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Condensed Phosphates in the Molten State

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Problems of the determination of the anionic composition of melts of condensed phosphates and the application of the "theory of the disordered reorganisation of condensed polymers" (Flory, Van Wazer) to them are considered. The part played by water in the formation and breakdown of polymeric chains and rings is noted. The liquidus diagrams of systems based on condensed phosphates of various anionic compositions are reviewed and compounds formed in the system are noted. The physical properties of phosphate melts (mainly surface tension, density, and their temperature coefficients) and their dependence on the type of equilibrium diagram, melt composition, and generalised moments of the cations and anions are examined. It is concluded that the interparticle interaction of polyphosphates in the liquid phase is reflected in their volume and surface properties. 157 references.

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I. INTRODUCTION

Melts of condensed phosphates are attracting attention not only for themselves but also as a comparatively easily investigated model of an inorganic polymer, especially of silicate melts. They are of interest to various branches of learning and technology: nuclear physics, fertiliser technology, metals, electrometallurgy, etc. Crystalline and vitreous substances with valuable physical properties are obtained from the melts. There has recently been an increasing number of papers on condensed phosphate melts. However, Van Wazer's monograph[1] and Thilo's review papers[2,3] did not devote much space to the properties of melts, what was said being distributed in various sections. It is interesting to systematise the available information in terms of physicochemical analysis.

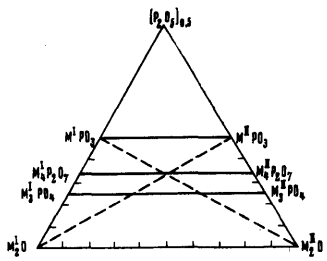


Figure 1. Composition triangle of the $M^{I}_{2}O-P_2O_5-M^{II}_{2}O$ system, where M is an equivalent of a metal.

Condensed phosphates are compounds in systems formed by phosphorus pentoxide with oxides of one or two metals; instead of one of the oxides they may contain water. The compositions are characterised by the ratio $R = M/P$, where M is the number of equivalents of the metal and P the number of phosphorus atoms. In the condensed phosphates PO_4 tetrahedra are connected through oxygen atoms with the formation of rings, chains, or networks. Although representatives of this class of compound were known at the start of the last century the study of the condensed phosphates became systematic only after the main feature of their structure as polymers was established. We will be interested in the part of the system (Fig. 1) corresponding to compositions with $R \geqslant 1$, not containing hydrogen. In Fig. 1 this part of the system is represented by the trapezium $M^{I}PO_3-M^{II}PO_3-M^{II}O-M^{I}_{2}O$. The compounds corresponding to this region are obtained by the thermal dehydration of acid phosphates or their mixtures with oxides or carbonates.

Compositions with $R = 1$ are termed "proper" metaphosphates, or simply metaphosphates. Their general formula is $(MPO_3)_n$, where $n = 3-8$.[2,4,5] They all have a ring structure. Condensed phosphates with $R > 1$ correspond to the general formula $(MPO_3)_n \cdot M_2O$ or $M_{n+2}P_nO_{3n+1}$ and have a chain structure. They are termed polyphosphates. Polyphosphates are the main constituent of melts. The initial member of the series of polyphosphates with very large values of n, that is, with a ratio R which is very little in excess of unity, is usually called metaphosphate, as are the ring phosphates. To distinguish the chain phosphates (with large n) from the ring phosphates with the same number of phosphorus atoms in the formula the word "meta" is inserted in the name when we are dealing with a ring phosphate, or the word "poly" when we are dealing with a chain; however, the word "poly" is sometimes omitted. Hence names such as "tetrametaphosphate" and "tetraphosphate" are obtained; the latter would be more accurately named a tetrapolyphosphate. The final term of the polyphosphate series ($R = 3$) is a compound with one PO_4 group, a monophosphate, better known under the name of orthophosphate; the penultimate term of the series ($R = 2$) is a di- or pyro-phosphate. In the polyphosphates where n is large two equivalents of metal are evidently replaced by hydrogen atoms which enter into the terminal groups with formation of hydroxyl groups. Hence the formula of the long-chain polyphosphates is more accurately written as $M_nH_2P_nO_{3n+1}$. †

† As lattice polyphosphates are almost absent from melts[6] we will not discuss their structure.

Some investigators do not take into account the hydrogen in the terminal groups and the polyphosphates are represented by formulae $M_{n+2}P_nO_{3n+1}$. These formulae are unconditionally applied to polyphosphates with n not exceeding 8–10, which are called oligophosphates[7].

II. ANIONIC COMPOSITION OF THE MELTS

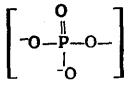
The anionic composition of phosphate melts is determined predominantly by investigating the glasses into which melts of many phosphates with $R < 2$ (that is, in the metaphosphate–diphosphate region) are readily converted. There is a possibility of bringing phosphate glasses into solution without change in anionic composition by the choice of appropriate solvents or by double decomposition with salts and complexones and also with the aid of ion-exchange resins. The anionic composition of the solutions obtained can be determined by chemical analysis[8], by the method of titration of terminal groups[9,10], and by the methods which are general for polymer physics: ultracentrifugation, dialysis, electrophoresis, light scattering studies, viscosity of dilute solutions in the presence of an indifferent electrolyte, etc. However, the greatest possibility was revealed by paper chromatography, applied to polyphosphates by Ebel[11], subsequently perfected and now widely used.

The identity of the structural units of melts and of glasses has been shown by several investigators[12-18] using Raman and infrared absorption spectra, unfortunately for not many compositions. These results showed that in glasses there are chain and a few ring phosphates, and that branching is almost absent. The anions were identified on the basis of a comparison of the spectra of glasses and melts with the spectra of crystals of individual phosphates the structure of which had been found by X-ray diffraction or other methods.

