CONDENSED PHOSPHATES AND ARSENATES

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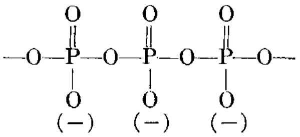
I. Introduction, History, and Nomenclature

A. INTRODUCTION

The concept of a 'condensed phosphate' embraces a group of pentavalent phosphorus compounds in which various numbers of tetrahedral PO_4

groups are linked together by oxygen bridges according to the scheme:



$$-O-\overset{\overset{\large O}{\|}}{\underset{\underset{\large O^{(-)}}{|}}{P}}-O-\overset{\overset{\large O}{\|}}{\underset{\underset{\large O^{(-)}}{|}}{P}}-O-\overset{\overset{\large O}{\|}}{\underset{\underset{\large O^{(-)}}{|}}{P}}-O- \qquad (1)$$

These substances, some of which were recognized more than two hundred years ago (though their special nature was not then realized) have repeatedly been the subject of chemical investigation and of much controversy. The principles underlying their structures were elucidated decisively for the first time in recent decades.

It is impossible to consider in a short article each of the publications relevant to this field which has appeared in the scientific and patent literature; they already far exceed a thousand in number. In the following pages only the basic outline of the development of this branch of research and the present state of our knowledge will be presented, primarily from the standpoint of preparative and structural chemistry.

Since the condensed arsenates and mixed condensed species, the so called arsenatophosphates, have played an essential role in elucidating the structure of some condensed phosphates, these will be considered in a special section. Derivatives of condensed phosphates in which oxygen is partly replaced by another element, such as nitrogen, will be mentioned only where necessary. In the more recent literature there are also a number of publications which are physico-chemical and theoretical in character. These will be considered only in so far as they contribute essentially to special problems of the structure of these substances or to the understanding of their most important properties.

B. HISTORY

1. *Early History up to Graham's Discovery*

When Thomas Clark (*52*, *53*) discovered that ordinary sodium phosphate, $Na_2HPO_4 \cdot 12H_2O$, when heated, loses at first only a part of its water and is transformed to a new compound, sodium pyrophosphate, only after giving up the last part, chemists of his time were presented with difficult

$$Na_2HPO_4 \cdot 12H_2O \xrightarrow{\text{sand bath}} Na_2HPO_4 + 12H_2O \qquad (2)$$

$$2Na_2HPO_4 \xrightarrow{\text{red heat}} Na_4P_2O_7 + H_2O$$

problems. According to the theory of Lavoisier, which was then current, salts were considered as compounds derived from basic and acid oxides and were characterized by the ratio of base to acid which they contained. All the water in a salt was thought of as water of crystallization and nonconstitutional. As a result, the familiar compound $Na_2HPO_4 \cdot 12H_2O$ ($= Na_4P_2O_7 \cdot 25H_2O$) and the new compound $Na_4P_2O_7$ were taken to be different forms of the same substance. A similar situation existed for the stannic acids and some organic compounds. Since no explanation of this could be given, Berzelius (*13*) sought to explain such relationships in terms of the concept of isomerism, which became so important later.

Thomas Graham (*103, 104*) recognized very clearly that water may have different functions in salts, and particularly in the phosphates. He discovered that the different phosphates differed from one another not only

$$NaH_2PO_4 \cdot H_2O, Na_2HPO_4 \cdot 12H_2O \quad \text{and} \quad Na_3PO_4 \cdot 12H_2O \tag{3}$$

in their base to acid ratio, but also in their behavior on heating. When heated, trisodium phosphate loses its water of crystallization without undergoing further change. Graham verified Clark's results for $Na_2HPO_4 \cdot 12H_2O$. For the dihydrogen phosphate, which he knew only in the form without water of crystallization, he observed it went over first of all to an acid pyrophosphate from which salts of a new type, which he called metaphosphates, were formed at a red heat. Since Graham, in common with the

$$2NaH_2PO_4 \xrightarrow{190°C} Na_2H_2P_2O_7 \xrightarrow{\text{red heat}} 2NaPO_3 + H_2O \tag{4}$$

chemists of his time, believed in Lavoisier's theory of salts, according to which there was only one "phosphoric acid," P_2O_5, he saw an explanation for his discovery in the assumption that water can also assume the function of a base and replace other bases in salts. In this way he was able to characterize the three types of phosphate by their different ratios of base to acid. The ordinary phosphates must then contain three molecules of base per molecule of P_2O_5, the pyrophosphates two, and the metaphosphates one, according to the formulas:

Ordinary Phosphates P_2O_5:Base = 1.3

$P_2O_5 \cdot 3Na_2O$	$P_2O_5 \cdot 2Na_2O \cdot H_2O$	$P_2O_5 \cdot Na_2O \cdot 2H_2O$	$P_2O_5 \cdot 3H_2O$

(5)

Pyrophosphates P_2O_5:Base = 1:2

$P_2O_5 \cdot 2Na_2O$	$P_2O_5 \cdot Na_2O \cdot H_2O$	$P_2O_5 \cdot 2H_2O$

Metaphosphates P_2O_5:
Base = 1:1

$P_2O_5 \cdot Na_2O$	$P_2O_5 \cdot H_2O$

All of the water in the salts other than that shown in these formulas was considered as true water of crystallization.

One important discovery by Graham could not be explained in this way. He observed that when NaH_2PO_4 was heated until all the water had been given off, three different forms of sodium metaphosphate resulted. One was a finely crystallized material, readily soluble in water, which we now know as trimetaphosphate, the second a form insoluble in water, the so-called Maddrell's salt, and the third form, Graham's salt, a water-soluble glass, formed by rapidly cooling molten NaH_2PO_4. These three compounds, which differ in many other properties in addition to their water solubility, presented new and difficult problems to the chemists who followed Graham.

2. Development of Current Views

Graham's ideas and his experiments which indicated the existence of different types of phosphates all had the dualistic theory of salts as their background. The first step leading to further progress stemmed from the view which was developed by Gay-Lussac, Davy, and Dulong at about the turn of the century, that acid oxides alone cannot be considered as acids. Acids were thought of rather as hydrogen compounds from which salts were formed when hydrogen was replaced by metals. This view was adopted by Liebig (*175*), who extended it to a theory of polybasic acids by his own observations on salts of organic acids and particularly on the basis of Graham's findings on phosphates. On this basis, the various phosphoric acids, which contain more than one hydrogen atom and which are transformed to acid or neutral salts by partial or complete replacement of the hydrogen atoms by metals, can also be transformed by elimination of water into compounds with a greater number of phosphorus atoms.

On this basis Fleitmann and Henneberg (*93*) started their celebrated study of Graham's metaphosphates. They considered that in the hypothetical series:

$$6Me_2O\cdot 2P_2O_5; \qquad 6Me_2O\cdot 3P_2O_5 \; . \; . \; . \; 6Me_2O\cdot 6P_2O_5 \qquad (6)$$

which Liebig had proposed, it should be possible to discover the compounds $6Me_2O\cdot 4P_2O_5$ and $6Me_2O\cdot 5P_2O_5$. They first attempted to prepare these substances by melting together the appropriate proportions of sodium pyrophosphate ($Na_4P_2O_7$) and Graham's salt ($NaPO_3$). From the solutions of such melts they believed they had obtained in a crystalline form the compounds which we now know as tetraphosphate, $Na_6P_4O_{13}$ (= $6Na_2O\cdot 4P_2O_5$) and decaphosphate, $Na_{12}P_{10}O_{31}$ (= $6Na_2O\cdot 5P_2O_5$). They described them, however, as very liable to decompose and incapable of being recrystallized.

We now know that Fleitmann and Henneberg did not handle these compounds. Their basic reasoning was, however, correct, for the compounds exist, though they belong not to a series with only six members, but to a series which, in principle, has an infinite number of members of the general composition shown below, which we now call polyphosphates,

$$\mathrm{Me}^{\mathrm{I}}_{n+2}(\mathrm{P}_n\mathrm{O}_{3n+1}). \tag{7}$$

The second part of Fleitmann and Henneberg's work dealt with the problem of the differences between the metaphosphates with the composition $NaPO_3$, which Graham had discovered. They started from Liebig's supposition that perhaps the difference between these substances was due to different degrees of polymerization of the acids which they contained. They first investigated the crystalline readily soluble salt, which is obtained by heating NaH_2PO_4 and may readily be purified by recrystallization, and obtained from it a series of salts with other cations which, for the most part, contained water of crystallization. They found that these salts could be formulated with simple whole number atomic ratios only if one assumed that the anion was a trimer. This assumption received particularly strong support from the fact that many double salts of constant composition could be prepared which were of the type of the well-crystallized $BaNa(P_3O_9)\cdot 4H_2O$. Although the argument of the simple whole number atomic ratio in a salt is not, in principle, proof of the degree of polymerization of the anion which it contains, Fleitmann and Henneberg were right in the case of the soluble sodium metaphosphate. The anion of this salt is a trimer and the salt is a member of a series of compounds, $\mathrm{Me}^{\mathrm{I}}_n(\mathrm{P}_n\mathrm{O}_{3n})$, which are called metaphosphates and which differ in their degree of polymerization.

Fleitmann (*92*) was less fortunate in a second investigation in which he tried in an analogous way to determine the degree of polymerization of the two other compounds described by Graham and of a further series of metaphosphates which had been discovered in the interim. Among these was a true tetramer, discovered by Maddrell (*181*) through the copper salt, the anion of which Fleitmann thought to be a dimer. To Graham's insoluble metaphosphate and a large number of analogous water-insoluble salts prepared by Maddrell, he very tentatively assigned monomeric anions, while for the anion of the Graham's water-soluble glass he thought formulation as a hexamer to be the most probable (see Section IV,E,*1*,*a*).

A large number of authors, among whom Tammann (*290*) may be mentioned, who attempted to establish molecular weights from the composition of single and double salts, from the conductivity of their solutions, or from cryoscopic molecular weight determinations in water were no more successful. A large number of interesting and important facts were discovered in the course of this work, but simultaneously many hypotheses were advanced, only a small proportion of which proved subsequently to be correct. On the whole, the chemistry of the metaphosphates remained a closed book until the beginning of this century, and appeared to become more difficult the more it was investigated. Details of this phase of the history of the condensed phosphates cannot be considered here, particularly as this part of the story, with all its by-ways and speculation, is fully described in a monograph by Karbe and Jander (*158*).

At about the beginning of this century three facts were recognized as probably established.

1. There is a group of metaphosphates with the exact composition $Me^{I}_{n}(P_nO_{3n})$ and relatively low molecular weight.

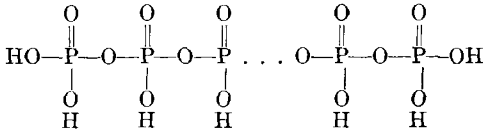
2. A second group embraces the pyrophosphates and the analogous sodium triphosphate, $Na_5P_3O_{10}$, discovered by Schwarz (*263*) and confirmed by Stange (*273*). These were formulated as salts of chain-like anions, as were derivatives with other cations.

3. A third group contains, in addition to the soluble Graham's salt, some of Maddrell's water-insoluble salts and the so-called Kurrol's sodium salt (*291*). These all have the analytical composition $(Me^{I}PO_3)_x$, but different molecular weights were assigned by each of the many authors. This situation was not changed by Pascal's attempt (*219*) to fit the then known "metaphosphates" into a simple but, as we now know, quite inadequate scheme. Indeed, new knowledge was necessary in order to progress.

First of all, Nylén (*209*) established by exact molecular weight determinations in aqueous solution that Fleitmann and Henneberg's 'trimetaphosphate' had indeed a trimeric anion, and that the second metaphosphate of this group was not a dimer, as some authors had supposed, but, as Warschauer (*334*) had found, a tetramer. Views on the nature of the Graham's salt, which had been believed to be a hexamer, were put on a new basis when Lamm and Malmgren (*168*) showed by ultracentrifuge measurements that its anion had a high molecular weight. These authors (*168*) found molecular weights between 100,000 and 140,000 for the "potassium metaphosphate" which was insoluble in water but soluble in solutions of salts of other cations. Shortly afterwards, Karbe and Jander (*158*) used diffusion measurements to establish that the molecular weight of the anion of Graham's salt was between 10,000 and 20,000 and depended on the temperature to which the melts prepared from NaH_2PO_4 had been heated before being quenched. In both of these investigations the compounds were held to be high molecular weight analogs of the trimeta- and tetrameta-phosphates of the composition $(Me^{I}PO_3)_x$.

Treadwell and Leutwyler (*328, 329*) found that, in solutions of Graham's salt, strongly and weakly dissociated acid groups were always detected together, and Rudy and Schloesser (*250*) recognized that the strong and weak acid groups were associated with Graham's salt itself and did not arise from the presence of impurities. All of the authors named, however, regarded Graham's salt as a high molecular weight metaphosphate.

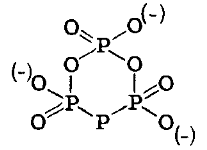
Samuelson (*254*) showed that low and high molecular weight phosphates may be separated with the help of ion exchange resins and that, in such separations, a certain part of the weakly acidic OH groups on phosphorus cannot under any circumstances be separated from the acids corresponding to Graham's salt as long as the acid itself remains undecomposed. These acids must therefore contain a number, mostly very small, of weakly acidic POH groups in addition to a more or less large number of strongly acidic groups. In order to explain this, Samuelson proposed for the acids corresponding to this sort of salt a chain form shown, where the weakly acidic OH groups represent the end groups of the chains. In proof of this formulation



$$\mathrm{HO{-}\underset{\underset{H}{O}}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{\underset{H}{O}}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{\underset{H}{O}}{\overset{O}{\overset{\|}{P}}}\;.\,.\,.\;O{-}\underset{\underset{H}{O}}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{\underset{H}{O}}{\overset{O}{\overset{\|}{P}}}{-}OH} \qquad (8)$$

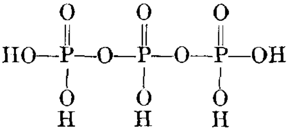
Samuelson was able to show that the ratio of strongly acidic POH groups, which can be titrated up to pH 4.5, to those titrated between pH 4.5 and pH 9, is a measure of the molecular weight of the corresponding acid and gives the same value as Karbe and Jander found and as had led Lamm and Malmgren (*168*) to the view that this group of "metaphosphates" probably possesses high molecular weight chain-like anions.

There are other grounds for considering that compounds of the type of Graham's salt do not belong to the same group as the trimeta- and tetrameta-phosphates. Rudy and Schloesser (*250*) had in fact found that the POH groups in the acid corresponding to the trimetaphosphate are all equally strong. As Treadwell and Leutwyler (*328, 329*) had done a little earlier, they proposed for the anion a ring structure of the type



(9)

In addition, Pauling and Sherman (*222*) had proposed a ring structure for the anion of aluminium tetrametaphosphate on the basis of a crystal structure determination. The triphosphate $Na_6P_3O_{10}$ must, then, have the chain structure already proposed by Schwarz (*263*), for Rudy and Schloesser (*250*) showed that the acid corresponding to the triphosphate has three strongly and two weakly acidic OH groups with the weakly acidic groups



$$\mathrm{HO{-}\underset{\underset{H}{O}}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{\underset{H}{O}}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{\underset{H}{O}}{\overset{O}{\overset{\|}{P}}}{-}OH} \qquad (10)$$

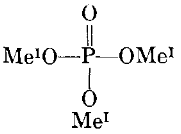
forming terminal groups, as in the long-chain compounds. This corresponds with the general experience that, with several acid OH groups attached to a central atom, the first is stronger than the second, which is stronger than the third, and so on.

C. NOMENCLATURE

Thus far it has been established that there are two types of polymeric phosphates:

1. Phosphates with ring-like anions which correspond exactly with the formula $\mathrm{Me}_n{}^{\mathrm{I}}(\mathrm{P}_n\mathrm{O}_{3n})$ found by Graham for the metaphosphates. Only these will be designated, following a usage developed in the meantime, as *metaphosphates*.

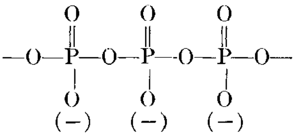
2. Phosphates with chain-like anions of the composition $\mathrm{Me}^{\mathrm{I}}_{n+2}(\mathrm{P}_n\mathrm{O}_{3n+1})$ or $\mathrm{Me}_n{}^{\mathrm{I}}\mathrm{H}_2(\mathrm{P}_n\mathrm{O}_{3n+1})$, which is almost equivalent at high values of *n* to Graham's formula MePO_3. Salts with high molecular weight anions (see Section IV,E), the terminal groups of which are generally POH groups, belong to this class, as do salts of the type of triphosphate (n = 3), pyrophosphate (n = 2) and orthophosphate, which is the monomeric first member of the series



$$\mathrm{Me^{I}O{-}\underset{\underset{\displaystyle Me^{I}}{\displaystyle O}}{\underset{|}{\overset{\overset{\displaystyle O}{\|}}{P}}}{-}OMe^{I}} \qquad (11)$$

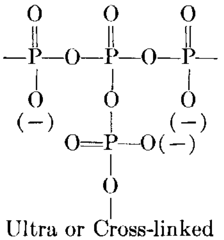
The corresponding monophosphoric acid has one strongly acidic POH group and two weakly acidic "end groups." The name *polyphosphate* is given to this second group of condensed phosphates and one can distinguish between species of low molecular weight, intermediate polymers (oligomers) and high polymers. Thus one refers to triphosphates, tetraphosphates etc., or, particularly in technical publications, to tripoly- and tetra-poly-phosphates and differentiates them from trimeta- or tetrameta-phosphates. A point common to both groups of polymeric phosphates is that they have a larger or smaller number of PO_4 tetrahedra joined together by common oxygen atoms.

