated that the above ideas are essentially correct. Thus the analytical results reported in Table I as well as the solubility data discussed here are found to agree reasonably well with the tripoly- and pyrophosphate content of the glasses computed from the Poisson distribution.

Acknowledgment.—Thanks are due to the Rumford Control Laboratory for carrying out the phosphorus pentoxide analyses used in this work. I also wish to thank Messrs. Albert Marshall, Raymond Copson and Bernard Starrs for their advice and constructive criticism.

Summary

The methods commonly used in the solubility fractionation of organic polymers have been applied to the separation of fractions from sodium phosphate glasses lying in the range between the meta and pyro compositions. The fractions were analyzed by *p*H titrations to find the ratio of the equivalents of total phosphorus to end-group phosphorus. Assuming that this ratio equals $^1/_2$ the average chain length of the polyphosphates making up each fraction, a chain length distribution curve could be plotted for each glass fractionated. These curves were found to agree satisfactorily with the chain length distributions discussed in the previous paper of this series.

The dissolution and solubility behavior of the various sodium phosphate glasses in water was also reported. According to the theoretical predictions, a minimum was found in the rate of dissolution near the $Na_2O \cdot 2P_2O_5$ composition. In addition it was found that precipitates consisting of mixtures of crystalline pyro- and tripolyphosphates were formed immediately upon the dissolution of glasses near the $5Na_2O \cdot 3P_2O_5$ composition.

RUMFORD, R. I. RECEIVED AUGUST 14, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF RUMFORD CHEMICAL WORKS]

Structure and Properties of the Condensed Phosphates. IV. Complex Ion Formation in Polyphosphate Solutions

BY JOHN R. VAN WAZER* AND DORIS A. CAMPANELLA

Very soon after the discovery[1] of the condensed phosphates, it was found that precipitates of metals other than the alkalies would redissolve in an excess of the alkali metal salts of certain condensed phosphoric acids,[2] which according to the conclusions reached in the earlier papers of this series we shall call polyphosphates. Before the turn of the century this phenomenon was ascribed[3] to the formation of a relatively stable, soluble complex between the metal and the phosphate. This concept of complex formation is still in vogue.

Because of experimental difficulties, the complexes between the metals and the polyphosphates have not yet been defined in terms of a chemical formula[4] and a dissociation constant. As the common cations, except those of the alkali metals, ammonia and the amines, form precipitates with most of the phosphates, the available range of concentrations is quite restricted and many of the standard methods of studying complexes cannot be applied. Thus the work reported here is limited to two experimental methods based on polarographic and electrometric *p*H techniques, respectively.

Structure of Complexes

From consideration of the structure of chains of interlinked PO_4 tetrahedra, it appears that a chelate ring[5] might be completed between any two adjacent PO_4 tetrahedra. We shall, therefore, find it convenient to advance the hypothesis that the strong complexing ability of the linear polyphosphates is due to the formation of chelate rings. Although it has been shown[6] that the formal valence bond structures do not make major contributions to the over-all resonance in simple PO_4 groups, the chelate structures[7] given

---

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

[1] Clark, *Edinburgh J. of Sci.*, **7**, 298 (1827); Graham, *Phil. Trans.*, **123**, 253 (1833).

[2] Persoz, *Ann.*, **65**, 163 (1848); Rose, *Phil. Mag.*, **34**, 321 (1849); Scheerer, *J. prakt. Chem.*, **75**, 113 (1858).

[3] Tammann, *ibid.*, **45**, (Ser. 2), 417 (1892).

[4] However, some purely empirical formulas have been suggested: *e. g.*, Chwala, "Textilhilfsmittel," Springer, Wien, 1939, p. 78 (reprinted by Edwards Bros., Ann Arbor, in 1943).

[5] Diehl, *Chem. Rev.*, **21**, 39 (1937); also Liebhafsky, *J. Chem. Ed.*, **23**, 341 (1946).

[6] Pauling, "Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1945, pp. 239–250.

[7] As shown in the formula the metal, M, is monovalent; but polyvalent metals can also enter into similar structures. Furthermore, the number of phosphorus pairs connected to each metal atom will be determined by the relative concentrations of metal