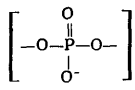
Chromatographic investigation of phosphate glasses was undertaken from the 1950's onwards over the widest front by the schools of Thilo[19-21], Van Wazer and Westmann[22-31], and Meadowcroft and coworkers[32]. In the fusion of even definite crystalline phosphates—tri- and tetra- (but not di-) phosphates—a mixture of anions is formed, in which an anion with a chain length one unit less than the mean chain length ($\bar{n}$) predominates; the mean chain length is easily related to the relative concentration of the oxides $R = M/P$ by the ratio $\bar{n} = 2/(R-1)$. The isolated PO_4^{3-} ion was observed only in melts with $n < 2$, that is, in melts of mixtures of diphosphate and orthophosphate (see Ref. 1, p. 477).

The investigation of the anionic composition of the glasses does not give any idea of the state of the melts, since in the latter, their viscosity being low in comparison with that of glasses, processes connected with the formation of radicals and reactions with participation of the latter are possible. According to some investigators[21,33], many conversions in polyphosphate melts are connected with the formation of intermediate products—the radicals $NaPO_3$, PO_3, etc.

A guideline in ideas about the anionic composition in melts of chain polymers was given by the application to phosphates of the "theory of the disordered reorganisation of condensed polymers", Flory[34] having investigated the polymerisation of organic liquids. He considered the statistical polymerisation of hydroxy-acids, by assuming exchange between the molecular constituents of their "segments". These concepts and methods were transferred by Van Wazer[1,35,36] to polyphosphates. A phosphate melt with a definite value of n is characterised by the retention of some unchanged number of terminal phosphate groups PO_4^{2-}



and of intermediate PO_4^- groups:



analogous to the "segments" of Flory. Van Wazer finally obtained the distribution function—an equation for the determination of the anionic composition with a specified mean chain length $\bar{n}$. If the electrolytic dissociation in the melt were high then the anionic chains would behave as "rigid rods", owing to the high concentration of negative charges; if the dissociation were small then the negative charges would be partly neutralised and the anions would behave as "flexible chains". In the absence of PO_4^{3-} ions and of unreacted oxides the distribution function, which characterises the weight distribution of phosphorus along chains of different length, at a mean chain length of $\bar{n}$ for "flexible chains" will have the form:

$$\omega_{(n)} = \frac{n}{n(n-1)} \left(\frac{n-2}{n-1}\right)^{n-2} \qquad (1)$$

where $\omega_{(n)}$ is the weight fraction of the phosphorus in chains containing n phosphorus atoms; $n \geqslant 2$. For "rigid rods" the distribution function becomes more complex. In some papers[26,28,32] the experimental and theoretical conclusions about the distribution of phosphorus along chains of different length have been compared for glasses of various compositions. The results of chromatographic experiment were treated theoretically on the basis of equations following the Flory theory. The experimental results lie between the calculated ones obtained assuming "flexible chains" and "rigid rods". In recent years the theory has been developed further[37,38]. However, the most significant conclusions yet were derived from Flory's original theory.

Meadowcroft and Richardson[32] attempted to arrive at the thermodynamic properties of polyphosphate melts by using Flory's theory, the equations of which acquired a form convenient for thermodynamic evaluation. The Flory distribution formula is represented in the form:

$$N_n = \left(\frac{\bar{n}-1}{\bar{n}}\right)^{n-1} \cdot \frac{1}{\bar{n}} \qquad (2)$$

where N_n is the mole fraction of the n-mer in the mixture, and $\bar{n}$ is the mean chain length. Each n-mer is in equilibrium with decomposition products:

$$2P_n = P_{n-1} + P_{n+1} \, . \qquad (3)$$

The equilibrium constant (K) of the reaction is given by

$$\frac{[P_{n-1}] \cdot [P_{n+1}]}{[P_n]^2} = K_n \, . \qquad (4)$$

The expressions in square brackets denote the mole fractions of each polymer. The $(n-1)$-mer and $(n+1)$-mer obtained also disproportionate:

$$2P_{n-1} = P_{n-2} + P_n \qquad (4a)$$

$$2P_{n+1} = P_n + P_{n+2} \text{ etc.} \qquad (4b)$$

Each of the equations is characterised by a definite equilibrium constant. When all the other mole fractions of the polymers remaining for the equilibrium constants from

Eqn. (2) are substituted in Eqn. (4) we find that all the constants are equal to unity. It was found[32] that the experimental values of the constants obtained by chromatography of a series of partitions ($n = 4$, 6; cations Na^+, Li^+, Ca^{2+}, Zn^{2+}) are not unity; this shows that the distribution of phosphate along chains of different length is not completely disordered. With increase in n the constants approach 1 and (in some instances) even exceed 1. The departure from 1 at the same mean chain length $\bar{n}$ decreases in the order Na–Li–Ca–Zn.

In the expression:

$$RT \ln K_n = \Delta G_n = \Delta H_n - T\Delta S_n \qquad (5)$$

Meadowcroft and Richardson[32] neglected the entropy term, for doing which there is some justification, since the disproportionating anion is extremely similar to those which are formed. From K_n they found ΔH_n, the heat of disproportionation, which was positive, that is, the process is accompanied by absorption of heat. For a given cation ΔH_n increases as $\bar{n}$ is reduced, that is, as the chain is shortened. This is understandable, since the less $\bar{n}$, the greater the difference between the neighbour n-mers. At a given value of $\bar{n}$ the heats of disproportionation decrease in the order K(Na)–Li–Ca–Zn. Since in the expression

$$d \ln K_n / dT = \Delta H_n / RT^2 \qquad (6)$$

ΔH_n is small, it follows that the temperature change of the anionic composition is insignificant. As experiment shows, it is almost undetectable with the present accuracy of partition chromatographic analysis of glasses.

III. WATER IN PHOSPHATE MELTS

In the formation and changes of condensed phosphates water plays a large part, since as noted above there are hydroxide ions in the terminal groups of long-chain phosphates. The participation of water has been best studied for sodium phosphates. During the dehydration of the dihydrogen phosphate at ~ 240°C in addition to trimetaphosphate chain polyphosphates are formed (crystalline Madrell's salt) and above 400°C these are completely converted into crystals of a cyclic trimetaphosphate[39], the chain closing into a ring with the release of water from the terminal groups. It partly volatilises and partly remains, possibly even forming clathrates. During fusion a large part of the trimetaphosphate is again converted into polyphosphates: water retained in the crystals allows the ends to unwind into long chains with hydroxyl groups at the ends. In the crystallisation of the melt trimetaphosphate is again obtained, with vaporisation of part of the water from the salt mass. On this is based the procedure for the dehydration of melts by alternate crystallisation and fusion.