A further group, the *ultra-polymeric or cross-linked-phosphates*, which were first mentioned by Kroll (*165*), are characterized by the fact that "tertiary" phosphate tetrahedra are present in addition to the ordinary P—O—P groupings. These are joined with other tetrahedra by three oxygen atoms and not by two, as in the meta- and poly-phosphates. They will be discussed in Section V.



$$-\mathrm{O}-\underset{\substack{|\\ \mathrm{O}\\ (-)}}{\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{P}}}-\mathrm{O}-\underset{\substack{|\\ \mathrm{O}\\ (-)}}{\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{P}}}-\mathrm{O}-\underset{\substack{|\\ \mathrm{O}\\ (-)}}{\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{P}}}-\mathrm{O}-$$

Meta- and Poly-phosphates



Ultra or Cross-linked Phosphates

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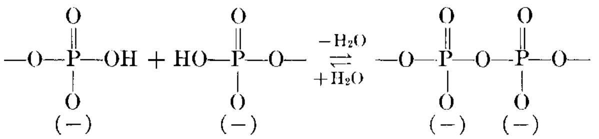
All three groups come under the heading of *condensed phosphates*, for the simplest method for their preparation is still by condensation reactions in which phosphate tetrahedra are condensed by elimination of water.



$$-\mathrm{O}-\underset{\substack{|\\ \mathrm{O}\\ (-)}}{\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{P}}}-\mathrm{OH}+\mathrm{HO}-\underset{\substack{|\\ \mathrm{O}\\ (-)}}{\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{P}}}-\mathrm{O}- \underset{+H_2O}{\overset{-H_2O}{\rightleftarrows}} -\mathrm{O}-\underset{\substack{|\\ \mathrm{O}\\ (-)}}{\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{P}}}-\mathrm{O}-\underset{\substack{|\\ \mathrm{O}\\ (-)}}{\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{P}}}-\mathrm{O}- \qquad (13)$$

It is also common to all condensed phosphates that, on appropriate treatment with water, they are hydrolytically broken down to ortho- or monophosphates, usually by a series of intermediate reactions.

Even before the above facts and structural considerations were generally appreciated by chemists, some of the polyphosphates, such as Graham's salt and the triphosphate, for example, had acquired major technical importance (*90*, *91*, *127*, *129*, *249*). About thirty years ago the study of condensed phosphates was taken up from many sides in attempts to determine their structures and, from their structures, to understand their properties. Preparative methods, physico-chemical investigations and theoretical considerations were all brought into play in order to develop this branch of inorganic chemistry to a point where, today, the perspective is clear and we can regard it as well-investigated.

In the following pages an attempt is made to depict the present state of our knowledge. In so doing, a systematic rather than a historical approach has been adopted. A recent comprehensive treatment of the whole field is also given in J. R. van Wazer's monograph "Phosphorus and its Compounds" (*340*). Older reviews are those of Topley (*326*) and Quimby (*232*).

II. Phase Relationships in Condensed Phosphates with Various Cations

A systematic investigation of phase relationships in the field of condensed phosphates is only just beginning, though there is an extensive literature on the subject. Two types of phase diagram are used. The first shows the interrelationship of substances formed by thermal treatment of given starting materials in the free atmosphere, and not necessarily under equilibrium conditions. The second type represents the relationship between substances occurring as stable phases under equilibrium conditions, and especially under particular pressures of water vapor. The first of these methods has the greater practical significance as yet (*125*).

A. CONDENSED PHOSPHATES IN THE SYSTEM $Na_2O—P_2O_5—H_2O$

The first attempt to set out a phase diagram of the first type for the system $NaH_2PO_4—NaPO_3$ in accordance with present ideas was made by Boullé (*21, 23, 24*). Later his diagram was several times amplified and improved (*218, 249, 302, 311, 340*) until, today, our knowledge of the substances which can be prepared from $NaH_2PO_4 \cdot H_2O$ can be represented by the following diagram (Fig. 1).

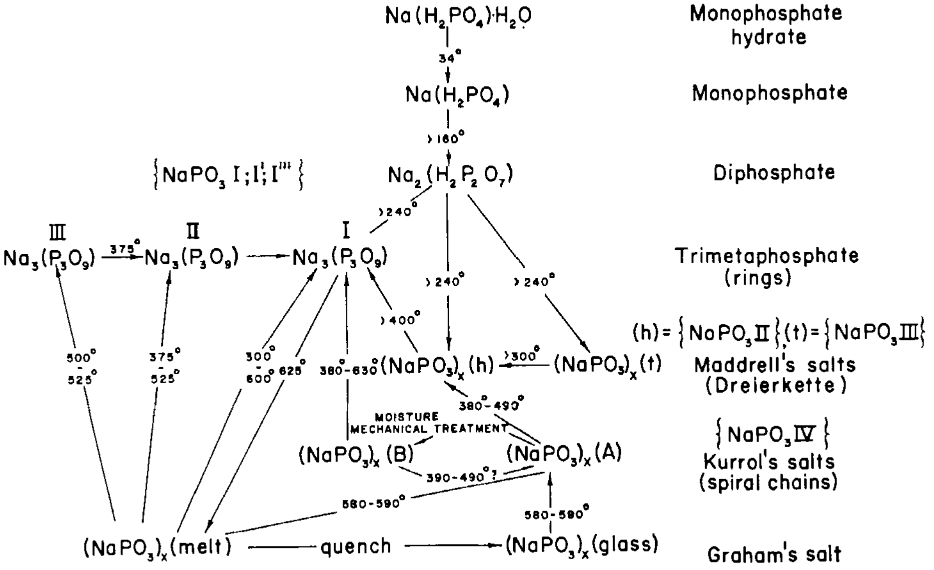
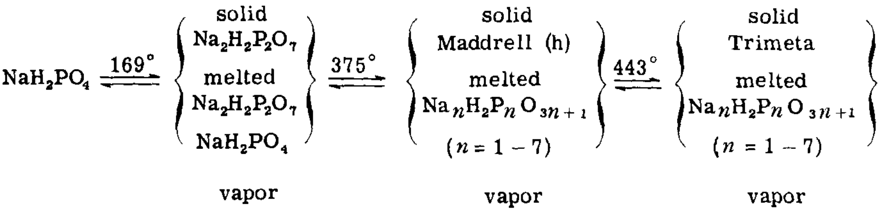


FIG. 1. Condensed phosphates prepared by heating $NaH_2PO_4 \cdot H_2O$ and their interrelationships.

On dehydration of sodium dihydrogen monophosphate in a normal atmosphere it first passes over completely to the acid diphosphate, $Na_2H_2P_2O_7$, without forming amorphous phases. From this at temperatures above 240°C trimetaphosphate I and Maddrell's salt are formed in proportions which appear to depend in the first place on the water vapor pressure (*229*). Usually the low-temperature form of Maddrell's salt is the primary product, though the high temperature modification (into which the low temperature modification is transformed above 300°C) often occurs as well. From the former the trimetaphosphate is formed from about 400°C, and this is the stable phase up to the melting point (625°C). If the melt is quenched, it solidifies to the glass-like Graham's salt, the mean chain length of which (see Section IV,E,*1*,*a*) depends on the water vapor pressure and the melting temperature (*364*). On tempering at a little below the melting point and inducing crystallization by local cooling with the help of any infusible foreign substance, the melt goes over into form A of Kurrol's salt, from which form B is produced by mechanical treatment or by exposure to moist air. Further cooling of form A gives Maddrell's salt (h), while form B yields trimetaphosphate (*316*). Two unstable forms of trimetaphosphate, formed by tempering the supercooled melt at ~525°C have been described (*114*, *173*).

Under an equilibrium pressure of water vapor the system looks much simpler.



$$NaH_2PO_4 \xrightleftharpoons{169^\circ} \begin{array}{c} \left\{\begin{array}{c} \text{solid} \\ Na_2H_2P_2O_7 \\ \text{melted} \\ Na_2H_2P_2O_7 \\ NaH_2PO_4 \end{array}\right\} \\ \text{vapor} \end{array} \xrightleftharpoons{375^\circ} \begin{array}{c} \left\{\begin{array}{c} \text{solid} \\ \text{Maddrell (h)} \\ \text{melted} \\ Na_nH_2P_nO_{3n+1} \\ (n = 1 - 7) \end{array}\right\} \\ \text{vapor} \end{array} \xrightleftharpoons{443^\circ} \begin{array}{c} \left\{\begin{array}{c} \text{solid} \\ \text{Trimeta} \\ \text{melted} \\ Na_nH_2P_nO_{3n+1} \\ (n = 1 - 7) \end{array}\right\} \\ \text{vapor} \end{array}$$

Applying the phase rule, it is found that, in the two component system $NaPO_3 + H_2O$, a maximum of four phases is possible at the quadruple points (*199*, *302*). In addition to, at the most, two crystalline substances and water vapor, an amorphous glass-like phase is always present. This phase consists of mixtures of polyphosphates, the chain length of which rises with increasing temperature. Only $Na_2H_2P_2O_7$, Maddrell's salt (h) and trimetaphosphate occur as stable solid phases in addition to NaH_2PO_4.

The second important section of the complete system Na_2O—P_2O_5—H_2O is the much-studied dry system $NaPO_3$—$Na_4P_2O_7$ (Fig. 2). In this system, in addition to trimetaphosphate, diphosphate, and melt, we find the triphosphate $Na_5P_3O_{10}$, which melts incongruently at 622°, forming crystalline diphosphate, $Na_4P_2O_7$ (*203*). It is therefore obtainable in the pure state only by tempering at below 622°C melts of the corresponding composition, which have solidified to a glass. (For details see Section IV,B,*1*).

B. Systems with Other Cations

The dry system K_2O—P_2O_5 is completely analogous to that with Na_2O (*202*). There is again a triphosphate, $K_5P_3O_{10}$, which melts incongruently at 641.5°C, forming the crystalline diphosphate $K_4P_2O_7$. On the other hand the salt KH_2PO_4 behaves differently from NaH_2PO_4 on heating in the free atmosphere. When it is heated stepwise to higher temperatures, the constitutional water is given off and the high molecular weight polyphosphate, the so-called Kurrol's potassium salt C (*213*), is produced without observable amounts of intermediate products. There is always an arrest point in the dehydration curve, which was at one time interpreted in terms of the supposed formation of di- or tetra-phosphate. The arrest point, however, arises from the fact that a solid crust of high-molecular polyphosphate forms round the crystallites of KH_2PO_4. This crust breaks down if the internal pressure due to water which has been set free becomes great enough. The high water pressure inside the crust also brings about disproportionation of oligophosphates, which are produced initially, into the two crystalline phases KH_2PO_4 and Kurroll's potassium salt. The intermediate

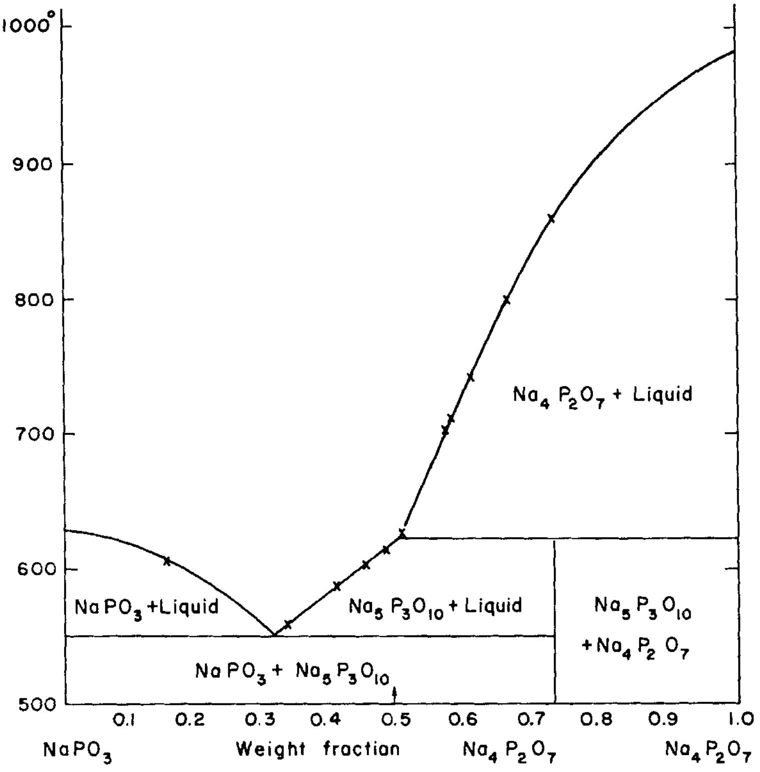


FIG. 2. Phase diagram of the system $NaPO_3$–$Na_4P_2O_7$ according to Morey and Ingerson (*203*).

oligophosphates are easily detected if the dehydration is done under increased water vapor pressure or if KH_2PO_4 is heated directly to higher temperatures. In the direct heating of KH_2PO_4 a lattice compound $2KH_2PO_4 \cdot K_2H_2P_2O_7$ (*25, 302*) occurs as an intermediate; this compound is obtained only by reaction in the solid state.

The compound $Li(H_2PO_4)$ (*215, 302*) and the acid $H(H_2PO_4)$ (*143, 149, 210, 314*) behave differently from the usual alkali hydrogen phosphates, though they resemble one another. Both are transformed gradually into a whole series of polyphosphates with continuous loss of water. As is shown in the chromatogram in Fig. 3, none of these products occurs alone at any time, and finally the whole sample is made up of high-molecular lithium polyphosphates or polyphosphoric acids. There are two crystalline forms of high molecular $Li_xH_2P_xO_{3x+1}$, the low temperature form always being metastable. The ammonium compound $NH_4H_2PO_4$ behaves similarly to LiH_2PO_4 except that ammonia is partly lost on heating. As a result part

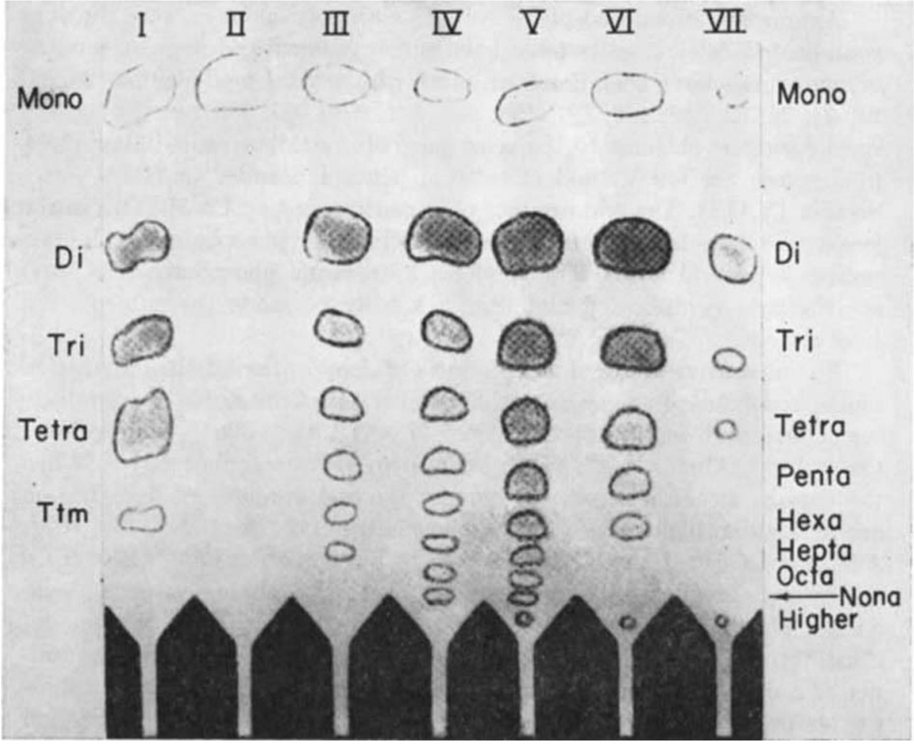


FIG. 3. Chromatogram of the dehydration products of LiH_2PO_4 obtained at various temperatures.

of the salt goes over into polyphosphoric acid and the rest into water-insoluble, high molecular ammonium polyphosphate (*302*). Dehydration of CsH_2PO_4 appears to be analogous to that of KH_2PO_4 (*215*).

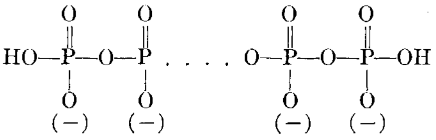
In the much-studied system $NaPO_3$—$Na_4P_2O_7$—$K_4P_2O_7$—KPO_3 the equilibrium phases occurring are the compound $Na_5P_3O_{10} \cdot K_5P_3O_{10}$, which, like its triphosphate components, melts incongruently at 512°C, and the compound $3NaPO_3 \cdot KPO_3$ (*200, 202*), which is recognized as a mixed trimetaphosphate, $K_3(P_3O_9) \cdot 3Na_3(P_3O_9)$ (*113*).

Among condensed phosphate systems with polyvalent cations, the very complicated calcium salts have been much studied and a great number of compounds have been detected, often with several modifications (*5, 27, 28, 34, 54, 79, 136, 137, 191, 198, 204, 211, 276, 305, 330*). In this system special interest attaches to the occurrence of crystalline cross-linked phosphates (see Section V) and of calcium pentaphosphate, $Ca_7(P_5O_{12})_2$ (see Section IV,D,*1*). The end-product obtained by heating $Ca(H_2PO_4)_2$ in the free atmosphere is the high-molecular calcium polyphosphate, which crystallizes in several forms. The condensed strontium phosphates (*246, 305*) are similarly complicated and cannot readily be made the subject of a brief review.

A comparative study of the products of dehydration of the dihydrogen monophosphates of polyvalent cations showed that the stable end-products for cations with ionic radii between 0.57 and 1.03 Å (Cu^{++}, Mg^{++}, Ni^{++}, Co^{++}, Fe^{++}, Mn^{++}, Zn^{++}, Cd^{++}, Al^{+++}) are tetrametaphosphates. When the cations are either larger or smaller the end-products of dehydration are crystalline high-molecular polyphosphates (Li^+, Be^{++}, K^+, Rb^+, Cs^+, Ag^+, Zn^{++}, Cd^{++}, Hg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Pb^{++}, Cr^{+++}, Fe^{+++}, Bi^{+++}). In the case of the alkali salts only sodium trimetaphosphate occurs as a condensed phosphate with a cyclic anion (*304, 305*). Up to the present, an alkali tetrametaphosphate has not been observed as the dehydration product of a dihydrogen monophosphate. Consequently, alkali tetrametaphosphates are obtainable only indirectly. Reference is made later (Section IV,C,*4*) to the fact that the tetraphosphates of barium, lead, and bismuth are formed as crystalline phases from melts of the corresponding composition. There are also reports of various forms of several condensed phosphates of tervalent iron and aluminum (*31, 242, 369*).

III. Condensed Phosphates with Cyclic Anions. The Metaphosphates

The group name "Metaphosphate" includes all compounds whose ions have the composition $(PO_3)_n{}^{n-}$. On the hypothesis, which, hitherto, has not been disproved by any experiments, that pentavalent phosphorus in its oxygen compounds always has a coordination number of 4 with respect to oxygen, these compounds can only have cyclic anions. It is true that analysis of high-molecular polyphosphates with chain-like anions yields values which may approximate closely to the composition $(PO_3)_x \frac{1}{z} Me_x^z$. In fact, however, the chain ends are always terminated by OH groups (*254*), so that the composition of the anions is $(H_2P_xO_{3x+1})^{x-}$ and not

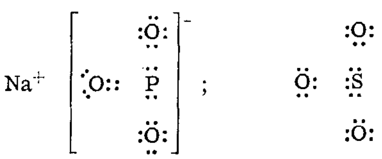


$$\mathrm{HO{-}\overset{\overset{O}{\|}}{\underset{\underset{O^{(-)}}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O^{(-)}}{|}}{P}}\;.\;.\;.\;.\;O{-}\overset{\overset{O}{\|}}{\underset{\underset{O^{(-)}}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O^{(-)}}{|}}{P}}{-}OH} \qquad (14)$$

$(PO_3)_x^{x-}$. Contrary to the old nomenclature (*340*), which is still often used, they should no longer be designated as metaphosphates. Such a change in nomenclature is all the more important since the high-molecular polyphosphates in question differ clearly from true metaphosphates in that solutions of true metaphosphates have a neutral reaction since they are salts of strong acids: those of polyphosphates are weakly acidic on account of the free OH end groups. In this review the term metaphosphate will be used only for condensed phosphates with cyclic anions.

A. THE HYPOTHETICAL MONO- AND DI-METAPHOSPHATES

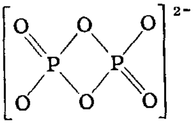
The fact that the old literature refers to compounds with the same name which we now know to be different, and also to identical substances by different names, is due to lack of knowledge of structures, inadequate experimental methods and, above all, to the difficulty of identifying different condensed phosphates. These factors are responsible for reports of the existence of what were thought to be mono- and di-metaphosphates, which are fully discussed in Karbe and Jander's comprehensive review (*158*) but which have proved later to be incorrect (*19, 81, 83, 117, 209, 317*). A *mono*-metaphosphate would have the structure,



(15)

where phosphorus would be tervalent and short of electrons. Such a compound would have the character of a radical, like SO_3, which is a monomer only in the gaseous state. No compound of this sort which is stable under normal conditions is known at the present time. Many indications, however, lead to the conclusion (*119, 120, 364*) that such monomeric radicals occur in the thermal transformation of condensed phosphates, e.g., in that of anhydrous potassium tetrameta- into trimeta-phosphate or of anhydrous sodium triphosphate into sodium diphosphate and high-molecular polyphosphates.

Dimetaphosphates would have the constitution



(16)

where two PO_4 tetrahedra are joined by two oxygen atoms, i.e., by a tetrahedral edge. In accordance with the prediction based on Pauling's rules (*220, 221*) that such polyhedral structures can hardly be stable, no dimetaphosphate is in fact known. Reports of the existence of such compounds have, without exception, proved to be incorrect (*81, 83, 317*). It must be borne in mind, however, that in many cases the designation dimetaphosphate has been used simply as a name which was not linked with a structural representation.

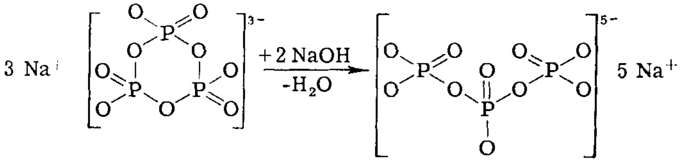
B. The Trimetaphosphates

1. *Preparation and Structure*

The chief representative of the metaphosphates is sodium trimetaphosphate, $Na_3(P_3O_9)$, which was discovered in 1834 by Graham (*102, 103*) as a product obtained by heating NaH_2PO_4, and was recognized as a trimer by Fleitmann and Henneberg (*93*) fifteen years later. The best method of preparing sodium trimetaphosphate is to temper Graham's glass with an exact sodium to phosphorus ratio of 1:1 between 300–600°, but best at 500°, and to recrystallize the resulting white crystalline mass from water. The trimetaphosphate separates at room temperature as the hexahydrate. Its purity can be established by the fact that the solution remains quite clear on adding silver nitrate and, in addition, by chromatography.

Among the salts of trimetaphosphoric acid other than $Na_3(P_3O_9)$, the double salts $Na_9K_3(P_3O_9)_4$ (*113, 200, 202*) and $CaNa_4(P_3O_9)_2$ (*198*) can, like $Na_3(P_3O_9)$, be obtained as stable solid phases from melts of the corresponding composition. The trimetaphosphates of potassium, rubidium, and cesium also may be obtained from mixed melts with other salts, particularly nitrates (*229*). Since the work of Fleitmann and Henneberg a large number of trimetaphosphates of other cations have been prepared, starting from the sodium salt, from solutions of the free acid (*119, 305*). Reference will be made here only to the fact that the pure and mixed alkali salts are easily soluble in water and the alkaline earth metal salts are not easily soluble, e.g., $Na_3(P_3O_9)$, 18% *(362)*; $Ba_3(P_3O_9)_2$, 1.03% *(131)*. The salts which are not easily soluble, however, separate only very slowly from supersaturated solutions. As a result, it is relatively easy to separate trimetaphosphate from polyphosphates which are precipitated from acid solution by Ba^{++}, though only in special cases is the separation quantitative *(71, 130)*. In the system Na_2O—P_2O_5—H_2O there are, in addition to the stable 'normal' form of anhydrous sodium trimetaphosphate *(199)*, which is stable above 443°C under an equilibrium pressure of water vapor, and which melts at 625°C *(198)*, two other metastable forms differentiated by their X-ray powder diagrams. They may be obtained by slowly cooling $(NaPO_3)_x$ melts *(57, 173)*. All three forms give identical solutions in water.

The possibility of preparing mixed salts of the type $CaNa(P_3O_9) \cdot 3H_2O$ led Fleitmann and Henneberg to the conclusion that the trimetaphosphate is a trimer. That this is in fact the case, first appeared likely from freezing point depression measurements with the aqueous solution *(209)* and was finally established cryoscopically in melting Glauber's salt (M_{found} 307–317; $M_{\text{calc.}}$ 306) *(19)*. Proof for the ring structure of the anion, a structure which has been postulated repeatedly in the past *(232, 250, 329)*, is provided by the observation that sodium trimetaphosphate is transformed quantitatively into sodium triphosphate by treatment with $2M$ NaOH *(90, 311)*.



(17)

$$Na_3(P_3O_9) + 2\ NaOH \longrightarrow H_2O + Na_5P_3O_{10}$$

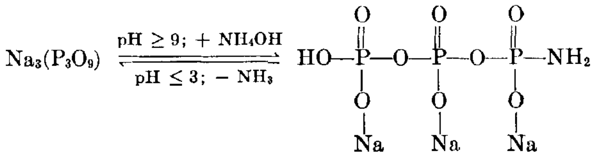
From the Raman spectrum in aqueous solution the anion ring was considered to be planar *(139, 268)*. On the other hand the infrared absorption spectrum *(57)* of crystals of the stable form was interpreted in favor of the more probable chair form *(36)*. The only X-ray study of the crystalline hexahydrate *(40)* published up to the present has proved to be incorrect *(212)*.

Attempts to bring about a direct reversal of the ring cleavage of the trimetaphosphate have so far been unsuccessful. However, ring closure was effected, though through a series of intermediate substances, by treating sodium triphosphate hexahydrate with a mixture of 3 volumes of glacial acetic acid and one volume of acetic anhydride at room temperature. The reaction

$$Na_5P_3O_{10}\cdot 6H_2O + (CH_3CO)_2O \rightarrow Na_3(P_3O_9)\cdot 1H_2O + 2CH_3COONa + 5H_2O \quad (18)$$

is quantitative after five days at 60°C (*306*).

The ring of the trimeta-anion is also broken by aqueous ammonia. The amidotriphosphate results and this reverts to the trimetaphosphate with loss of ammonia on acidifying the solution (*234*).



$$Na_3(P_3O_9) \underset{pH \leq 3;\ -\ NH_3}{\overset{pH \geq 9;\ +\ NH_4OH}{\rightleftharpoons}} HO-\underset{\underset{Na}{|}}{\underset{O}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{Na}{|}}{\underset{O}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{Na}{|}}{\underset{O}{|}}{\overset{\overset{O}{\|}}{P}}-NH_2 \quad (19)$$

The formation of potassium trimetaphosphate by condensation reactions at ordinary temperatures, and acid sodium trimetaphosphate, are dealt with in Sections VI,B,*3* and V,A, respectively.

2. Hydrates of the Trimetaphosphates

In addition to sodium trimetaphosphate-6-hydrate, which loses its water of crystallization on exposure in the air without change in the anion, a 1.5 hydrate and two forms (I and II) of a 1 hydrate have been described. The monohydrates undergo partial cleavage of the anion on thermal dehydration (*306, 307, 320*). The hydrate $Li_3(P_3O_9)\cdot 3H_2O$ undergoes a similar hydrolytic cleavage when it is dehydrated (*119*). Determination of space groups and of the elementary cells have been made for anhydrous $Na_3(P_3O_9)$ and the hydrates apart from form I of the monohydrate, the existence of which is doubtful (*212*).

3. Physicochemical Properties of Trimetaphosphate Solutions

Solutions of trimetaphosphates of strong bases have a neutral reaction. The acid from which they are derived behaves on titration as a strong monobasic acid (*62, 250, 294*). Differences in the dissociation constants of the three OH groups have not hitherto been detected with certainty. Measurements of electrical conductivity on trimetaphosphate solutions and determinations of the solubility products of slightly soluble salts of other cations in presence of sodium trimetaphosphate have led to the conclusion that ion pairs such as $Na(P_3O_9)^{2-}$ and $Me^{II}(P_3O_9)^{-}$ are produced. Dissociation constants for these are given in Table I (*62, 152*). The refractive index of solutions of the sodium salt corresponds with that of sodium polyphosphate solutions with a very large anion chain length (*110*).

TABLE I

DISSOCIATION CONSTANTS ($K \times 10^{-4}$) OF ION PAIRS CONTAINING THE TRIMETAPHOSPHATE ANION [$(P_3O_9)^{2-}$]

Cation	Dissociation constant with $(P_3O_9)^{2-}$ anion
Na^+	0.06_8
Ca^{++}	3.5_6
Sr^{++} (*196*)	4.4_4
Ba^{++}	4.5_6
Mg^{++}	4.8_9
Mn^{++}	2.7_2
Ni^{++}	6.0_3
La^{+++} (*197*)	2.0

4. Hydrolytic Degradation of the Trimetaphosphate Anion

Solutions of alkali trimetaphosphates are practically stable under neutral conditions and at 20°C or below. At a lower pH they are hydrolyzed according to a first order law and transformed via tri- and di-phosphates to monophosphates (*10, 33, 51, 130, 238, 244, 293*).

$$(P_3O_9)^{3-} \xrightarrow{H_2O} H_2P_3O_{10}^{3-} \xrightarrow{H_2O} H_2P_2O_7^{2-} + H_2PO_4^- \xrightarrow{H_2O} 3H_2PO_4^- \qquad (20)$$

Each of the reaction rate constants is strongly pH- and temperature-dependent and this dependence is different for the successive reactions. Thus at pH 8 and 80° the hydrolysis constant of sodium trimetaphosphate is so much smaller than those for the tri- and di-phosphate, that the latter compounds are practically undetectable. On the other hand in strongly alkaline solution, at pH 10 and 40°C, the hydrolysis constant of the trimetaphosphate is so much greater than those of its degradation products that it is transformed practically quantitatively into triphosphate (*130, 322*) [Eq. (17)]. For the energy of activation of the hydrolysis of trimetaphosphate pH-dependent values between 19.6 kcal (pH 7) and 21.8 kcal (pH 3) have been given (*33, 130, 322*); in the case of heat of hydrolysis for the fermentative cleavage of the (P—O—P) bond in trimetaphosphate, a value of −6.2 kcal at pH 7 and 33°C has been found for the change in enthalpy, the change in free energy being −7 kcal (*193*).

As in the hydrolysis of polyphosphates (Sections IV,B,*6* and IV,E,*1*), hydrolysis of the trimetaphosphate anion is catalytically accelerated by added cations. Their effect is attributed, as in the case of the polyphosphates, to the formation of "complex ions" of the type $Ca(P_3O_9)^-$ or $Ba(P_3O_9)^-$ and $Na_x(P_3O_9)^{3-x}$ (*130, 144, 146*).

5. *Analysis of the Trimetaphosphate Anion*

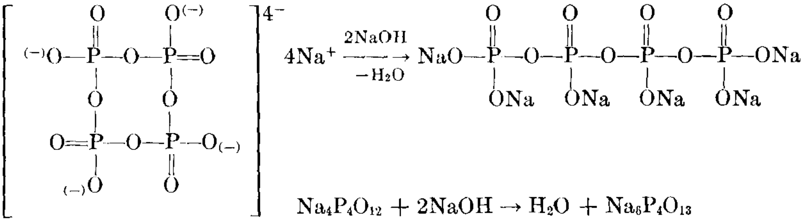
As described in Section VII, only chromatography is dependable for determining the $(P_3O_9)^{3-}$ anion quantitatively in presence of other condensed phosphates. However, since trimetaphosphate does not rapidly form a sparingly soluble precipitate with any other cation, especially in acid solution, an approximately quantitative determination is possible after precipitation of all other phosphates with barium (*71*, *130*), provided tetrametaphosphate is not present. It can also be determined by quantitative evaluation of infrared spectra (*58*) and, when only crystalline substances are present, by Debye X-ray photographs (*178*).

C. THE TETRAMETAPHOSPHATES

1. *Preparation and Structure*

Whereas sodium trimetaphosphate is easily obtained by tempering Graham's salt, the water-soluble alkali tetrametaphosphates are made only by indirect routes. One is by way of the water-insoluble tetrametaphosphates of polyvalent cations with ionic radii between 0.57 and 1.03 Å (Cu^{++}, Mg^{++}, Ni^{++}, Co^{++}, Fe^{++}, Mn^{++}, Zn^{++}, Cd^{++}, Al^{+++}), which are formed by heating the corresponding di-acid monophosphate with a small excess of phosphoric acid (*304*). From there the best route is, as Fleitmann (*92*) and many later workers have observed, to treat the copper salt with a solution of sodium sulfide and so obtain copper sulfide and a solution of sodium tetrametaphosphate (*3*, *8*, *334*). The tetrahydrate, $Na_4(P_4O_{12})\cdot 4H_2O$ is obtained pure from the solution by recrystallization. The sodium salt is more conveniently obtained by careful hydrolysis of the readily volatile modification (P_4O_{10}) of phosphorus(V) oxide by means of cold caustic soda or sodium bicarbonate solution (*8*, *12*, *33*, *50*, *238*, *244*, *321*, *326*, *327*, *331*, *356*). Yields of $Na_4(P_4O_{12})$ are strongly dependent on the quality of the phosphorus(V) oxide used. Alkali salts of tetrametaphosphoric acid are soluble in water. The salts of barium, lead, and many organic amines, such as benzidine and toluidine, are not easily soluble and may be precipitated from aqueous solution (*87*, *131*).

The molecular size of tetrametaphosphates was not clear for a long time. It was first established that these substances are derived from a tetrameric acid by determining the molecular weight from measurements of the freezing point depression of an aqueous solution of the sodium salt (*209*) and by cryoscopy in melting Glauber's salt (M_{found} 395–418; $M_{\text{calc.}}$ 408) (*12*, *17*). Final proof that tetrametaphosphate consists of a ring of four PO_4 tetrahedra came from a determination of the structure of $Al_4(P_4O_{12})_3$ (*222*) and the practically quantitative transformation of $Na_4(P_4O_{12})$ by caustic soda into tetraphosphate. This follows a second order rate law (*233, 312*).



(21)

$$Na_4P_4O_{12} + 2NaOH \rightarrow H_2O + Na_6P_4O_{13}$$

The tetrametaphosphate anion is transformed into the amidotetraphosphate, $(P_4O_{12}NH_2)^{5-}$, by concentrated ammonia solution just as the anion ring of trimetaphosphate is cleaved by ammonia to amidotriphosphate. Acidification of the solution results in partial reconversion to the tetrametaphosphate anion, but there is also partial hydrolysis to NH_4^+ and tetraphosphate ions as well as to amidomonophosphate and triphosphate ions, with simultaneous formation of trimetaphosphate (*300*). A complete structure determination has been made for ammonium tetrametaphosphate (*1*) from which the cyclic structure of the anion is evident (*245*). The diacid salt $Na_2H_2(P_4O_{12})$ (*108*) (see Section V,A) is also undoubtedly a tetrametaphosphate (*150*) (for structural data, see Section IV,E,*3*).