According to some investigators[40,41] the vapour pressure of water over the melts determines the type of polymers formed and the lengths of the anions present in the melt. Fig. 2 gives the change in the mean chain lengths as a function of the time of holding the melts in air[41]. A melt of dehydrated trimetaphosphate absorbs water from the air and the chains are shortened. The points characterise the change in the melt obtained by dehydration of monosubstituted orthophosphate. The melt loses water in the air and the chains lengthen. After 24 h both melts arrive at the same mean chain length, corresponding to the partial pressure of water in the air. The isotherms shown in Fig. 3 give the decrease in mean length with increase in the partial pressure of water vapour in the atmosphere, At constant pressure a rise in temperature brings about lengthening of the $(NaPO_3)_n.H_2O$ chain, evidently owing to removal of part of the water from the melt.

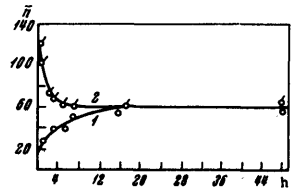


Figure 2. Dependence of the mean chain length ($\bar{n}$) of Graham's salt on the time kept at 650°C at a water vapour pressure of 55.3 torr[4]: *1*) salt obtained from NaH_2PO_4; *2*) salt obtained from anhydrous phosphate.

Prolonged crushing of condensed phosphate crystals or glasses has also been observed[42] to lead to a decrease in chain length. The water from the surrounding atmosphere evidently participates in this process.

The partial pressure of water also affects the relative composition of the dehydration products of crystalline modifications of a single phosphate, as is shown by the example of sodium tripolyphosphate[43]; this is connected with the formation of polyphosphate phases as intermediate compounds; their length is determined by the water vapour pressure. The ability to absorb and liberate water in the formation of different phases is also shown by condensed phosphates of other metals[44–49].

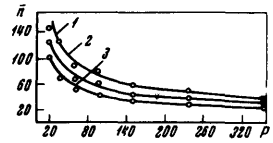


Figure 3. Dependence of the mean chain lengths of sodium polyphosphate melts on temperature and water vapour pressure[41]: Temperatures: *1*) 850°C; *2*) 750°C; *3*) 650°C. $\bar{n}$ = mean chain length; P = water vapour pressure, torr.

The quantitative determination of water present in polyphosphate melts and glasses is difficult and only a few papers‡ give the quantity of water in the melts.

Van Wazer (see Ref. 1, p.593) noted that fusion of NaH_2PO_4 at 700°C gives a preparation of $NaPO_3$ with n = 20–50; on holding the melt at 700–800°C for a month n is increased to 250–500, which corresponds to a water content of 0.07–0.03 wt. %.

‡ For example, according to Owens and Mayer[49] an analysis of a preparation of $NaPO_3$ by the zinc oxide method indicated < 0.2 wt. % H_2O.

The water present in molten metaphosphates is reactive. When molten $NaPO_3$ is held for 2 h at 800°C and then mixed with NaCl, predominantly HCl is liberated. In a melt of KPO_3 + NaCl mixture the liberation of HCl ends after almost 2 h. Judging by the quantity of HCl liberated the formula of the initial preparation was $(KPO_3)_{114}.H_2O$. The preparation of $NaPO_3$ contained more water and the reaction had not ceased after 2 h.[48]

IV. LIQUIDUS DIAGRAMS

1. Metaphosphate–Oxide of the Same Metal Systems

Metaphosphate–oxide systems with a single cation correspond to the sides of the triangle (Fig.1) from the figurative points of the metaphosphates downwards. The diagrams of these systems have been studied mainly by the methods of quenching and thermography; systems with the following oxides have been studied: Li_2O;[50] Na_2O;[51,52] K_2O;[53] MgO;[54] CaO;[55,56] SrO;[57] ZnO;[58] CdO;[59] PbO;[60-62] NiO and CoO;[63] Fe_2O_3.[64] The liquidus curves of all these systems have a chain or ring metaphosphate branch and also diphosphate and orthophosphate branches§.

In systems with Na_2O [51,52] and K_2O,[53] in addition to the diphosphate and orthophosphate branches there is a branch for the tripolyphosphate $M_5P_3O_{10}$; in the system with CaO there is a short branch for a phase of variable composition (tremelite), which was shown to be[65] a hexapolyphosphate with the anion $(P_6O_{19})^{8-}$. In systems with SrO [57] and PbO [66] there are branches for the tetrapolyphosphates $M_3P_4O_{13}$; the analogous Ba compound was obtained from melts and investigated chromatographically[67]. In systems with PbO a compound intermediate between the diphosphate and orthophosphate was also found: $Pb_5P_4O_{15} = 2Pb_2P_2O_7.$ $.PbO$.[62] In the systems with CaO, CdO, PbO, Fe_2O_3, and SrO there is yet another compound, different from those mentioned above, and richer in basic oxides than orthophosphates.

In systems with oxides of tervalent elements: B_2O_3,[68] Al_2O_3,[69] and Ga_2O_3 [79] orthophosphates are observed; however, in the diphosphate region only the system with Al_2O_3 has been studied, in which there is a eutectic between $Al(PO_3)_3$ and Al_2O_3. The orthophosphates of Fe^{3+},[71] Al,[72] and B, according to Schulze[73] and to Dachill and Dentglasser[74], are similar in structure to the modifications of SiO_2. According to Van Wazer[1], $AlPO_4$ and BPO_4 are most correctly considered as mixed anhydrides and not orthophosphates. The compound $Bi_3P_4O_{13}$ was isolated and the structure of its anion found chromatographically[68]. In the $Bi_2O_3-P_2O_5$ system, which was investigated by other authors[75] up to 12 mole % P_2O_5, solid solutions based on the high-temperature modification of Bi_2O_3 were found. In the interval between the branches of this phase and of the tetraphosphate there should be a branch of the orthophosphate $BiPO_4$; bismuth diphosphate is stable only in the solid phase.