The infrared and Raman spectra of sodium tetrametaphosphate differ little from those of the trimetaphosphates (*57, 139*). The Raman spectra of crystalline tetrametaphosphates vary with the nature of the cation (*275*) and, from the infrared spectra, different symmetries are assigned to the anions of different salts.

2. Tetrametaphosphate Hydrates

A deca-hydrate of sodium tetrametaphosphate is known, which goes over above 25°C into the low-temperature form of the tetrahydrate. This, in turn, gives the high-temperature form above 54°C and the anhydrous salt is formed above 75°C (*12*). From 250°C the anhydrous salt takes up small amounts of water from the atmosphere and passes over into Maddrell's salt with long chain-like anions (*119, 241, 326*). The lithium salt crystallizes with four molecules of water of crystallization, two of which are given up above 60°C. The remaining two are much more difficult to remove and there is simultaneous hydrolytic cleavage of the anion. The products, when further heated, change preferentially to tetra- and octaphosphate and finally to high-molecular polyphosphate (*119*).

Potassium tetrametaphosphate crystallizes with two molecules of water and becomes anhydrous at 100°C. Above this temperature the anhydride takes up water from the atmosphere and goes over to the high-molecular

Kurrol's potassium polyphosphate through a whole series of intermediate polyphosphates. The fact that potassium trimetaphosphate is formed by direct heating of $K_4(P_4O_{12})$ to temperatures above 200°C is an indication of the occurrence of radical-like fragments as intermediate products (*119*).

3. Physicochemical Properties of Solutions of Tetrametaphosphates

Tetrametaphosphoric acid behaves in aqueous solution as a strong acid (*326, 334*), the fourth H^+ ion of which is, however, appreciably more weakly dissociated than the first three (*62*). Solutions of their alkali salts are neutral.

Measurements of the electrical conductivity and solubility of difficultly soluble salts in sodium tetrametaphosphate solutions (*62*, *151*, *196*, *197*) and potentiometric titrations lead to the assumption of the existence of "complexes" of the type of $Na^+(P_4O_{12})^{3-}$; Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, Mn^{++}, Ni^{++}, $Cu^{++}(P_4O_{12})^{2-}$; $La(P_4O_{12})^-$; $Cu(P_4O_{12})_2^{6-}$ and $Ni(P_4O_{12})_2^{6-}$. No comparable dissociation constants for these have so far been given, though in any case they will be smaller than for the corresponding ion pairs of the trimetaphosphate anion (*145*).

4. Hydrolytic Degradation of the Tetrametaphosphate Anion

The alkali tetrametaphosphates are stable in aqueous solution at or below room temperature provided the pH is between approximately 5 and 10 (*61*). Temperatures of about 40°C and higher, or lower pH values, bring about hydrolysis to monophosphate through several intermediate stages

$$\text{Tetrameta} \rightarrow \text{Tetra} \rightarrow \text{Tri} + \text{Mono} \rightarrow \text{Di} + \text{Mono} \rightarrow \text{Mono} \qquad (22)$$

(*12, 33, 50, 61, 244, 312, 322, 355*)

In strongly alkaline solution hydrolysis of sodium tetraphosphate takes place so much more slowly than that of the tetrametaphosphate that tetraphosphate accumulates in the solution in a practically pure state

TABLE II

DECOMPOSITION HALF-LIVES FOR SODIUM TRIMETA- AND TETRAMETAPHOSPHATE ANIONS IN AQUEOUS SOLUTION AT 60°C AS A FUNCTION OF pH

pH	Trimeta	Tetrameta
1	17 minutes	2.48 hours
3	1.7 days	6.5 days
7	69.3 days	116.5 days

(*312*). In acid solution, where the hydrolysis proceeds according to a first order law as long as the pH is constant (*33*), all the intermediate products may first be detected chromatographically. The energy of activation in acid solution is 20 kcal, i.e., very similar to the trimetaphosphate value (19.6–21.8 kcal). The stability of tetrametaphosphate under comparable conditions (e.g., at 60°C), however, is greater than that of the trimetaphosphate, as may be seen from the half-lifetimes (*322*) (Table II). That hydrolysis of the tetrameta ion is catalytically accelerated by added cations, at least in alkaline solution, is shown, for example, by the effect of the Na^+ ion (*145*).

D. Metaphosphates with More than Four Phosphorus Atoms in the Anion

It seemed probable, from the early results of chromatography, that the hydrolyzate from Graham's salt contains metaphosphates with more than four phosphorus atoms in the anion ring (*350*). A little later (*186*) the metaphosphate content of a freshly prepared solution of Graham's salt with a mean chain length $\bar{n}$ of 100–125 was given as:

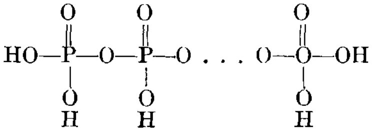
TABLE III
Percentage of Metaphosphates with Various Numbers of Units in the Anion Ring in Graham's Salt

Number of P atoms in the ring	3	4	5	6	≥7
Per cent	3–9	2.5	0.75	0.5	<0.5

With a chromatographic liquid more suited to the separation of the meta- from the polyphosphates (*15*), the existence of pentameta- and hexametaphosphates was shown conclusively, though they have not yet been isolated on a preparative scale and their constitutions have not been proved.

IV. Condensed Phosphates with Chain Anions. The Polyphosphates

The polyphosphates include all compounds with the composition $Me^{I}_{n+2}P_nO_{3n+1}$, or $Me_n{}^{I}H_2P_nO_{3n+1}$. The first members are the dihydrogen monophosphates, $Me^{I}H_2PO_4$, which are stable and go over into members of the series with higher molecular weight by condensation. Their anions are chain-like.



$$HO-\underset{\underset{\displaystyle H}{\underset{|}{O}}}{\overset{\overset{\displaystyle O}{\|}}{P}}-O-\underset{\underset{\displaystyle H}{\underset{|}{O}}}{\overset{\overset{\displaystyle O}{\|}}{P}}-O\ \ldots\ O-\underset{\underset{\displaystyle H}{\underset{|}{O}}}{\overset{\overset{\displaystyle O}{\|}}{O}}-OH \qquad (23)$$

The free acids carry a strongly dissociated acid OH group on each phosphorus atom and each of the two ends of the chain has a weakly dissociated

OH group. Solutions of their "neutral" alkali salts, therefore, have a weakly alkaline reaction, while the "acid salts" in which the terminal OH groups are not replaced by cations, are weakly acid.

Only the members with low molecular weight can be prepared directly in a pure form: all those of higher molecular weight occur as mixtures of individual members of the homologous series of polymers. Starting with the chain length $n = 3$, all polyphosphates are distinguished by their ability to bind polyvalent cations so firmly that they can no longer be detected by ordinary precipitating agents. Among other properties, their absorption on solid surfaces of all sorts is specially important (cf. Section IV,E,*1*,*d*).

A. DIPHOSPHATES

1. *Recent Advances*

Pyro- and di-phosphates, the simplest members of the group of condensed phosphates, are so well known that only the results of recent investigations will be described here, and only in so far as they bear on the chemistry of condensed phosphates. Thus, ever since Clark's investigations (*52*), it has been common knowledge among chemists that diphosphates are obtained by heating monohydrogen phosphates, or by double decomposition of other diphosphates. It was unexpected, however, to find that an equilibrium

$$2H_2PO_4^- \rightleftharpoons H_2O + H_2P_2O_7^{2-} \qquad (24)$$

is established from both sides in concentrated aqueous solutions of sodium dihydrogen mono- or di-phosphate at 80°C or above with about 6000 parts of NaH_2PO_4 and 16 parts of $Na_2H_2P_2O_7$. The enthalpy of the hydrolysis reaction is -4.7 kcal, the free energy of hydrolysis of the P—O—P system is -3.2 kcal, and the activation energy for the formation of $H_2P_2O_7^{2-}$ is about 30 kcal (*261*). An enthalpy of -5.81 ± 0.13 kcal has been found by direct calorimetry for the enzyme-catalyzed hydrolysis at pH 7.3 (*100*).

It has now been clearly established (*179*) by a complete structure determination on $Na_4P_2O_7 \cdot 10H_2O$ that the oxygen valency angle in pyrophosphates is not 180° (*172*, *370*), but 134° (see also Section IV,E,3). The existence of two different forms of $Na_2H_2P_2O_7$ has been reported (*30*, *170*). It has also been proved that the two phosphorus atoms are equivalent (*227*).

2. *Complex Formation by the Diphosphate Anion*

The existence in diphosphoric acid of two strongly and two weakly dissociated H^+ ions has been known for a long time. New determinations of the separate dissociation constants have given the values:

TABLE IV
ELECTROLYTIC DISSOCIATION CONSTANTS FOR DIPHOSPHORIC ACID

K_1	K_2	K_3	K_4	Reference
0.107	7.58×10^{-3}	1.45×10^{-6}	9.81×10^{-9}	*(60)*
—	—	$1.5\text{–}2.5 \times 10^{-6}$	40×10^{-9}	*(44)*
—	—	0.9×10^{-6}	4.07×10^{-9}	*(140)*

Not only hydrogen ions are relatively strongly bound to the pyrophosphate anion. Thus, for example, the salt $Ba_2P_2O_7$, which is not easily soluble in water, is brought into solution by an excess of pyrophosphate. Furthermore, electrometric and conductimetric studies have established *(16, 140)* that most polyvalent cations and also the Tl^+ ion *(265)* are bound in "complexes" of various sorts. Quantitative studies show that the formation constants for the "calcium complexes" of the $P_2O_7^{4-}$ ion have values which are about a power of ten smaller than those for the corresponding "complexes" of the triphosphate anion *(148)*. (For data, see Section IV,B,*8*.)

3. Hydrolysis of the Diphosphate Anion

Alkali diphosphates are practically stable in alkaline and neutral solutions, but they are more and more rapidly hydrolyzed with decreasing pH. Over the whole pH range, however, they are more stable, under the same conditions, than all other condensed phosphates. Hydrolysis is accelerated by an increasing temperature or ionic strength *(44, 346)*. The table below shows the dependence of the rate constant for the hydrolysis on pH at 65.5°C. This dependence is attributed to the differing sensitivity to hydrolysis of the various pyrophosphate anions *(44, 60)* which can be differentiated by their infrared spectra *(208)*.

TABLE V
RATE CONSTANTS FOR DIPHOSPHATE HYDROLYSIS AS A FUNCTION OF pH

pH	2.0	2.8	3.0	4.9	5	6	9.3	10.9	Reference
$k \times 10^4$ (min^{-1})	5.4	—	3.31	—	—	1.25	0.1	0.048	*(60)*
	—	4.04	—	2.99	2.90	—	—	—	*(270)*

B. TRIPHOSPHATES

1. Preparation

The most important compound in the series of low molecular weight polyphosphates is the sodium salt of triphosphoric acid, $Na_5P_3O_{10}$, which was first reported in detail by Topley (*326*). It is formed, as Schwarz (*263*) (its discoverer) and, somewhat later, Stange (*273*) showed, when any mixture of sodium phosphates with a $Na_2O:P_2O_5$ ratio of 5:3 is melted and the melt is cooled, though the cooling should not be too slow. The yield of triphosphate depends on the way of cooling (*4, 142, 203, 218*).

$$x\mathrm{Na_5P_3O_{10}} \xrightarrow{622^\circ\mathrm{C}} x\mathrm{Na_4P_2O_7} + (\mathrm{NaPO_3})_x \tag{25}$$

The triphosphate melts incongruently at 622°C and decomposes in so doing into crystalline diphosphate and a polyphosphate melt in which the diphosphate gradually dissolves as the temperature is raised further until, at 860°C, the whole mass is a homogeneous liquid. On quenching, this melt solidifies to a glass. If cooling is carried out moderately rapidly, fine crystalline needles of diphosphate separate in the polyphosphate glass. On cooling slowly, on the other hand, coarse diphosphate crystals separate together with more or less triphosphate and some trimetaphosphate. The residue remains as a glass. To prepare triphosphate in this way it is best to quench the melt and then temper it at a temperature below the incongruent melting point (<622°C). In this process a modification (I), which is undesirable for technical purposes, crystallizes above $\sim$470°C, and the technically important form (II) crystallizes below this temperature.

The glass which is formed by heating triphosphate was formerly thought to contain a single "metaphosphate." Experiments with paper chromatography have shown, however, (*115*) that above the incongruent melting point it consists of a mixture of oligophosphates with chain lengths between $n = 2$ and > 10, and that the mean chain length n decreases progressively with rising temperature as more diphosphate is dissolved by the melt. When molten triphosphate at $\sim$630°C is cooled rapidly, the glass contains relatively large amounts (up to 20%) of high molecular weight polyphosphates (*120*) which are formed by polymerization of the monomeric radical-like $NaPO_3$ groups formed initially [Eq. (25)]. They first react with the other polyphosphates in the melt when the temperature is increased until, above 860°C, the equilibrium distribution of chain lengths has been established.

Preparation on a technical scale now starts, in general, from solutions containing mixtures of Na_2HPO_4 and NaH_2PO_4 in which the $Na_2O:P_2O_5$ ratio is 5:3. In the "Sprühtrocken" process these solutions are evaporated and the resulting salt is calcined in a rotating furnace at 300–400°C. This process gives a product containing 85–94% of triphosphate, but small proportions of diphosphate, trimetaphosphate, and some polyphosphate glass are always present

$$2\mathrm{Na_2HPO_4} + \mathrm{NaH_2PO_4} \rightarrow \mathrm{Na_5P_3O_{10}} + 2\mathrm{H_2O} \tag{26}$$

The mechanism of reaction (26), leading to triphosphate formation, is complicated (*88*, *133*, *190*, *231*). It occurs through two intermediate stages which depend on the nature and amount of the water content of the melt, the atmosphere, and the mode of heating. In any case the presence of water is necessary for triphosphate formation in order to hydrolyze again the P—O—P bonds of high-molecular anions and to catalyze the crystallization of triphosphate. The main reaction, however, consists in all probability in the primary formation of the double salt $Na_3H_3(PO_4)_2$. After that, $[HP_2O_7]^{3-}$ ions are formed which finally condense with $[HPO_4]^{2-}$ ions to give triphosphate anions, with elimination of water

$$[HPO_4]^{2-} + [HP_2O_7]^{3-} \rightarrow [P_3O_{10}]^{5-} + H_2O \tag{27}$$

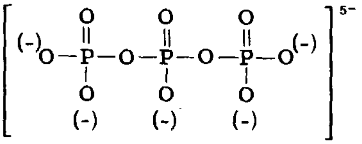
A third method of preparing triphosphate (*311*), which is suitable for laboratory purposes, involves alkaline hydrolysis of the readily available trimeta phosphate (see Section III,B,*1*). Cleavage of the trimeta ring takes place according to reaction (29), leading to the formation of $Na_5P_3O_{10}\cdot 6H_2O$ (*233*, *317*), which is obtained with a purity of 99–99.5% by dissolving in water and precipitating with alcohol (*233*, *235*).

2. The Two Modifications (I and II) of Sodium Triphosphate

Huber (*142*) first suspected that sodium triphosphate occurs in two modifications when he observed that quenched triphosphate melts, after tempering at high temperatures ($<622°C$), broke up during cooling into a fine powder. Proof of the existence of a high- and low-temperature form of $Na_5P_3O_{10}$, I and II, was obtained by Andress and Wüst (*4*) from Debye diagrams. However, the relationship between these two forms is still not clear. The transition I $\rightleftarrows$ II at 417 ± 8°C is reversible in a sealed tube only if water is present (*201*). With finely powdered preparations the transition II → I is observed at about 470° but not the transition I → II, irrespective of whether one works in a dry or a moist atmosphere (*230*). This seems to be inconsistent with the frequently observed transition from I to II accompanied by disintegration which occurs, though not invariably, and for the most part not completely, on cooling crystallites of the high temperature form which first separate from the melt. These relationships appear to be similar (*326*) to those in the transition β-$Ca_2SiO_4 \rightarrow \gamma$-$Ca_2SiO_4$ (*97*, *123*, *301*, *368*). In both cases the transformation from the high- to the low-temperature form occurs with an increase in volume; $Na_5P_3O_{10}$(I) has a density $\rho_I = 2.62$ and $Na_5P_3O_{10}$(II) a density $\rho_{II} = 2.57$ g/cm^3. It is not yet clear why the high temperature form I is also produced occasionally at temperatures which are far below ~400°C.

3. The Structure of the Triphosphate Anion $[P_3O_{10}]^{5-}$

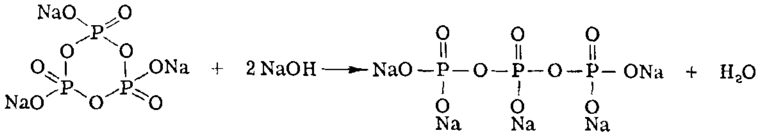
Proof for the structure of the triphosphate anion comes from its composition and the cryoscopic molecular weight in molten Glauber's salt [values found, 372 (*19*) and 364 (*317*): calculated, 367.9]. Assuming that phosphorus has a coordination number of four with respect to oxygen, the anion structure can only be represented by the formula



$$\left[\begin{array}{ccccccccc} & & O & & O & & O & & \\ & & \| & & \| & & \| & & \\ {}^{(-)}O & - & P & -O- & P & -O- & P & - & O^{(-)} \\ & & | & & | & & | & & \\ & & O & & O & & O & & \\ & & (-) & & (-) & & (-) & & \end{array}\right]^{5-}$$

(28)

This formula also corresponds with the fact that dissociation is strong in three and weak in two of the five H^+ ions in triphosphoric acid (*250*). The correctness of the structural formula is also supported by the quantitative formation of triphosphate from trimetaphosphate on cleaving the anion ring with strong alkali (*90, 311*). Final proof for the structure of the triphosphate anion is furnished by determination of the crystal structure of the two forms of $Na_5P_3O_{10}$(I) (*63*) and (II) (*56*). The anions of the two forms



(29)

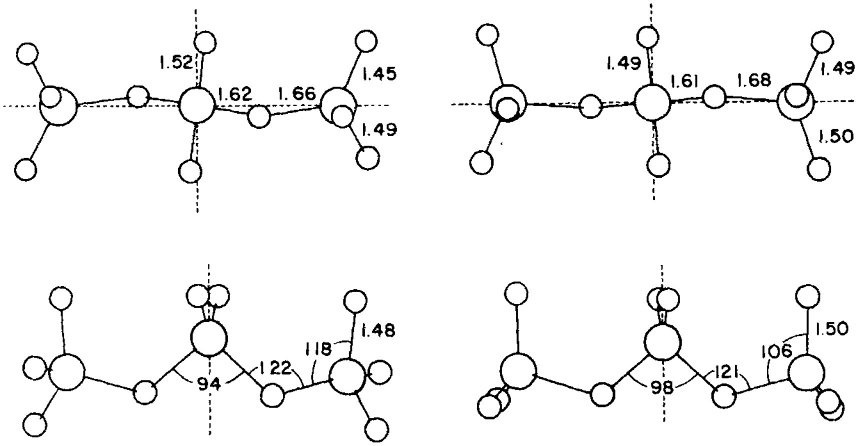


FIG. 4. Structure of triphosphate anion in the two crystalline forms of $Na_5P_3O_{10}$ (I and II), according to Corbridge (*56*).

are similarly constituted of three not completely regular PO_4 tetrahedra joined to one another through oxygen (Fig. 4). Both have a *trans* configuration and are exceedingly similar in all essential structural details. Only the coordination of the Na ion is significantly different in the two forms and this difference is discussed in the next section. Reports of the existence of a "polymeric" form of the triphosphate (*161*) have been found to be incorrect (*340*).

4. Hydration of the Two Forms of Sodium Triphosphate

The same hexahydrate, $Na_5P_3O_{10} \cdot 6H_2O$ separates as a stable solid phase from aqueous solutions of forms I and II of $Na_5P_3O_{10}$. Below 20° and with rapid evaporation of the solvent an octahydrate can also form (*19*, *141*), though this passes over into the hexahydrate on exposure to air, or over sulfuric acid.

The behavior of the two forms on solution is very different. $Na_5P_3O_{10}$(I) cakes rapidly when treated with water forming a tough hard mass which dissolves only slowly. This modification is therefore undesirable as a constituent of detergents. Modification II, on the other hand, dissolves normally. This difference in behavior is due (*189*, *326*) to the fact that modification I is very rapidly hydrated on contact with water and separates as hexahydrate. The high concentration of the solution near the surface of modification I gives rise to a high concentration of seeds of the hexahydrate and a corresponding rapid formation of the crystalline solid phase $Na_5P_3O_{10} \cdot 6H_2O$. Modification II has a much smaller solution rate and, as a result, no high concentrations of solution or seeds occur near the crystallite surfaces, though supersaturated solutions form readily. Preparations of II with a high surface area approximate in their behavior to $Na_5P_3O_{10}$(I). A corresponding behavior is observed on exposure of the two forms to water vapor at 50°; for example, I is completely transformed to hexahydrate in 5 days whereas II requires 25 days (*126*, *371*).

The reason for the different behavior of the two crystalline forms of $Na_5P_3O_{10}$ does not lie in a difference in the constitution of the anions. As chromatography shows, both modifications give identical solutions. The anions are also practically identical in the crystal (see Fig. 4). Their relative situations in the lattice are also hardly different, but the coordination of the Na ion does vary. In modification II, which hydrates slowly, all Na^+ ions are surrounded octahedrally by oxygen, but in the rapidly hydrated form, I, (see Fig. 5), on the other hand, part of the Na^+ ions are only tetrahedrally coordinated. It is conceivable that the low coordination of Na^+ ions and the desire to increase this is the cause of the great tendency to hydration of $Na_5P_3O_{10}$; whether essential changes in the lattice as a

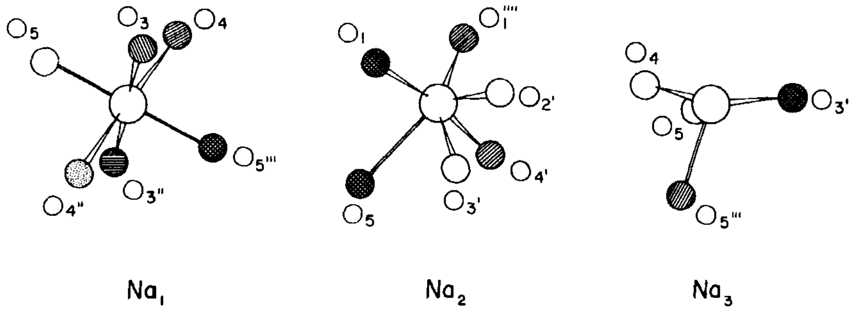


FIG. 5. The oxygen coordination of the Na^+ ions in the form I of sodium triphosphate, $Na_5P_3O_{10}$.

whole are associated with this hydration can be decided only when the structure of the hexahydrate is known.

5. The Thermal Decomposition of the Hexahydrate $Na_5P_3O_{10}\cdot 6H_2O$

Both forms of anhydrous sodium triphosphate are unstable with respect to combination with water, and cannot therefore be prepared from aqueous solution. Likewise they cannot be obtained by dehydration of the hexahydrate (*19, 141, 142, 326*) as long as the dehydration temperature is less than ~150°C. When the hexahydrate is heated in an open atmosphere to about 120° it first loses only about five molecules of water (*238, 317*). The residual molecule of water simultaneously causes hydrolysis and splits the triphosphate anion to crystalline diphosphate and amorphous monophosphate, perhaps according to the equation:

$$Na_5P_3O_{10} + H_2O \rightarrow Na_4P_2O_7 + NaH_2PO_4 \qquad (30)$$

Decomposition of the hexahydrate is certainly not represented by such a simple equation (*233, 266, 372*). In general the ratio di- to mono-phosphate is greater than unity and, after prolonged tempering, crystalline $Na_3HP_2O_7\cdot H_2O$ and Na_2HPO_4 can be detected in addition to $Na_4P_2O_7$. As in the case of the preparation of $Na_5P_3O_{10}$ from $Na_2HPO_4 - NaH_2PO_4$ solutions, the course of the thermal dehydration of $Na_5P_3O_{10}\cdot 6H_2O$ is dependent on many factors, such as water vapor pressure, temperature, the mode of heating, crystallite size, and so on (*296*).

The low temperature form of the triphosphate, $Na_5P_3O_{10}$(II), is formed with the loss of residual water from the mixture of decomposition products by raising the temperature to ~130–150°C. Direct dehydration to $Na_5P_3O_{10}$(II) also occurs, partially at least, by simply and directly heating the hexahydrate in vacuum or in boiling toluene (110.8°C) (*266, 372*).

The triphosphate reacts with substances which are relatively basic in character in a way which is similar to its reaction with water. Thus, it reacts with sodium fluoride in the melt with partial formation of Na_2PO_3F (*134*) and with Na_3PO_4, even in the solid state, from 260°C, to form $Na_4P_2O_7$ (*228*).

6. *Hydrolysis of the Triphosphate Anion in Aqueous Solution*

In aqueous solution at pH 7–9 at room temperature the triphosphate anion, like the anions of all polyphosphates, is practically indefinitely stable. With increasing temperature and decreasing pH, however, it undergoes increasingly rapidly a hydrolytic breakdown involving a first reaction step which leads to formation of monophosphate and diphosphate.

$$[P_3O_{10}]^{5-} + H_2O \rightarrow [HP_2O_7]^{3-} + [HPO_4]^{2-} \qquad (31)$$

In the second step diphosphate is further hydrolyzed to monophosphate at about a third of the rate (*4, 10, 326*). Both hydrolytic processes occur independently (*270*) according to a first order reaction at a constant pH (*60, 166, 233*).

The hydrolysis undergoes strong catalytic acceleration by added cations, provided the solution is not too acid (*6, 7, 106, 346, 348, 361*). The mode of action of the cations, which include the H^+ ion, is likely to be similar to that in the hydrolytic degradation of high-molecular polyphosphates (see Section IV,E,*1*,*c*). Added cations have a retarding effect in strongly acid solution (*96*). The hydrolysis reaction is accelerated in strongly alkaline solutions (*60*), but this is attributed to the cations introduced with the alkali and not to OH^- ions (*346, 348*). Suspensions of various sorts of enzymes and living cells can also accelerate hydrolysis greatly (*160*). Hydrolysis data for the triphosphate can be well presented nomographically for practical purposes (*111*).

7. *Triphosphates with Other Cations*

a. The potassium salt. A compound $K_5P_3O_{10}$, analogous to $Na_5P_3O_{10}$, may be prepared by the method used in the case of the sodium salt (*19, 205, 213*). It melts incongruently at 641.5°C and forms crystalline $K_4P_2O_7$ and a melt in which, as with $Na_5P_3O_{10}$, the $K_4P_2O_7$ dissolves with increasing temperature until the whole mass is liquid at ~940°C (*200*). Potassium triphosphate is hygroscopic and very readily soluble in water (*19*). On exposure to the atmosphere it takes up two molecules of water to form an α-form of the dihydrate. A second or β-form, which is different in its chemical behavior, is produced by precipitation of the aqueous solution with methanol (*205*). Proof of the existence of a compound $Na_5P_3O_{10}{\cdot}K_5P_3O_{10}$ is provided by the melting point diagram of mixtures of the two components (*202*).

b. Acid triphosphates and triphosphoric acid. A crystalline acid triphosphate $Na_5P_3O_{10} \cdot Na_3H_2P_3O_{10} \cdot 3H_2O$ (= $Na_4HP_3O_{10} \cdot 1 \cdot 5H_2O$) is precipitated by alcohol from an acetic acid solution of $Na_5P_3O_{10}$ (*141*). When heated it decomposes, like the neutral salt, into di- and mono-phosphate (*238*). From a hydrochloric acid solution of $Na_5P_3O_{10}$ crystalline $Na_3H_2P_3O_{10} \cdot 1 \cdot 4H_2O$ is formed and this gives $Na_2H_2P_2O_7$ and Maddrell's salt on heating (*30*). An analogous compound, $K_3H_2P_3O_{10} \cdot 1\text{–}2H_2O$, which is very hygroscopic and thermally unstable, is also known (*26*, *67*). The acid salts $Ca_2HP_3O_{10}$ and $Ca_3(H_2P_3O_{10})_2$, which are formed by heating $Ca(H_2PO_4)_2 \cdot H_2O$ (*137*, *206*, *211*, *305*), and the compound $AlH_2P_3O_{10} \cdot 2H_2O$ (*31*) have also been described.

Free triphosphoric acid has hitherto been obtained only as an aqueous solution prepared by ion exchange from the sodium salt. The dissociation constants are (*337*): K_1 = very high; $K_2 = 10^{-1.1}$; $K_3 = 10^{-2.3}$; $K_4 = 10^{-6.26}$; $K_5 = 10^{-8.90}$. These values verify the old observation that triphosphoric acid has three strongly dissociated and two weakly dissociated H^+ ions and explains why aqueous solutions of alkali triphosphates have an alkaline reaction.

c. Triphosphates with polyvalent cations. A large number of triphosphates with polyvalent cations are mentioned in the literature. Those most commonly occurring are of the types $Me_3{}^{I}Me^{II}P_3O_{10} \cdot aq$, $Me^{I}Me_2{}^{II}P_3O_{10} \cdot aq$, $Me_5{}^{II}(P_3O_{10})_2 \cdot aq$ and $Me_5{}^{III}(P_3O_{10})_3 \cdot aq$, which are slightly or extremely slightly soluble in water but, in most cases, dissolve in excess of triphosphate (*16*, *18*, *19*, *39*, *45*, *76*, *98*, *99*, *233*). Special mention may be made of the well crystallized compound $NaZn_2P_3O_{10} \cdot 9H_2O$, described by Schwarz (*263*) and Huber (*141*, *142*), which is valuable because of its low solubility for the rapid identification of triphosphates. Triphosphates also give precipitates of low solubility such as $(Co(en)_3)H_2P_3O_{10} \cdot 2H_2O$ with complex cobalt cations (*187*, *188*, *352*). The compound $Na_3MgP_3O_{10} \cdot 12H_2O$ has been fairly fully investigated (*66*).

8. *The Bonding of Cations to Triphosphate and Diphosphate Anions*

The fact that most triphosphates of polyvalent cations which are difficultly soluble in water are soluble in excess of triphosphate, and that such polyvalent cations (e.g. Ca^{++}) are either not precipitated or not quantitatively precipitated by the usual reagents from solutions of their salts containing triphosphate, has become of great commercial importance in water softening (*90*). The term "sequestration" is used in this connection. Numerous publications have appeared which are not mentioned in detail here, and which attempt to determine this property quantitatively. In general, the effect is attributed to the formation of relatively stable "ion pairs" or "complexes," the stability of which is defined by the formation constants K or K'.

TABLE VI

Selection of Most Important Formation Constants for Complexes, Expressed as p_K Values (= $-\log K$)

A. Triphosphate Complexes

Ionic strength	$NaP_3O_{10}^{4-}$	$SrP_3O_{10}^{3-}$	$CaP_3O_{10}^{3-}$	$MgP_3O_{10}^{3-}$	$CaHP_3O_{10}^{2-}$	$MgHP_3O_{10}^{2-}$
0	2.8 (*366*)	7.2 (*366*)	8.1 (*366*)	8.6 (*184*)	—	3.7 (*184*)
	—	—	6.90 (*148*)	—	—	—
0.1	—	—	4.95 (*184*)	5.80 (*184*)	3.78 (*148*)	—
	—	—	6.41 (*148*)	—	3.1 (*184*)	—
1	1.64 (*336*)	—	5.44 (*335*)	5.83 (*167*)	3.01 (*335*)	3.34 (*167*)
	—	—	5.36 (*148*)	—	3.30 (*148*)	—

B. Diphosphate Complexes

Ionic strength	$NaP_2O_7^{3-}$	$SrP_2O_7^{2-}$	$CaP_2O_7^{2-}$	$MgP_2O_7^{2-}$	$CaHP_2O_7^{-}$	$MgHP_2O_7^{-}$
0	2.3 (*366*)	8.9 (*366*)	6.8 (*366*)	7.2 (*366*)	—	—
	2.35 (*195*)	—	5.60 (*148*)	—	—	—
	2.22 (*64*)	—	—	—	—	—
0.1	—	—	5.39 (*148*)	—	—	—
1	—	—	4.95 (*335*)	5.41 (*157*)	2.30 (*335*)	3.06 (*167*)
	—	—	4.89 (*148*)	—	2.22 (*148*)	—
					3.32 (*148*)	

$$K = \frac{[\mathrm{Me}^{n+}][\mathrm{P_3O_{10}}^{5-}]}{[\mathrm{MeP_3O_{10}}^{(5-n)-}]} \text{ or } K' = \frac{[\mathrm{Me}^{n+}][\mathrm{HP_3O_{10}}^{4-}]}{[\mathrm{MeHP_3O_{10}}^{(4-n)-}]} \tag{32}$$

In essence there are three ways of determining these constants, namely, conductimetry (*195, 336*), potentiometry (*184, 289, 337, 366*), and the determination of the solubility of sparingly soluble metallic salts in presence of triphosphate (*148, 167, 335*).

The method using pH determinations, for example, depends on the fact that the pH of a solution of sodium triphosphate is decreased by the addition of salts containing the cation under investigation—e.g., NaCl or $CaCl_2$ (*95, 248, 345*). The quantity of H^+ ions set free in this way is determined potentiometrically and the formation constant of the complex is determined on the basis of the equilibria involved, such as:

$$\mathrm{H^+ + P_3O_{10}{}^{5-} \rightleftharpoons HP_3O_{10}{}^{4-}} \text{ and } \mathrm{Ca^{2-} + P_3O_{10}{}^{5-} \rightleftharpoons CaP_3O_{10}{}^{3-}} \tag{33}$$

The following values have been given for these constants, which often show good agreement for the different methods (Table VIa). It will be seen that the $\mathrm{Me^{II}P_3O_{10}{}^{3-}}$ complexes are more stable than those of the type $\mathrm{Me^{I}HP_3O_{10}{}^{2-}}$, that their stability increases in the order $Na^+ < Sr^{++} < Ca^{++} < Mg^{++}$ (i.e., with increasing charge and decreasing radius of the rare gas-like cation), and that increase in ionic strength of the solution diminishes the stability of the complex strongly. If one compares the recent data given here with corresponding values for diphosphates (see Table VIB) it is found that the pK values for the triphosphates are in general about 0.5–1 pK unit greater than those for diphosphates. This represents about a factor of three in the strength of binding of the cation in triphosphate complexes compared with that for the diphosphates.

TABLE VII

FORMATION CONSTANTS $p_K(= -\log K)$ FOR COMPLEXES OF TRIPHOSPHATES WITH IONS NOT HAVING THE RARE GAS CONFIGURATION

Ionic strength	$\mathrm{ZnP_3O_{10}{}^{3-}}$	$\mathrm{CdP_3O_{10}{}^{3-}}$	$\mathrm{Hg_2{}^{I}(P_3O_{10})_2{}^{8-}}$
0	9.7 ± 0.5 (*366*)	9.8 ± 0.5 (*366*)	—
0.75	—	—	11.32 (Triphosphate) (*367*) 12.38 (Diphosphate)

Ions which do not have a rare gas configuration appear not to fit into this rule. They are much more firmly bound than the alkali and alkaline earth cations. A dependence on radius is not observed and for Hg(I) the binding is stronger with the diphosphate anion than with triphosphate (*366*). (See, also the binding of cations by highmolecular polyphosphates, Section IV,E,*1*,*d*.) For the analysis and determination of triphosphates, see Section VII,B.