In systems with the oxides of quadrivalent elements: SiO_2,[76,77] TiO_2,[78] UO_2 [79] there are branches for compounds with the composition of diphosphates: SiP_2O_7, TiP_2O_7, and UP_2O_9. In the first of these compounds various methods have shown the existence of the diphosphate ion[78,80,81,82]. An orthophosphate is not formed in the system with SiO_2; other investigators have not confirmed the report[76] of its formation. The separation of crystalline compounds with composition intermediate between the diphosphate and orthophosphate is characteristic: $Si_2P_2O_9 = SiP_2O_7.SiO_2$; $U_2P_2O_9 = UP_2O_7.UO_2$, close in composition to the $2Pb_2P_2O_7.$ $.PbO$ mentioned above[62]. These compounds and others which contain more basic oxide that the orthophosphate do not correspond to the formula of the chain polyphosphates $M_{n+2}P_nO_{3n+1}$.

In the $MoO_3-P_2O_5$ system compounds corresponding to the formulae $MoO_2(PO_3)_2$ (part of the Mo has a lower valency) and $(MoO_2)_2P_2O_7$ have been isolated[83]. As chromatography showed, the first is a polyphosphate with long chains, the second, according to the chemical analysis, is a diphosphate. Compounds of analogous composition but not isomorphous with the Mo compounds are also obtained with WO_3;[83] the composition of their anions could not be found. Schulz's results[83] suggest that the branch of the compounds with the diphosphate formula should extent to the trioxide branch, that is, orthophosphates are not formed in this or in the other system. But since the equilibrium diagrams have not been studied this conclusion needs to be checked.

2. "Metaphosphate–Oxide of Another Metal" Systems

Systems formed from the metaphosphate of one metal and the oxide of another metal constitute the diagonals of the trapezium in the lower part of Fig. 1 and can be represented as sections of the M^I, $M^{II} \parallel O$, PO_3 reciprocal systems. The correctness of this conclusion is confirmed by the experimental results[84-86] on the systems in which M^I = Na or K and M^{II} = Zn: the melts corresponding to the point of intersection of the diagonals appear to be saturated with the same phase (the mixed diphosphate $Na_2ZnP_2O_7$ or $K_2ZnP_2O_7$) irrespective of the initial components: $Zn(PO_3)_2$ and alkali metal oxides, or ZnO and alkali metal metaphosphates. But unlike many well-known salt systems in the present systems both the diagonal sections are stable, that is, they correspond to binary systems having one common branch of mixed diphosphate; its figurative point corresponds to the intersection of the diagonals of the square which represents the reciprocal system. The remaining branches of both sections, apart from the branches of the components, belong to the products of the initial substances—mixed phosphates, which are distinguished in the present systems by the ratio of the cations and even by the anions. In the Na, $Zn \parallel O$, PO_3 system the $NaPO_3-ZnO$ diagonal section[84] has $Na_3ZnP_3O_{10}$ and $NaZnPO_4$ branches (in addition to the branch of the mixed diphosphate); the $Na_2O-Zn(PO_3)_2$ diagonal section[85,86] probably the branches of $Na_2Zn_4P_8O_{25}$ (the structure of the anion was not established) and tentatively, the branch of the mixed orthophosphate. In the K, $Zn \parallel O$, PO_3 system[85,86] on the KPO_3-ZnO and $K_2O-Zn(PO_3)_2$ diagonal sections the compounds $K_3ZnP_3O_{10}$, $KZnPO_4$ and respectively $K_4Zn_3(P_3O_{10})_2$ and (probably) $K_4Zn(PO_4)_2$ are formed.

In the rest of the "$NaPO_3$–basic oxide of another metal" systems studied (M^{II} = Mg;[84] Cd, Pb, Mn;[87] Fe^{3+};[88] Al;[89] Ce, Nd, Sm [90]) mixed salts are also formed: diphosphates (in all the systems with a doubly-charged cation) of the $Na_2M^{2+}P_2O_7$ type; diphosphates with a triply charged cation $Na_6Al_2(P_2O_7)_3$ and $Na_6Ce_2(P_2O_7)_3$; triphosphates $Na_3MgP_3O_{10}$, $Na_3PbP_3O_{10}$, $Na_9Al_2(P_3O_{10})_3$, and $Na_9Fe_2(P_3O_{10})_3$; the orthophosphates of all bivalent metals

§ The system with Fe_2O_3 has not been studied in the range close to $R = 1$. The diagrams of some systems (for example $LiPO_3-Li_2O$) have not been studied in detail: the compounds were obtained by fusing appropriate amounts of the components.

$NaM^{III}PO_4$; the orthophosphates of tervalent metals $Na_3Fe_2(PO_4)_3$ and $Na_3Al_2(PO_4)_3$. It is characteristic that in the Ce and Nd systems mixed orthophosphates are obtained with an excess of the base $(M^{3+}PO_4)_2.Na_2O$. The structure of the compounds with triply-charged cations is probably not reflected in the formula given since tervalent metals can enter into the anion to some extent judging from their role in the Al and B orthophosphates (see above).

In the dissolution of WO_3 and MoO_3 in $NaPO_3$ only one compound (1 : 1) is isolated, as the equilibrium diagram shows [87,91]. A chromatographic investigation of these compounds obtained preparatively somewhat earlier [92] showed them to be mixed orthophosphates of dioxotungsten $(WO_2)^{2+}$ or dioxomolybdenum $(MoO_2)^{2+}$ and sodium.

In the systems mentioned the phases obtained are mixed salts containing both cations. Not one of the diagrams of diagonal sections obtained has branches for compounds formed in the binary systems (that is, represented by points on the sides of the square of the diagram of the reciprocal system). The formation of mixed Na triphosphates by the Mg, Zn, Pb, Al, and Fe^{3+} cations, which do not give triphosphates in the absence of Na, is characteristic. The absence of a mixed diphosphate in the $NaPO_3 - Fe_2O_3$ diagonal section is noteworthy.