C. TETRAPHOSPHATES

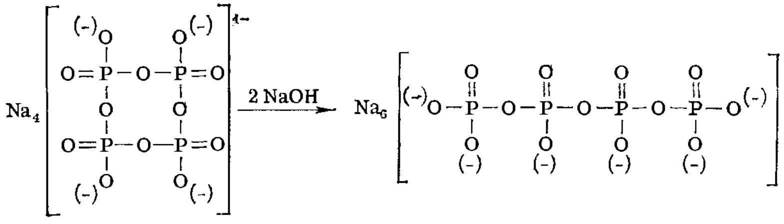
1. *Formation and Preparation*

It has been shown repeatedly (*4, 19, 20, 142, 263*) that, contrary to earlier reports, pure sodium tetraphosphate, $Na_6P_4O_{13}$, cannot be obtained in a crystalline form from aqueous solutions of melts of the corresponding composition (*94, 253*) or by thermal dehydration of $Na_3HP_2O_7$ (*217*). The only crystalline phase to separate from such melts is the triphosphate, $Na_5P_3O_{10}$; the residue is a glassy mixture of various condensed phosphates (*203, 218*). Nevertheless, all glasses obtained by quenching melts in which the Na:P ratio is over 2:1 contain considerable quantities of tetraphosphate in addition to other poly- and meta-phosphates. Chromatographic analysis of such glasses gave the following tetraphosphate contents. It has not so far proved possible to isolate pure tetraphosphate from such glasses in more than milligram quantities (see also Section VII,D).

TABLE VIII
CONTENT OF TETRAPHOSPHATE IN POLYPHOSPHATE GLASSES, EXPRESSED AS PERCENTAGE OF THE TOTAL PHOSPHORUS

Na:P	H. Grunze (*115*) 1956	Westman and Gartaganis (*354*) 1957
5:3	21.3	20.41
6:4	26.6	27.43
7:5	20.9	19.93
8:6	15.5	14.59
9:7	—	11.59
11:9	—	7.34

Pure or very nearly pure sodium tetraphosphate is obtained in the bimolecular reaction involving alkaline cleavage of the cyclic anion of sodium tetrametaphosphate in aqueous solution at temperatures up to 40°C (*233, 312, 355, 356*). The tetraphosphate $Na_6P_4O_{13}$·aq



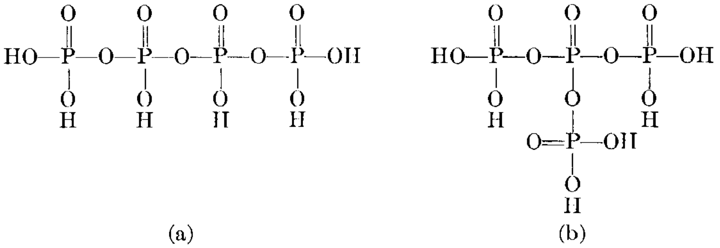
(34)

$$Na_4(P_4O_{12}) \xrightarrow{2\,NaOH} Na_6P_4O_{13}$$

may be obtained from the aqueous solution in a state of considerable purity by repeated reprecipitation with acetone or alcohol.

2. Constitution and Properties of Sodium Tetraphosphate

The tetraphosphates of Na^+ and K^+, which have not hitherto been obtained in the crystalline state, are obtained on precipitation in the form of colorless oils with a variable water content. The acid from which they are derived, $H_6P_4O_{13}$, has four strongly and two weakly dissociated H^+ ions, which proves the ion to be a linear chain and discounts the idea of an isoform (b) with a branched chain. The iso-form would have three strongly and three weakly dissociated H^+ ions. Tetraphosphate, therefore, fits correctly into the sequence of linear polyphosphates in chromatography (*81, 117, 355*) (see Section VII,C).

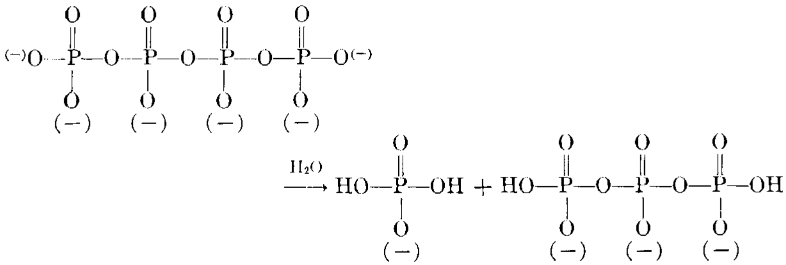


(35)

In keeping with the presence of two weakly acidic end groups, "neutral" alkali tetraphosphates are faintly alkaline in solution (pH 9). The ions Ag^+, Zn^{++}, and Ca^{++} in excess yield difficultly soluble amorphous precipitates of $Ag_6P_4O_{13}\cdot aq$, $Zn_3P_4O_{13}\cdot aq$ and $Ca_3P_4O_{13}\cdot aq$, which are soluble in excess of phosphate. No precipitate is formed by tetraphosphate with $(Co(en)_3)^{3+}$ ions (*233*). The dihydrogentetracridinium salt and the neutral hexaguanidinium salt may be obtained reproducibily in the crystalline form from formamide- and alcohol-containing solution (*233*).

3. Hydrolytic Degradation of Alkali Tetraphosphates

The tetraphosphate anion is practically stable in neutral and alkaline solution at room temperature but at 65.9°C it is about half a power of ten less stable than the triphosphate anion over the whole pH range (*61*). Tetraphosphate has its maximum stability at 65.5°C at pH 10 and this is why it can be prepared from tetrametaphosphate at such temperatures. Its stability becomes smaller with decreasing pH. Apparently during the hydrolysis of an aqueous solution, which follows a first order law at constant pH, the tetraphosphate is cleaved initially exclusively at the end of the chain, to form mono- and tri-phosphate.



$$^{(-)}O-\overset{\overset{O}{\|}}{\underset{\underset{(-)}{O}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{(-)}{O}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{(-)}{O}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{(-)}{O}}{P}}-O^{(-)} \xrightarrow{H_2O} HO-\overset{\overset{O}{\|}}{\underset{\underset{(-)}{O}}{P}}-OH + HO-\overset{\overset{O}{\|}}{\underset{\underset{(-)}{O}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{(-)}{O}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{(-)}{O}}{P}}-OH \quad (36)$$

Further hydrolysis of triphosphate in the usual way then follows as a secondary reaction (*61*). Cleavage of the middle P—O—P bond to yield two pyrophosphate molecules has been observed in a sodium tetraphosphate oil containing water after it had been dried to a glassy consistency (*312*).

$$Na_6P_4O_{13} + 3H_2O \rightarrow 2Na_3HP_2O_7 \cdot 1H_2O$$

4. Crystalline Tetraphosphates of Polyvalent Cations

While no crystalline tetraphosphates of polyvalent cations have so far been obtained from aqueous solutions, crystalline $Ba_3P_4O_{13}$ and $Pb_3P_4O_{13}$ are formed by heating the appropriate mixtures of $Me^{II}HPO_4$ and $Me^{II}(H_2PO_4)_2$ to 550°C, just as sodium triphosphate is formed by calcining mixtures of $NaH_2PO_4 + 2NaHPO_4$ (*169*, *214*). In addition, crystalline $Pb_3P_4O_{13}$ and $Bi_2P_4O_{13}$ have been made by tempering melts with the tetraphosphate composition at 400° or 700°C (*262*). The bismuth salt decomposes at 810°C to yield crystalline $BiPO_4$ and acid melts in which the $BiPO_4$ formed initially dissolves above 900°C. The lead salt melts incongruently at 700°C. Attempts to prepare crystalline tetraphosphates of Zn^{++}, Cd^{++}, and Li^{+} in a similar way have met with no success.

D. THE OLIGOPHOSPHATES WITH A CHAIN LENGTH $n > 4$

In this section the group of polyphosphates with a chain length of $n > 4$ which undergo definite migration in paper chromatography is considered. They include compounds with $(P_nO_{3n+1})^{(n+2)-}$ anions having chain length up to $n \sim 9$.

1. Calcium Pentaphosphate

Apart from tri- and tetra-phosphates, which, like the familiar pyrophosphates, belong to this group, only calcium pentaphosphate has been obtained in a crystalline form. It is formed as so-called trömelite in the form of plates or fibrous crystals on tempering melts of the corresponding composition at temperatures between 920 and 990°C (*136*). That trömelite is in fact a pentaphosphate $Ca_7(P_5O_{16})_2$ can be proved by paper chromatography after the compound has been brought into solution with the aid of ethylenediaminetetracetic acid (*211, 351*).

2. Oligophosphate Glasses

The oligophosphates occur in general as mixtures of salts with anions of various chain lengths corresponding with the homologous series $(P_nO_{3n+1})^{(n+2)-}$. The most studied compounds of this class up to the present are the sodium salts, which are obtained as optically clear glasses by melting together any phosphate mixture with the corresponding $Na_2O:P_2O_5$ ratio. Van Wazer first showed that these glasses must consist of mixtures of linear polymeric phosphates both from theoretical considerations (*338, 349*) and by enriching the components in separate fractions by fractional precipitation of solution with organic liquids, such as acetone (*339*). The degree of fractionation occurring was found by titration of the end groups in the separate fractions (*254*). The mean chain length $\bar{n}$ is given by the equation:

$$\bar{n} = [2 \times (\text{number of P atoms})]/\text{number of end groups}$$

or

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

It is necessary in this case to make the proviso that these glasses shall not contain any ortho- or meta-phosphate. A similar fractionation may be obtained using barium ions (*72, 73*) or organic bases such, for example, as naphthylamine, phenylenediamine or benzidine (*37, 86, 87*), at various pH values. In this case the material of high molecular weight is precipitated from the more strongly acidic solutions and material of lower molecular weight under less acidic conditions. Complete separation into the components and the quantitative determination of the latter is possible only by paper chromatography or ion exchange chromatography (see Section VII).

a. Composition of oligophosphate glasses. Quantitative evaluation of chromatograms by determining the content of separate polymer homologues in the glass with radioactive P^{32} (*115, 192*), or by colorimetric determination after eluting the chromatogram with ammonia (*353, 354*), has given results which are in extensive agreement. As was predicted by van Wazer (*338*), none of the glasses contained mono- (i.e., ortho) phosphate and none contained only a single component. All were mixtures of compounds in the series $Na_{n+2}P_nO_{3n+1}$. In general, the most abundant component is that with a chain length n corresponding with the mean chain length $\bar{n}$.

A series of attempts to calculate theoretically the distribution of anions of different chain length (*216, 339, 340*) has so far led to results which are approximately but not generally valid (*354*). One theory represents better the distribution of low molecular weight species (up to $n \sim 3$) and another is better for $n = 5$–9. None, however, explains why, with the same mean chain length, the distribution of the separate chain lengths depends on the nature of the cation Na^+, K^+, Li^+ (*354*), H^+ (*143, 314*) or Ca^{++} (*211*). The chief shortcoming of the distribution theories advanced up to the present is that they are based on the assumption that the bond strength in the separate P—O—P bonds is independent of the chain length and the nature of the cation. This will certainly be true only if the mean chain length assumes high values as in Graham's glasses, in which the $Na_2O:P_2O_5$ ratio is very close to unity.

b. Constitution and chemical properties of oligophosphates. The presence in the anions of oligophosphates with a chain length $n > 4$ of unbranched chains of PO_4 tetrahedra, as in the anions of tri- and tetraphosphates, was deduced originally from the linear plot of the logarithms of R_f or P_k values for oligophosphate glasses in paper chromatography (*118*) (see Section VII,C) and also from regularities in the physical properties of their melts and solutions (*42, 110*). When weighable quantities of the pure separated components were obtained in solution by ion exchange chromatography (*38, 105*) direct chemical proof of the constitution was advanced. It was found (*358*) that when the individual polyphosphates of chain length n were degraded hydrolytically in weakly alkaline solution (pH 8; 60°C), monophosphate and a polyphosphate with chain length $(n - 1)$ were formed as the primary products in addition to small amounts of trimetaphosphate. The compounds thus represent a true homologous series of polymers showing continuity in their chemical properties with tri- and tetraphosphates.

Alkali oligophosphates are soluble in water either individually or when in the form of glass-like mixtures, and their solutions form precipitates with polyvalent cations which are soluble in excess of the phosphate. Their physical properties are described in Section IV,E,*1*,*e* since they are related to those of glasses of the type of Graham's salt with anions of large chain length.

c. Hydrolytic degradation of oligophosphates. As has been mentioned already, the stability of oligophosphates decreases with the pH. Figure 6 shows the dependence of the first order constants for the rate of hydrolysis on the pH of the solution as determined by Crowther and Westman (*60, 61*).

These values reveal that the rate of hydrolysis in the alkaline range up to pH ~ 9 is very small and practically constant, but that it then rises rapidly with decreasing pH. It is also evident that the stability of oligophosphates to hydrolytic degradation decreases in the order diphosphate > triphosphate > tetraphosphate. Degradation experiments with small quantities of oligophosphates with chain lengths $n = 4$–8 show (*358*) that stability decreases further up to the octaphosphate (see Fig. 7). (The

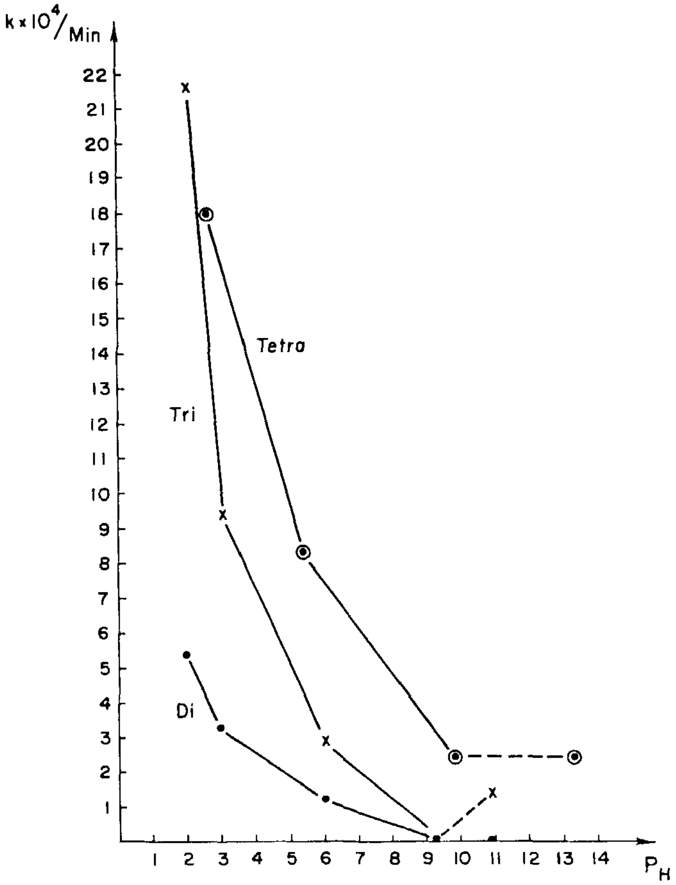


Fig. 6. Dependence of first-order rate constants for the hydrolysis of oligophosphates on pH, according to Crowther and Westman (*60*).

K-values of van Wazer *et al.* (*348*) are used for the di- and tri-phosphate.) As already mentioned, these degradation experiments also showed that, starting from the pentaphosphate, formation of trimetaphosphate with a

TABLE IX

Yield of Trimetaphosphate on the Degradation of Polyphosphates in Aqueous Solution at pH = 8 and at 60°C

Chain length *n*	2	3	4	5	6	7	8	∞
% P as Trimetaphosphate after complete degradation	0	0	0	5–8	15–17	~25	~38	≧60

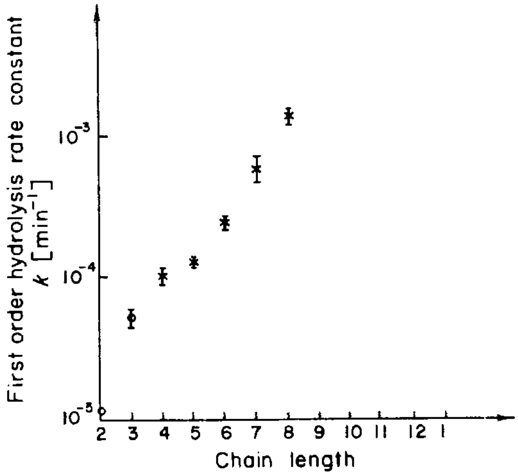


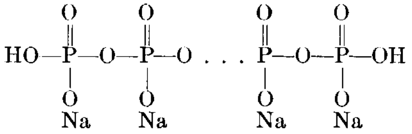
FIG. 7. Dependence of hydrolysis rate constants of oligophosphates at pH = 8 and 60°C on chain length, according to Wieker (*358*).

cyclic anion occurs in addition to cleavage of monophosphate. More trimetaphosphate is produced as the phosphate chain length increases. The amounts of trimetaphosphate present when the phosphate taken originally has disappeared completely are given in Table IX (*358*). The processes leading to formation of trimetaphosphate in the breakdown of polyphosphates and the conclusion to be drawn regarding the configuration of the chains will be considered in Section IV,E,*1*,*b*.

E. HIGHMOLECULAR POLYPHOSPHATES

1. Glasslike Graham's Salts

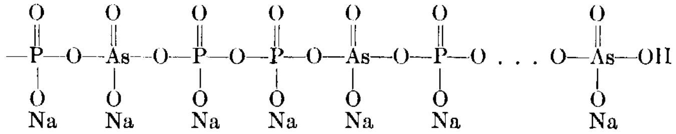
a. Preparation and constitution. The chief representative of this group of compounds is Graham's salt, to which Graham, its discoverer, ascribed the formula $NaPO_3$ (*103*). It is formed as a somewhat hygroscopic glass which is readily soluble in water when sodium dihydrogen monophosphate, NaH_2PO_4, is heated to its melting point (620°C) and the melt is quenched. Fleitmann and Henneberg (*93*) concluded that this compound was a hexamer from their observation that when Graham's salt was treated with ammonia solution, a maximum of $5/6$ of the sodium was replaced by ammonium. Since then Graham's salt has been incorrectly called a hexametaphosphate, and this term is still often used. The incorrectness of this conclusion became apparent after the high molecular weight had been determined by means of the ultracentrifuge (*168*) and by diffusion measurements (*158*). Samuelson (*254*) deduced from this and from the detection of acid end OH groups (*250, 328*) that Graham's salt is a mixture of salts with anions made up of PO_4 tetrahedra having OH groups on the chain ends.



$$\mathrm{HO{-}\underset{\underset{Na}{O}}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{\underset{Na}{O}}{\overset{O}{\overset{\|}{P}}}{-}O\ .\ .\ .\ \underset{\underset{Na}{O}}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{\underset{Na}{O}}{\overset{O}{\overset{\|}{P}}}{-}OH} \qquad (39)$$

The end groups which can be determined titrimetrically (pH 4.5–9) provide a measure of the mean chain length $\bar{n}$ of the salt mixture $Na_n(H_2P_nO_{3n+1})$. The same conclusion was reached by van Wazer from theoretical considerations (*338, 339*).

Chemical proof that the anions in Graham's salt are linear chains of PO_4 tetrahedra follows from the observation that arsenato-phosphate glasses analogous to Graham's salt (see Section VI) are broken down on aqueous hydrolysis into ortho arsenate and mixture of low molecular polyphosphates with a mean chain length dependent only on the P:As ratio in the glass (*295, 308*).



$$\mathrm{{-}\underset{\underset{Na}{O}}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{\underset{Na}{O}}{\overset{O}{\overset{\|}{As}}}{-}O{-}\underset{\underset{Na}{O}}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{\underset{Na}{O}}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{\underset{Na}{O}}{\overset{O}{\overset{\|}{As}}}{-}O{-}\underset{\underset{Na}{O}}{\overset{O}{\overset{\|}{P}}}{-}O\ .\ .\ .\ O{-}\underset{\underset{Na}{O}}{\overset{O}{\overset{\|}{As}}}{-}OH} \qquad (40)$$

In addition, solutions of Graham's salt prove to be identical in their chemical behavior with those of Maddrell's salt (*295, 316*), the chain-like nature of the anions of which has been clearly established chemically by a study of the arsenato-phosphate analogs (*309*) and later by crystal structure analysis (*78*). (See also Section IV,E,*2*.) Anions of Graham's salt show their high molecular character by their failure to migrate in paper chromatography (*82, 84*).

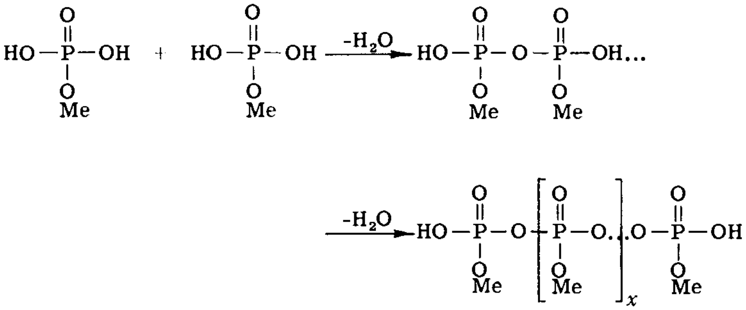
Physical properties of solid polyphosphate glasses and their melts are also in accord with the conclusions drawn from chemical studies. The X-ray diffraction pattern shows the polyphosphate anions to consist of long chains of PO_4 tetrahedra (*32*) and the same conclusion is reached by studying the double refraction of fibers formed by rapidly drawing supercooled melts of Graham's salt (*101*).

Apart from salts with homologous polymer anions, Graham's glass always contains trimeta- (6–10%), tetrameta- (up to ~4%) and very small amounts of pentameta- and hexametaphosphate (see Section IV,D) with cyclic anions and also, to a small extent, cross-linked phosphates with tertiary PO_4 tetrahedra (see Section V) (*284, 285, 364*).

The linear polymer components of Graham's salt are high molecular members, $Na_nH_2P_nO_{3n+1}$, of the series of di-acid polyphosphates, the initial members of which are the dihydrogen monophosphate, acid diphosphate, triphosphate etc.

$$NaH_2PO_4;\quad Na_2H_2P_2O_7;\quad Na_3H_2P_3O_{10}\ \ldots\ Na_nH_2P_nO_{3n+1} \tag{41}$$

All result from thermal condensation of dihydrogen monophosphates.



$$\mathrm{HO{-}\overset{\overset{O}{\|}}{\underset{\underset{Me}{O}}{\underset{|}{P}}}{-}OH + HO{-}\overset{\overset{O}{\|}}{\underset{\underset{Me}{O}}{\underset{|}{P}}}{-}OH \xrightarrow{-H_2O} HO{-}\overset{\overset{O}{\|}}{\underset{\underset{Me}{O}}{\underset{|}{P}}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{Me}{O}}{\underset{|}{P}}}{-}OH\ldots}$$

$$\mathrm{\xrightarrow{-H_2O} HO{-}\overset{\overset{O}{\|}}{\underset{\underset{Me}{O}}{\underset{|}{P}}}{-}O{-}\left[\overset{\overset{O}{\|}}{\underset{\underset{Me}{O}}{\underset{|}{P}}}{-}O.\right]_{x}.O{-}\overset{\overset{O}{\|}}{\underset{\underset{Me}{O}}{\underset{|}{P}}}{-}OH} \tag{42}$$

Equilibrium conditions for the chain length distribution are set up in these reactions, the mean chain length $\bar{n}$ of the anion being greater the higher the temperature used in the preparation and the lower the water

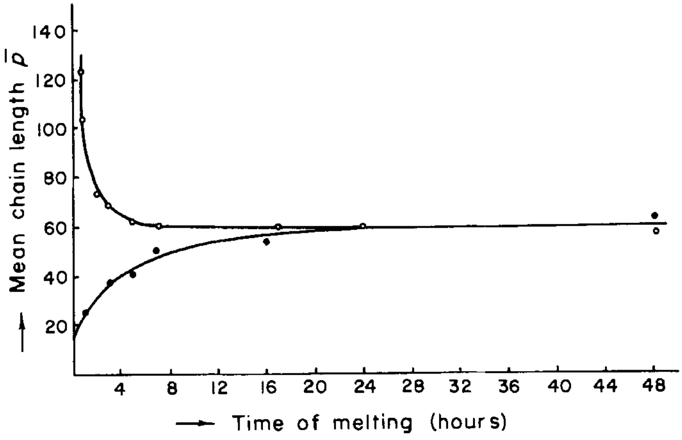


FIG. 8. Mean chain lengths in the formation of Graham's salt. T = 650°C; P_{H_2O} = 55.3 Torr.

vapor pressure in the surrounding atmosphere (see Fig. 8 points). The same equilibrium as in the condensation reaction is established if anhydrous trimetaphosphate is heated to the same temperature and with the same water vapor pressure (*364*) (see Fig. 8 circles).

$$\frac{n}{3}\,Na_3(P_3O_9) + H_2O \rightleftharpoons Na_n[H_2P_nO_{3n+1}] \tag{43}$$

The mean chain length $\bar{n}$ given by:

$$\bar{n} = (K/p_w)^{1/2} \tag{44}$$

may be deduced from the mass action law, p_w denoting the external water vapor pressure. The equilibrium constant K satisfies the van t'Hoff equation $\log_e K = (Q/RT) + \text{Const.}$ Both relationships are given by the expression,

$$\bar{n} = \exp\,[8.87 - (5100/RT) - (\log_e p_w/2)] \tag{45}$$

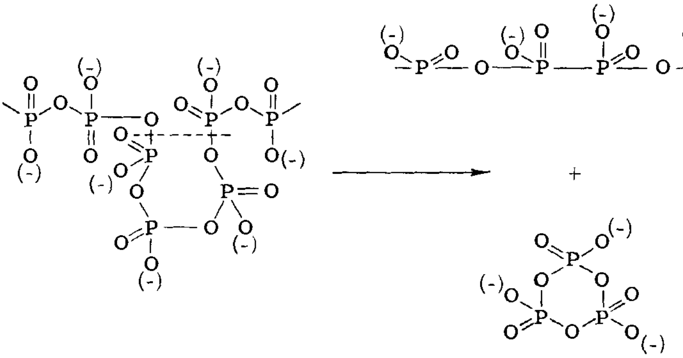
from which the mean chain length in the glass may be calculated with an accuracy of ±5%. A "heat of hydrolysis" of the P—O—P linkage by water vapor between 650° and 850°C of ~10 kcal is obtained from the temperature dependence of K (*364*).

b. The transformation of Graham's salt to Trimetaphosphate. When any sodium dihydrogen polyphosphate with a Na:P ratio of 1:1 is tempered in the free atmosphere at between ~400° and 600°C, the reaction (43) is reversed. Water is split off and quantitative formation of trimetaphosphate occurs.

The kinetics of the transition from Graham's glass to trimetaphosphate crystals follow Stranski and Kaischew's theory of crystallization (*157*, *277*) and yield an activation energy of 62.9 kcal/mole (*124*). Trimetaphosphate occurs as the equilibrium phase in the system $NaPO_3$—H_2O at between ~450° and 620°C (*199*).

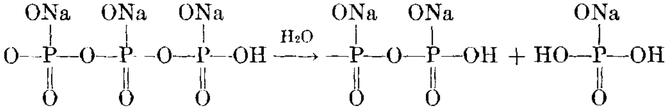
Formation of trimetaphosphate anions from those of Graham's salt also occurs in solution. In water this process is not associated with hydrolytic cleavage of the P—O—P bonds, as was at first assumed (*10*, *322*), but is independent of it (*361*). Thus polyphosphates of long-chain amines which are soluble in benzene form trimetaphosphate quantitatively on warming the anhydrous solution (*359*). This transformation follows Ostwald's rule for successive transformations, since trimetaphosphates are more stable than polyphosphates (*322*).

Perhaps the formation of trimetaphosphate and small quantities of tetrametaphosphate from dissolved polyphosphates, which can amount to ~70% in presence of Mg^{++} ions, is an indication of the form in which the anion chains are present in the solution. In any case this formation of trimetaphosphates is not, contrary to what was proposed initially (*293*, *326*), an argument for the assumption that trimetaphosphate rings constitute a structural unit in the polyphosphates. Thus in solutions of Maddrell's salt, the anions of which are known to be linear chains from crystal structure determination (*78*) (see Section IV,E,*2*), up to 50% yields of trimetaphosphate are produced as a product of degradation in aqueous solution (*316*). The formation of trimetaphosphate could be understood readily if it were assumed that polyphosphate anions with more than a certain number of members ($n = 5$) are present in solution as spiral chains with a repeating unit in the spiral of, on the average, $3PO_4$ tetrahedra which can also be coiled (see Section IV,E,*1*,*e*). Formation of trimetaphosphate can then be considered as a simple transformation and it is possible to understand that trimetaphosphate formation is in no way linked with the formation of fresh OH groups (*361*). The process is accelerated catalytically by cations added to the solution and this effect is greater than that of added cations on the hydrolytic cleavage of P—O—P bonds (*323*, *358*). (See Sections IV,E,*1*,*c* and *d*.)



(46)

c. Hydrolytic Degradation of High-Molecular Polyphosphates. Formation of trimetaphosphate in aqueous polyphosphate solutions is always accompanied by hydrolytic degradation of the anion chains according to a first-order law. Two types of cleavage may be distinguished (*186*, *322*). The first is like that occurring with low-molecular oligophosphates and entails the splitting off of monophosphate from the ends of the chains. This is a first-order reaction.



$$O-\underset{\underset{O}{\|}}{\overset{\overset{ONa}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{ONa}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{ONa}{|}}{P}}-OH \xrightarrow{H_2O} -\underset{\underset{O}{\|}}{\overset{\overset{ONa}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{ONa}{|}}{P}}-OH + HO-\underset{\underset{O}{\|}}{\overset{\overset{ONa}{|}}{P}}-OH \qquad (47)$$

High-molecular polyphosphates are practically stable in aqueous solution at room temperature and a pH near the neutral point. At 60°C the half-life is about 50 days but it decreases rapidly with rising temperature. The hydrolysis constant of the high-molecular phosphates at 60°C and pH 8 has the value $K = 0.9 \times 10^{-4}$ and is about a power of ten smaller than that of octaphosphate and roughly equal to that of hexaphosphate (see Fig. 7).

Polyphosphates seem to pass through a minimum of stability for a chain length of about $n = 10$ (*359*). Decreasing the pH accelerates hydrolysis. Thus, for example, the following values of $t_{1/2}$ are found for high-molecular anions at 60°C with varying pH. Added cations have a similar action to H$^+$ ions. Addition of 0.164 milli-equivalents of cations per millimole of $NaPO_3$ increases the rate constant K for the degradation of polyphosphates at pH 8 and 60°C by the following factors relative to the constant K_0 in absence of added salts (*361*).

TABLE X

INFLUENCE OF PH ON THE HALF-LIFE FOR POLYPHOSPHATE DECOMPOSITION

pH	1	3	5	8
$t_{1/2}$	22.8 m	6.7 h	4.4 d	45.4 d

TABLE XI

CATALYTIC ACTION OF VARIOUS CATIONS ON THE RATE OF HYDROLYSIS OF POLYPHOSPHATES

Cation	K^+	Na^+	Li^+	Ba^{++}	Sr^{++}	Ca^{++}	Mg^{++}	Al^{+++}
K/K_0	~1	~1	1.08	1.56	1.69	2.78	3.52	7.50

The hydrogen ion probably falls, for a corresponding concentration, between Li$^+$ and Ba^{++}, and the ions of metals such as Ag, Cu, Zn, Pb, and Bi, or the rare earths, have a much stronger catalytic effect (*6*) which is further increased if the dielectric constant of the solvent is decreased by adding organic liquids such as acetone or dioxane (*323*). The degrees of dissociation (Table XII) and the exchange constants (Table XV) of the cations are also related to their catalytic activity (cf. Section IV,E,*1*,*d*).

It is very probable, though not yet quite certain, that a second type of hydrolytic cleavage occurs at very high hydrogen ion concentrations. This involves cleavage of high-molecular anions from inside the chain and the formation of polyphosphates of smaller chain length (*186*, *322*). This type of cleavage apparently occurs preferentially in presence of enzymes (*147*). In addition to the hydrolytic cleavage of the P—O—P bonds of the anion chain and independently of it, there is a much slower hydrolysis of the trimetaphosphate formed initially to di- and mono-phosphate until finally the whole of the phosphate is present as monophosphate.

d. Complexing of Ions by High-Molecular Polyphosphates. When solutions of salts of polyvalent cations are treated with a polyphosphate solution a precipitate is generally formed which redissolves on adding an excess of polyphosphate. The polyvalent cation is either not precipitated from this solution by the usual reagents or precipitation is no longer complete. This property forms the basis of a technically important application of this group of compounds (*91, 127*). Thus if a sufficient quantity of polyphosphates (usually triphosphate or Graham's salt) is added to hard water the alkaline earth cations contained in the water can no longer be precipitated and the water is therefore softened.

The composition of the precipitates formed by polyphates depends on the way in which they are produced. If a solution of the precipitating cation is added to a polyphosphate solution, or if the solid polyphosphate is treated with the salt solution, only part of the cation of the phosphate taken is, as a rule, replaced by the precipitating cation (*92, 290, 291*). Conversely, when precipitation occurs by adding polyphosphate to a concentrated solution of the salt precipitates are formed which contain only the cation of the salt (*177, 324*).

The consistency of these precipitates with polyvalent cations depends on the cation radius. Precipitates with large cations ($r > 1.1$ Å: Ba^{++}, Sr^{++}, Pb^{++}, Ag^{+}, Bi^{+++}, ZrO^{++}, UO_2^{++}, Hg_2^{++}) are flocculent solids, whereas those with smaller cations ($r < 1.1$ Å: Ca^{++}, Mg^{++}, Zn^{++}, Cd^{++}, Mn^{++}, Ni^{++}, Co^{++}, Fe^{++}, Fe^{+++}, Cr^{+++}, Hg^{++}, Cu^{++}) are oily (*316*). All these precipitates, and also alkali polyphosphates obtained by "salting out" contain a lot of water (7–10 molecules H_2O/PO_3 group) which they do not lose completely on drying over desiccating agents. It is assumed that the polyvalent cations are linked to only one anion chain in the oily precipitates, such as that with Mg^{++}, but are linked simultaneously to more than one in those which are flocculent and thus produce cross-linking (*225*).

Partial replacement of cations when using excess of alkali phosphate was at first interpreted by supposing that the cations were in part bound as a "complex" with the polyphosphates. This led to incorrect conclusions regarding the molecular size of polyphosphates, which persist even now in the designation of Graham's salt as "hexametaphosphate." The correct interpretation of these very complicated relationships stems from the discovery that in dilute solutions of polyphosphates even salts of the alkali metal ions are only partially dissociated—up to a maximum of 30–40% (*260, 280, 282, 288, 333*). The degree of dissociation α for alkali polyphosphates depends on many factors. Thus, for example, the effective degree of

TABLE XII

DEPENDENCE OF THE DEGREE OF DISSOCIATION OF HIGH-MOLECULAR POLYPHOSPHATES ON THE NATURE OF THE CATION

Cation	Li^+	Na^+	K^+	Cs^+
α	0.34	0.37	0.39	0.4

dissociation of 0.01 *M* (on empirical formula) solutions of high-molecular alkali polyphosphates increases in the sequence Li → Cs with increasing cation radius (*282*). With increasing chain length the degree of dissociation first decreases rapidly and then more slowly to a limiting value at a chain length of about 100. Polyphosphoric acids in 0.01 *N* solution show almost the same degree of dissociation as the sodium salts, as shown below (*360*).