The reactions of the compounds which form the equilibrium diagrams of the metaphosphate–oxide systems reflects a characteristic property of the polyphosphate chains to add an oxygen ion. In doing this one initial anion gives two shorter anions and two intermediate groups are converted into two terminal ones. The scanty thermodynamic results suggest that this reaction is exothermic.

However, the formation of a new anion does not always lead to the stabilisation of the diagonal sections. Li and Na [93] and Li and K [94] diphosphates form simple eutectic systems. The diagonal sections of the Li, Na(K) ‖ O, PO_3 reciprocal systems cannot be binary systems, since at oxide concentrations permitting the formation of the P_2O_7 anion instead of the mixed diphosphates characteristic for stable sections the simple ones will be isolated.

As already shown [95] the breakdown of the $P_3O_{10}^{5-}$ anion into $P_2O_7^{4-}$ and PO_4^{3-} leads to the formation of mixed phosphates only when the oxides of doubly-charged cations of small radius—Mg^{2+}, Cd^{2+}, Zn^{2+} (and, according to de Carli [87], also Pb^{2+}) dissolve in sodium triphosphate. When SrO and BaO dissolve, Sr(Ba) diphosphate and sodium diphosphate are obtained separately [95]. Therefore unstable diagonal sections are possible in the Na, Zr(Ba) ‖ O, PO_3 systems. Other phenomena are associated with the instability of the diagonal sections in the K, Na ‖ PO_3, P_2O_7 system [96]; the system passes through the field of the mixed tripolyphosphate $Na_5P_3O_{10}.K_5P_3O_{10}$, the figurative point of which lies off the diagonal sections.

The interaction of $NaPO_3$ with basic oxides does not exhaust the reactions of the compound observed in recording heating curves of annealed melts. When TiO_2, Fe_2O_3, CdO, CuO, PbO, or Sb_2O_3 are held for a long time in $NaPO_3$ melt substances were isolated which could be regarded as products of the replacement of part of the Na in the hypothetical compound $Na_{15}P_7O_{25}$ by another metal; these substances are double decomposition products [97]. During this the melt is enriched in basic oxides, which in one or another form should be separated in further crystallisation of the melt [88].

In the high-temperature treatment of metals by pressure using $NaPO_3$ as lubricant substances were also found [98] which could not be represented as products of the reaction of the metaphosphate with iron(III) oxide but have another polymeric structure.

It has been observed [99,100] that silicon, on being dissolved in $NaPO_3$ melt separates in the form of cristobalite. According to Schwarz [101], notwithstanding earlier statements, silicon does not form a compound with $Na_4P_2O_7$, which separated from the melt as cristobalite. However, $NaPO_3 - SiO_2$ glasses were found by X-ray diffraction [102] to have the P–O–Si bond, that is, are silicophosphates. Thermodynamic calculations also showed experimentally [103] that SiO_2 displaces P_2O_5 from $Ca_3(PO_4)_2$. An even more acid oxide—liquid SO_3—is reported [104,105] to displace P_2O_5 from meta-, tri-, di-, and ortho-phosphates even below 100°C, with the formation of $Na_2S_2O_7$ and $K_2S_3O_{10}$.

3. Systems of Two Polyphosphates with a Common Anion

Systems of two phosphates with a common anion correspond to horizontal sections in the composition triangle (Fig. 1). The common anion in metaphosphates is conventional, therefore at a single figurative point it corresponds to ring phosphates with various n, and chain phosphates. As all the experiments show, these systems are binary. The following metaphosphate systems have now been studied¶: Li–Na, Li–K, Li–Cs, Na–K, [106,107] Na–Ca, [108,109] K–Ca, [110,111] K–Mg, [111] K–Cu, [112] Na–Zn, K–Zn, [113] Mg–Zn, [114] Cd–Zn. [115] In these systems except for the first and the last two, there is a single congruently melting compound $2NaPO_3.KPO_3$, $4NaPO_3.Ca(PO_3)_2$, $2KPO_3.CU(PO_3)_2$ and the 1 : 1 type. In the $LiPO_3 - NaPO_3$, $Mg(PO_3)_2 - Zn(PO_3)_2$, and $Cd(PO_3)_2 - Zn(PO_3)_2$ systems there are extensive ranges of solid solutions up to a continuous series.

These facts show that the formation of mixed polyphosphates is favoured by a difference in the generalised moments of the cations† ($\mu = Z/r$ where Z is the charge, and r the radius of the ion) as in the halide systems in which, during the formation of the compounds, complex anions with covalent bonds are formed to a certain extent. The formation of the compounds $4NaPO_3.Ca(PO_3)_2$, [109,118] $KPO_3.MgPO_3$, and $KPO_3.Ca(PO_3)_2$, [111] which was studied chromatographically, is accompanied by the reorganisation of the anions: all three double salts are trimetaphosphates, whereas $Mg(PO_3)_2$ isolated from melts or glasses is a tetrametaphosphate [19] and $Ca(PO_3)_2$ and KPO_3 have chain anions. Many compounds obtained by fusing oxides with monosubstituted phosphates (for example, by Mehrotra and Gupta [119]) only partly reflected by the equilibrium diagrams in earlier papers, do not contradict the above observations about the connection of the formation of the compounds with the ratios of the crystal-chemical characteristics of the cations.

Polyphosphates do not differ from other salts as regards the conditions of formation of solid solutions. The difference in the anions (chains in $LiPO_3$ and rings in $NaPO_3$), is evidently of no significance, despite the view of Tamman and Ruppelt [120] who associate the absence of solid solutions in the $KPO_3 - NaPO_3$ system with the difference in the anions: $NaPO_3$ is isolated from the melts as trimetaphosphate, that is, with a cyclic anion, KPO_3 as Kurrol's salt, which has a chain anion. The compound which is formed in the $KPO_3 - NaPO_3$ system is similar to that from the system of the sulphates of these metals.

¶ We mention only the most complete investigations.

† Semenchenko [116,117] first showed the value of μ, which characterises the interaction of the species in ionic liquids; we have used this term.

In the Cd, Mg, Zn ‖ PO_3 ternary system, which has been partly investigated[115], solid solutions with $Mg(PO_3)_2$ structure predominate.

In the system of the incongruently melting sodium and potassium tripolyphosphates, which has been studied as a section of the K, Na ‖ PO_3, P_2O_7 reciprocal system[96] the compound $Na_5P_3O_{10}.K_5P_3O_{10}$ is formed it melts incongruently with the formation of solid solutions of diphosphates.

New anions do not arise in the diphosphate systems that have been studied. These systems do not differ from the usual systems with a common anion (see, for example, Refs. 93 and 94).

V. PHYSICAL PROPERTIES OF MOLTEN PHOSPHATES

1. Individual Phosphates

Of the physical properties of molten phosphates, the surface tension σ and the density ρ have been studied most. In 1917 Jaeger[121] first applied a method he had developed for measuring σ and ρ at high temperatures to $NaPO_3$ and KPO_3 melts. Callis and coworkers[122] measured σ and ρ for $NaPO_3$ and calculated the degree of polymerisation by the Eötvös equation in the Foreland form, and using the Sugden parachor, to be 9 and 1 respectively. With allowance for the assumptions made, they considered their results as "weak confirmation of the theory of disordered reorganisation". The values of σ and ρ for $NaPO_3$, KPO_3, and $Ca(PO_3)_2$ explained[123] the decrease in σ along the Ca, Na, K series by the decrease in the "coefficient of extension of the oxygen anion" analogous to that of the generalised moments μ (see p. 866).

Results obtained[124-126] on σ for Li, Na, K, Cs, Ca, Sr, Ba, Zn, and Mg metaphosphates were used for constructing a plot of the surface tension of the metaphosphates against μ for the cations (Fig. 4); the same smooth curve was obtained as for halides, nitrates, etc., but with the difference that unlike these salts there was not a sharp maximum in the region of Sr and Ba. From the curve for the variation of σ for salts with a common cation with the generalised moments of the anions it is found[127] that the value of μ for alkali metal metaphosphates approximately corresponds to the generalised moment of the terminal PO_4^{2-} groups, irrespective of the thermodynamically estimated radius of the orthophosphate ion.

The negative values of the temperature coefficients $d\sigma/dT$ of metaphosphates on an absolute scale are several times less than for other salts. From the values of the temperature coefficients $d\sigma/dT$ the cations of the metaphosphates can be arranged in the following order for the decrease in absolute values of this quantity: K > Na > Ca, and when μ is plotted as a function of the cations a straight line is obtained[123]. This relation was extended[125] to metaphosphates with other cations. $Zn(PO_3)_2$ has[125] a positive $d\sigma/dT$, like B_2O_3 in certain silicates but differing from most of the salts studied. According to Krivovyazov[86] positive values of $d\sigma/dT$ for $Zn(PO_3)_2$ are due to the chains in its melts being mainly connected ("cross-linked") through the Zn atoms, which have fourfold coordinations in this respect.

These ideas follow from the investigations of Zn phosphate glasses[128-130]. With rise in temperature the concentration of the "cross-linked" chains, which are surface active in relation to the other constituents of the melt decreases, which is contrary to the decrease in σ brought about by the decrease in the interparticle interaction as the temperature is raised. The release of Zn from fourfold coordination on heating is also reflected in the volume properties of $Zn(PO_3)_2$. As has been shown[86], the absolute value of $d\rho/dT$ of $Zn(PO_3)_2$ is only a fifth of $d\rho/dT$ of $NaPO_3$ and a tenth the value for the unpolymerised salts. The explanation is that the non-cross-linked chains, the concentration of which increases on heating, permit more compact packing than the "cross-linked" chains, which counteracts the thermal expansion. The more compact packing of the chains is accompanied by greater disorder, which can be explained by a decrease in entropy as the surface increases, which follows from the positive temperature coefficients $d\sigma/dT = -\Delta S$. This explanation is, for $Zn(PO_3)_2$, better founded than the ideas about elongation[131,132], the smoothing out of buckling during the increase of the surface and crumpling of the chains of the surface layer. The formation of the $Zn(PO_3)_2$ surface should take place with liberation of heat, because $\Delta S < 0$. The results[133] on σ and ρ for Li, Na, Ca, and Zn metaphosphates confirms the relation between $d\sigma/dT$ and μ; as Krivovyazov and coworkers[125] found, $d\sigma/dT$ for $Zn(PO_3)_2$ is positive, whereas $Ca(PO_3)_2$ has a small negative temperature coefficient.

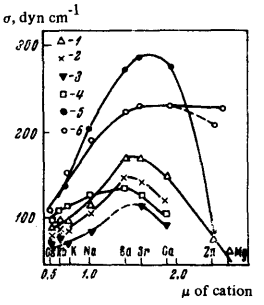


Figure 4. Dependence of the surface tension of metaphosphates on the generalised moments of the cations[122]: *1*) chlorides; *2*) bromides: *3*) iodides; *4*) nitrates; *5*) borates; *6*) metaphosphates.

The internal friction η was studied only for $NaPO_3$; according to Arndt[134] it is 200 times η for NaCl at the same temperature, but only one thirty-fifth that for B_2O_3 heated to 1000°C. The results[135] on η for $NaPO_3$, also calculated by the Bachinskii equation, showed that the viscous flow cell contains not more than eight PO_2 groups—a number close to that found[122] for the degree of polymerisation by the Eötvös equation. Whether the chain segments move separately or the number of PO_4 units in the cell corresponds to a mean length of the reconstructed chains, is thought to be uncertain[122]. On this basis[49,136] it has been found with the aid of the Bachinskii equation that the viscous flow cell contains 30 groups. The values obtained are several orders of magnitude less than found by the investigation of solutions and crystals[137-139].

The vapour pressure of molten phosphates has been studied very little. According to Storonkin and Bobrov's results[140] the vapour pressure of $Al(PO_3)_3$ at 1450°C reaches 115 mmHg. As regards the vapour pressure or dissociation pressure of other metaphosphates there are only notes made in passing that the pressure of some metaphosphate

melts is "insignificant"[49], that dissociation is not noted on heating a melt for 8 h at 1000°C;[141] on the other hand there is a report that above 1000°C "after some time" there is an appreciable loss of P_2O_5;[123] loss of P_2O_5 by calcium metaphosphate has also been noted[55]. Information on the electrical conductivity of molten metaphosphates has been given[142].

2. "Metaphosphate–Oxide" Systems

Of the properties of "metaphosphate–oxide of the same metal" melts the attention of investigators has been mostly directed towards surface and volume properties. The $NaPO_3$–Na_2O system has been studied[122]; the increase in σ and ρ (at constant temperature) with increase in R is explained by the shortening of the chains, this conclusion being drawn from the titration of terminal groups of aqueous solutions of the quenched glasses. Similar conclusions were drawn[123] for the $NaPO_3$–Na_2O, and KPO_3–K_2O systems, studied up to $R = 2$, and the $Ca(PO_3)_2$–CaO system studied up to $R = 1.66$. The slope of the straight lines showing the variation of σ with R increases with increase in μ for the cation. The increase in σ with R is explained by the increase in the "bond density" near the surface. With increase in R there is a decrease in $d\sigma/dT$ for every system‡, that is, the absolute values of $d\sigma/dT$ increase.

A rise in σ with increase in the concentration of the oxide was found in the $Ca(PO_3)_2$–CaO system[143]. An increase in σ with increase in R was also observed for the $Zn(PO_3)_2$–ZnO system[86]; at $R = 2$ a break is found, due[86,143] to the appearance at this concentration of surface inactive PO_3^- anions. The increase in $d\sigma/dT$ on adding ZnO is explained by the favourable action of the oxide on the breaking at elevated temperature of the surface-active "cross-linked" polyphosphate anions. Only on reaching a certain oxide concentration $R = 1.43$, when few "cross-linked" chains are left does $d\sigma/dT$ decrease with increase in R, remaining positive within the range of ZnO concentrations investigated.

σ and the molar volumes v of binary systems of Li, Na, Ca, and Zn metaphosphates and oxides with the same components for compositions with $R = 1$, 1.5, and 1.66 have been studied[133]. The value of σ increases with R for lithium, sodium, and calcium systems; for the zinc system σ was almost independent of R; $d\sigma/dT$, which is negative for the systems with Li and Na and positive for the systems with Ca and Zn, decreases with rise in R. The positive values of $d\sigma/dT$ were thought to be connected with the tendency of Ca and Zn to give covalent bonds with an oxygen atom and also with the fact that at the same values of R in these systems the chain length is greater than in systems which contain Li and Na, as was shown chromatographically[31]. Objections were raised[133] against the application to phosphates of the explanation[144] connecting the $d\sigma/dT$ of silicates with the subdivision of the anions of polymers on heating, since according to the polarographic determination, the anionic composition of polyphosphates varies little with temperature.

In all the studies made the isotherms of the properties investigated do not reflect the formation of alkali metal triphosphates and calcium hexapolyphosphate shown by the equilibrium diagrams. The formation of diphosphates has been noted only in the system with ZnO. The break found[143] in the $Ca(PO_3)_2$–CaO isotherm corresponds to the $(P_4O_{13})^{6-}$ anion.

The shortening of the chains on the introduction into Li, Na, K, and Ca polyphosphates of oxides with a common cation was shown[17] by investigating the infrared spectra of the glasses. The addition of oxides shifts the peak to higher frequencies. These results confirm the above explanation of the dependence of σ on R and μ.

σ and θ of melts of diagonal sections of the Na, Zn ‖ O, PO_3 and K, Zn ‖ O, PO_3 systems have been studied[85,86]. The isotherms of σ for $Zn(PO_3)_2$–K_2O (or Na_2O) sections have minima which differ from the isotherms described above for the binary systems with a single cation. The formation of mixed oligophosphates, shown by the equilibrium diagrams, does, as in the metaphosphate—(oxide of the same metal) systems, not determine the form of the σ isotherm. On adding Na or K oxide to $Zn(PO_3)_2$ σ does not increase—as in the $Zn(PO_2)_2$–ZnO system—but decreases. In the opinion of these investigators[85,86] the decrease is due to the formation of anionic complexes, the nature of which is uncertain, but which are determined by the tendency of Zn to form covalent bonds. In parallel with this there is the shortening of the polymer chains usual on the introduction of an oxide into the melt[144,145]. Starting from a certain concentration the effect of the latter process on σ predominates—σ starts to increase. The course of the temperature coefficients $d\sigma/dT$ can also be explained by its decreasing on adding Na_2O and K_2O but in some concentration ranges it changes very little since as the temperature is raised the surface-active anionic complexes decompose with the formation of inactive ones. The presence of new anionic complexes in the melts is demonstrated by the positive $\Delta\theta$ of mixing, similar to that which is observed in salt systems[146] in which the formation in the melts of anionic complexes with covalent bonds leads to positive values of $\Delta\theta$. The extensive chemical interactions during the dissolution in $NaPO_3$ melt of the oxides of bivalent and tervalent metals also show the excessive changes in free energies noted[147-149] in studying the chemical and concentration cells containing solutions of Pb, Bi, Ni, and Sb oxides in molten $NaPO_3$.

3. Systems with a Common Anion

The Table gives data on the fusion characteristics, the σ isotherm, $d\sigma/dT$, and $\Delta\theta$ for metaphosphate systems. Systems 1, 2, and 3 were classified as ideal by their investigators[152]; the Zhukhovitskii equation[153] in the form given by Guggenheim[154] was taken as a criterion of the ideality for σ; it has shown[141,155] that in most parts of the salt systems with formation of a compound the singular points on the σ isotherms alter. The behaviour (see Table) of system 3 in melts can be placed in accordance with the fact that from the infrared spectra[150] only the components are present in quenched melts, that is, the compounds dissociate during fusion. The same can also be suggested for system 2. Chromatograms of quenched melts of systems 1, 2, and 3 show the additivity of the anionic composition[133]. System 4 represents a change to the systems containing undissociated compounds in the melts; there are no singular points, but there is a negative departure of σ from that calculated by the Guggenheim formula[133,141]. Systems 5 and 7, the diagrams of which show the formation of compounds[86], and also system 6, for which there are grounds for expecting the formation of compounds by analogy with other systems which contain the same cations, have σ isotherms with minima or breaks

‡ Subsequently the increase in the absolute values of negative quantities will also be termed the loss function.

Isotherms of the properties of binary systems of metaphosphates.

No.	System	Type of diagram, compound	σ isotherm	$d\sigma/dT$	θ or $\Delta\theta$ isotherm
1	$LiPO_3$—$NaPO_3$	eutectic [106, 107]	weakly convex to the composition axis	—	straight line [133, 141, 152]
2	$LiPO_3$—KPO_3	$LiPO_3 \cdot KPO_3$ [106, 107]	ditto [152]	—	—
3	$NaPO_3$—KPO_3	$2NaPO_3 \cdot KPO_3$ [106, 107]	ditto [152]	—	convex away from the composition axis [150, 151]
4	$NaPO_3$—$Ca(PO_3)_2$	$4NaPO_3 \cdot Ca(PO_3)_2$ [108, 109]	ditto [133, 141]	—	ditto [133, 141]
5	$NaPO_3$—$Zn(PO_3)_2$	$NaPO_3 \cdot Zn(PO_3)_2$ [86]	minimum at 50 mole % $NaPO_3$	sign change [86]	with inflection [86, 133, 151]
6	KPO_3—$Ba(PO_3)_2$	—	minimum at ~70 mole % KPO_3 [141]	—	—
7	KPO_3—$Zn(PO_3)_2$	$KPO_3 \cdot Zn(PO_3)_2$ [86]	minimum at ~70 mole % KPO_3 [86, 151]	sign change [86]	with inflection [86, 151]
8	$Ca(PO_3)$—$Zn(PO_3)_2$	—	convex away from the composition axis [133]	—	—

(Fig. 5). The chromatograms of systems 4 and 5 show [133] an increase in the chain length on adding the metaphosphate of a bivalent metal to $NaPO_3$ melt. On this basis it is thought [133] that the change in anionic composition during the formation of compounds in polyphosphate melts leads to lengthening of the chain; the constancy of σ in the region of the minima is attributed to constancy of the concentrations of short and long chains.

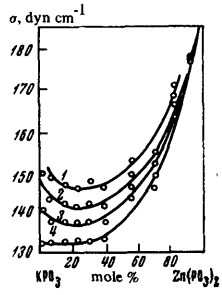


Figure 5. Surface tension of the KPO_3—$Zn(PO_3)_2$ system [86]. Temperature, °C: 1) 800: 2) 900; 3) 1000; 4) 1110.

Melts of systems 4, 5, and 7 are formed from the components with an increase in volume [133]. This is attributed to an increase in the concentration of the long chains under the influence of the doubly-charged cation. According to Krivovyazov [86] the change in $\Delta\theta$ in the last two systems is more complex: at low alkali metal concentrations the $\Delta\theta$ curve is concave ($\Delta\theta < 0$, mixing of the liquid components is accompanied by contraction), at high concentration it is convex away from the abscissa axis ($\Delta\theta > 0$). The shape of the $\Delta\theta$ and $d\Delta\theta/dT$ curves and also the minima on the σ isotherms are explained [86,141,151] by the superposition of effects: the first portions of alkali metal metaphosphate added to $Zn(PO_3)_2$ decrease σ owing to the surface activity of Na (or K) and the formation of surface-active anionic complexes which markedly affect σ. However, during this the volume is not increased§, but reduced, since the destruction of the "cross-linked" $Zn(PO_3)_2$ chains which takes place on the addition of $NaPO_3$ (or KPO_3) has a greater effect than the appearance of a few anionic complexes. Only when there is a high concentration of alkali metal metaphosphates is the concentration of anionic complexes sufficient for the appearance of a $\Delta\theta$ maximum; σ is not sensitive to the appearance of surface-active species, less sensitive to the increase in the concentration of surface-inactive products of the destruction. Only at high alkali metal concentrations does σ increase owing to the accumulation in the melt of surface-inactive cross-linked $Zn(PO_3)_2$ chains and the approach of the composition to pure $NaPO_3$ (or KPO_3).

§ For salts systems in which anionic complexes with predominance of covalent bonds are formed, an increase in volume on mixing is typical [146].

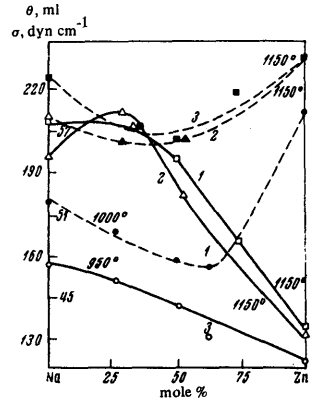


Figure 6. Molar volume (continuous lines) and surface tension (broken lines) of systems of sodium and zinc polyphosphates [133]. R: 1) 1; 2) 1.5; 3) 1.66.

Hence in systems consisting of Zn or Ca metaphosphates and Na or K metaphosphates the change in chain length goes in parallel with complex formation. These connect the phosphate melts with melts of $ZnCl_2$—M^ICl systems [156,157].

σ and θ for binary systems corresponding in composition to the Na and Zn tri- and tetra-polyphosphates have been studied [133]. The nature of the σ isotherms is the same as for systems of the metaphosphates of the same metals (Fig. 6); they have minima. The θ isotherm of the system of tripolyphosphates has a sharply expressed maximum, the system of tetraphosphates a positive departure of θ from a straight line.

The action of Zn and Ca on the change in properties of the alkali metal metaphosphates is thought [133] to be explained solely by the change in the length of the polymeric chains. This point of view is based on chromatographic

results, whereas the conclusion about complex formation[86,151] rests on results of physicochemical analysis. We note that ionic complexes can be decomposed in the dissolution of glasses for the chromatography. Furthermore, the chromatographic behaviour of the polyphosphate ionic complexes is unknown and to deny their existence on the basis of chromatographic results alone is premature.

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