TABLE XIII

DEPENDENCE OF THE DEGREE OF DISSOCIATION OF POLYPHOSPHORIC ACIDS ON THEIR CHAIN LENGTH

Mean chain length $\bar{n}$ of the polyphosphoric acids	3	$\overline{30}$	$\overline{50}$	$\overline{85}$	$\overline{180}$
Degree of dissociation, α, at 0°C	0.89	0.49	0.36	0.33	0.32

In addition, the degree of dissociation becomes smaller as the phosphate concentration is increased. The same rules apply in principle for polyvalent cations except that they are much more strongly bound than the alkali metal ions. This is particularly true of the transition elements Mn^{++} and Zn^{++} etc., and Bi^{+++} etc., (*182, 271, 345*). The negative logarithms of the dissociation constants of the Ca^{++} ion in polyphosphate solutions containing tetramethylammonium bromide have the following values at 25°C and pH 10–12 (*148*).

TABLE XIV

DEPENDENCE OF THE NEGATIVE LOGARITHMS OF THE DISSOCIATION CONSTANTS OF CALCIUM POLYPHOSPHATES ON THE ANION CHAIN LENGTHS AND THE IONIC STRENGTHS OF THE SOLUTIONS

	Anionic chain length					
Ionic strength	1 (*271*)	2	3	$\bar{6}$	$\overline{14}$	$\overline{60}$
1	—	4.89	5.36	5.78	5.80	5.80
0.2	1.7	—	—	—	—	—
0.1	—	5.39	6.41	6.8	6.77	6.99
0	—	5.60	6.90	7.28	7.23	7.54

The value for $CaHPO_4$ has been included for purposes of comparison (*271*). Taking $\alpha = 0.33$ a p_K value of about 0.7 may be calculated for the dissociation of Na^+ ions in solutions of high-molecular sodium polyphosphates. The strength of bonding of polyvalent cations decreases with increasing ionic strength, i.e., with increasing concentration of added salts.

Numerous experimental and theoretical studies of problems in this field have appeared and these have been reviewed under the title "Metal Complexing by Polyphosphates" by van Wazer (*342*). The phenomena which have been mentioned may be considered in general as due to "complex formation." However, a simple qualitative and quantitative description of the facts may also be obtained if solutions of high-molecular polyphosphates are considered as micro-heterogeneous systems and if the bonding of polyvalent ions is interpreted as involving ion exchange phenomena on the polyphosphate chains (*77*, *313*, *319*, *324*).

The exchange of H^+ ions in the free polyphosphoric acids with chain lengths $\bar{n}$ between 28 and 180 with metallic cations, for example, follows the equation of Rothmund and Kornfeld (*247*),

$$[(H^+)^z/(Me^{z+})]_{\text{solid}}{}^{\sigma} = K[(H^+)^z/(Me^{z+})]_{\text{soln}} \qquad (48)$$

where the constants K and σ at 0° at a mean chain length $\bar{n}$ of 100 have the following values (*360*).

TABLE XV

EXCHANGE CONSTANTS OF THE PROTONS OF POLYPHOSPHORIC ACIDS WITH VARIOUS CATIONS

Constant	K^+	NH_4^+	Na^+	Li^+	Alkaline earth
K	13.8	7.6	5.75	5.13	≤ 2.5
σ	2.3	(0.77)?	1.43	0.79	0.5

If the exchange constants for the cations are compared with their catalytic activity (Table XI) and the order of their degrees of dissociation in polyphosphate solutions (Table XII), a considerable measure of correlation will be recognized. It follows that the cations become more active catalytically as they become more strongly bonded to the polyphosphate anions. This also accords with the increase in their effectiveness as the dielectric constant of the solvent is decreased.

In addition to the ability of polyphosphates to bond cations they also possess the important property of hindering the formation of large crystallites of $CaCO_3$ and of solid boiler scale, even when present at very small concentrations (*239*). This property, which is used in the threshold or innoculation process, is based on the bonding or adsorption of polyphosphate chains on the surface of the crystal nucleus. These then hinder its further growth or aggregation. The effectiveness of detergents to which polyphosphates have been added must also be related to their adsorption on the surface of solid particles, which then become hydrophilic (*89, 163, 194, 341*).

e. Physico-Chemical Properties of Polyphosphate Solutions. There is also a continuous transition in the physical properties of solutions of polyphosphates in passing from the low- to the high-molecular compounds. Apart from the initial members they all exhibit the typical properties of polyelectrolytes. The number of investigations on this subject is very large. A review entitled "The Inorganic Phosphates as Polyelectrolytes" has appeared (*41*), but this may be extended by the new investigations described here.

The physical property which has been studied most accurately is the viscosity of polyphosphate solutions (*252, 283, 287*). As with all polyelectrolytes, the specific viscosity of solutions increases with increasing dilution. This is explained by supposing that the polyphosphate chains are only slightly dissociated in concentrated solution and are therefore coiled, whereas they are more highly charged in dilute solution and therefore stretch. Molecular weights may be calculated from the "intrinsic" viscosity extrapolated to zero concentration and the values are in good agreement with those calculated from light scattering (*251, 287*) and from the determination of end groups. The solutions show streaming double refraction which becomes more pronounced as the dilution is increased and as the chain length in the phosphate under study is increased. These solutions also show anisotropy in their electrical conductivity (*132, 256, 257, 258*), which follows similar laws to the streaming double refraction. From the two properties the end-end distance of the polyphosphate anions may be deduced, thereby leading to the conclusion reached from other measurements that polyphosphate anions are rod-like rather than spherical and are coiled to only a small extent. Data obtained up to the present do not contradict the hypothesis (see Section IV,E,*1*,*b*) that the anion chains are primarily spiral-like in shape and are coiled to a greater or lesser extent as a secondary effect. Results of diffusion and sedimentation measurements in the ultracentrifuge agree with those obtained by other methods. Unequivocal proof of the strong bonding of cations of all sorts to the polyanions comes from electrical conductivity measurements (*46, 259*), transport measurements, electrophoretic phenomena (*278, 279*), and also from salting-out effects. Densities and refractive index values for the solutions are also in accord with the picture which has emerged (*110*).

2. Crystalline Alkali Polyphosphates

A range of high-molecular alkali polyphosphates occur in several crystalline forms. In the case of the sodium and potassium compounds the trivial names Maddrell's and Kurrol's salts have been adopted and these have been applied to other crystalline polyphosphates without any attempt at following a systematic nomenclature. Thus for sodium one speaks of a high- and a low-temperature form of Maddrell's salt (*23*) and these are also called $NaPO_3(II)$ and $NaPO_3(III)$. Similarly there are two forms, A and B, of Kurrol's sodium salt (*316*) [= $NaPO_3(IV)$ (*340*)], three forms of Kurrol's potassium salt (*22, 29, 298*) and of Kurrol's rubidium and cesium salts (*54*). In addition all of these salts are also called metaphosphates (*340*) because their analytical composition corresponds with the formula $(M^IPO_3)_x$. In fact, they are all high-molecular polyphosphates, $Me_n{}^IH_2(P_nO_{3n+1})$, with a high degree of condensation ($\bar{n}$ = ~100 to >10,000) (*281*). All these crystalline polyphosphates and also those of lithium and ammonium (*291, 302*) are practically insoluble in water. They swell, however, when treated with solutions of salts of other cations and are then soluble in water. They are best brought into solution by shaking in water with an ion exchange resin charged with another cation (*224, 257*). It is notable that the crystalline sodium and potassium polyphosphates, which are separately insoluble in water, go into solution when they are taken together in about 1:1 *M* ratio and shaken with water. This effect depends on the ion exchange properties of these crystalline species, which may also be directly detected for Maddrell's salt (*243*).

Since the solutions of these salts are like those of the corresponding glassy compounds in almost all properties (*316*), their low solubility must arise from their lattice energy, as in the case of most silicates. In solution they may be differentiated from the corresponding glasses only by the higher molecular weights and their possibly smaller polydispersion (*183, 224*). Once brought into solution, they cannot generally be obtained again in the crystalline form by precipitation or crystallization. Only the potassium, rubidium and cesium salts can be precipitated from solutions in the form of very small crystals which contain water (*162, 291*).

3. Crystal Structures of Condensed Phosphates

Proof that the anions of the substances mentioned really consist of long chains of PO_4 tetrahedra has been supplied by complete structural analyses of crystals. Four different types of such chain-like anions, differing in shape and inner periodicity, have so far been recognized. In the low temperature form of lithium polyphosphate, which has the same type of structure as lithium polyarsenate and diopside $[Ca, Mg(SiO_3)_2]_x$ these are extended chains which (see Fig. 9a) as in enstatite have a *Zweierperiodizität* (*138*) (see also ref. *66* in Table XVI). Rubidium polyphosphate has quite similar *Zweierketten* (*55*) (see Fig. 9b and ref. *63* in Table XVI) except that the PO_4 tetrahedra are somewhat rotated with respect to Form a. In the high

TABLE XVI

A. CRYSTAL STRUCTURES OF CONDENSED PHOSPHATES AND ARSENATES

Substance	Literature	Lattice constants in Å or degrees						Space group	Z
		a	b	c	α	β	γ		
$Na_4P_2O_7 \cdot 10H_2O$	(*179*)	17.93	6.96	14.85		118.5		$I2/c$	4
$Na_5P_3O_{10}I$	(*80, 56*)	9.61	5.34	19.73		112		$C2/c$	4
$Na_5P_3O_{10}II$	(*63, 80*)	16.00	5.24	11.25		93		$C2/c$	4
$(RbPO_3)_x$ Rb-polyphosphate	(*55*)	12.12	4.23	6.48		96.3		P^21/n	4
$(NaPO_3)_x$ A. Kurrol A.	(*153, 155*)	12.12	6.20	6.99		92.0		P^21/n	8
$(AgPO_3)_x$ Ag-Polyphosphate	(*154, 155*)	11.86	6.06	7.31		93.5		P^21/n	8
$(NH_4)_4(P_4O_{12})$ Tetrameta	(*245*)	10.42	10.82	12.78				$Cmca$	4
P_4O_{10} Vapor	(*128*)			Electron diffraction					
P_4O_{10} Crystal	(*66*)	7.44	—	—	87			$R3c$	2
$(P_2O_5)_x$ Stable form	(*65*)	16.3	8.14	5.26				$Fdd2$	8
$(LiAsO_3)_x$ Polyarsenate	(*138, 302*)	10.18	9.43	5.25		110.5		$C2/c$	8
$(NaAsO_3)_x$ Maddrell-Type	(*174*)	8.07	7.44	7.32	91.5	90	104	$P\bar{1}$	6

B. INCOMPLETE CRYSTAL STRUCTURE DETERMINATIONS GIVING INFORMATION ON THE P—O—P FRAMEWORK

Substance	Literature	a	b	c	α	β	γ	Space group	Z
$(NaPO_3)_x$ Kurrol B	(*156, 54*)	11.37	6.01	7.63		86		P^21/n	8
$(NaPO_3)_x$ Maddrell h	(*78*)	15.30	6.96	7.05		93.3		P^21/n	12
$(KPO_3)_x$ Polyphosphate	(*2, 54*)	14.02	4.54	10.28		78.5		P^21/a	8
$(CsPO_3)_x$ Polyphosphate	(*54*)	12.71	4.32	6.83		83		P^21/n	4
$((PbPO_3)_2)_x$	(*2*)	7.29	7.95	17.28		89.5		P^21/c	8
$(P_2O_5)_y$	(*180*)	9.23	7.18	4.94		—		$Pnam$	4

temperature form of Maddrell's sodium salt $(NaPO_3)_x$, which has the same type of structure as sodium polyarsenate and β-wollastonite (*78*) there is a *Dreierkette* (see Fig. 9c and refs. *65* and *174* in Table XVI), in which each third tetrahedron is opposed to the two others. In the fourth type (see Fig. 9d and Table XVI, refs. *55*, *138*, and *153*) the anions are arranged on a screw pattern, each fourth PO_4 tetrahedron having the same orientation as the first. This type of anion has so far been identified in both the A and B forms of Kurrol's sodium polyphosphate and in silver polyphosphate (*54*, *153*, *155*, *156*). It is conceivable that spirally-wound anions of this sort

	Distances in A.		Valency angle		Distance parallel to the chain axis
Form	P—O— Bridge	P=O	O / \ P P	P / \ O O	P—O—P A
Angle	1.63	1.45-1.48	133.8°	99-116°	
Short chain	1.62; 1.66	1.45-1.52	121.8°	94-118°	
Short chain	1.61; 1.68	1.49-1.50	121.5°	98-116°	
Zweierkette	1.62	1.44-1.47	129°	95.9-123°	2.11
Spiral	1.57-1.64	1.47-1.48	124-136°	99-117°	1.55
Spiral	1.56-1.62	1.45-1.46	125-134°	101-118°	1.52
Ring	1.59-1.63	1.44-1.51	132°	100-122°	
Tetrahedron	1.62	1.39	123.5°	101.5-116.5°	
Tetrahedron	1.60-1.64	1.40-1.42			
Space structure	1.61-1.62	1.39	120.1-129.7		
	—As—O—	—As=O	O / \ As As	As / \ O O	
Zweierkette	1.73-1.81	1.60	128.6°	97.9-122°	2.62
Dreierkette	1.76-1.79	1.67-1.71	127.7-131.4°		2.48

Spiral	1.50
Dreierkette	2.32
Zweierkette	
Zweierkette	
Unknown	2.27
Layers	2.16

made the formation of trimeta- and tetrameta-phosphate possible in solution.

Table XVI summarizes both the crystallographic data for these high-molecular polyphosphates and also all data in the structures of other condensed phosphates from which unambiguous deductions can be made. It will be seen that two P—O distances can be distinguished in all these compounds. One set of values represents the distance in the bridging P—O—P bond. These lie between 1.56 and 1.68 Å. The second group corresponds with bonds to isolated oxygen atoms and here the bond distance is appreciably

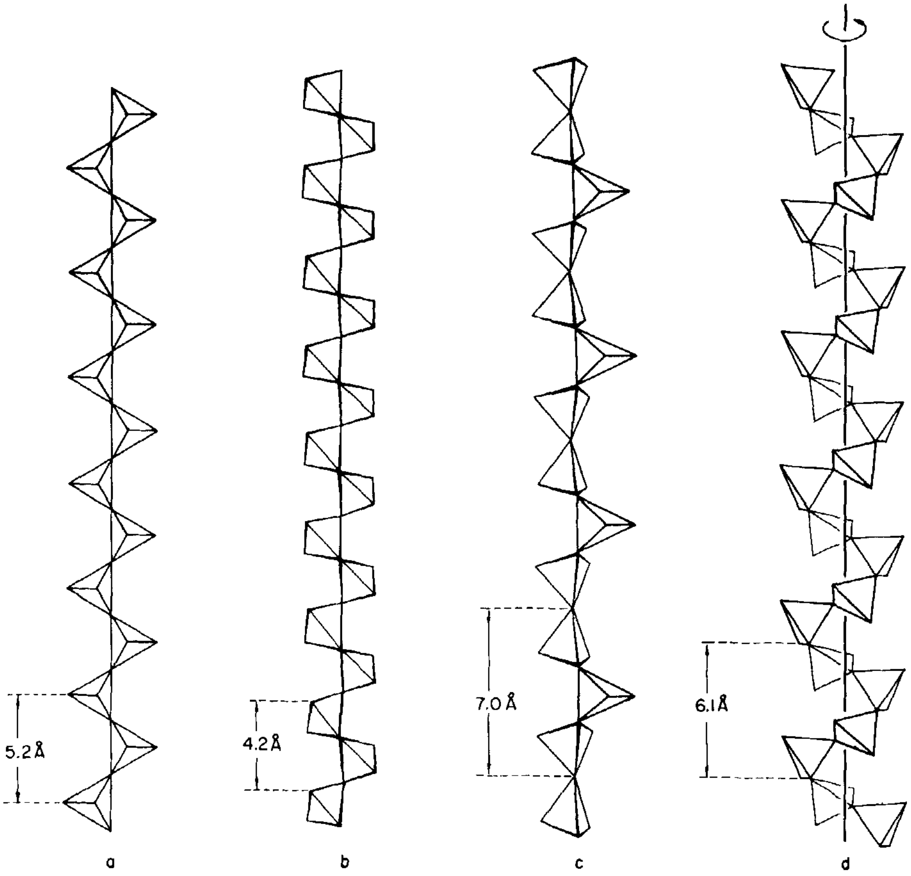


FIG. 9. Various chain types in crystalline high-molecular phosphates: (a) $(LiPO_3)_x$ low temperature form; (b) $Rb(PO_3)_x$; (c) $(NaPO_3)_x$ Maddrell's salt (high temperature form); (d) $(NaPO_3)_x$ Kurrol's salt.

shorter (1.39–1.52 Å). In the old terminology these two sets of values correspond with single and double bonds between pentavalent phosphorus and oxygen. In all cases the (P—O—P) and (O—P—O) bonds are nonlinear. The oxygen valency angle lies between 120° and 136°, with a mean of 127°. The (O—P—O) angle in the PO_4 tetrahedra varies from 94° to 125°, with a mean of 102°. The distance between the P atoms of two PO_4 tetrahedra linked by O measured by projection onto the direction of the chain is also interesting. For anions with linear chains it is between 2.11 and 2.32 Å, and in the chains with a screw configuration between 1.51 and 1.55 Å. In any case it is less than the value of 2.5 Å which has been assumed so far in discussion of the end-end distances in the coiled anions.

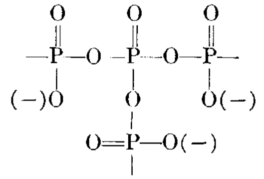
It is also noteworthy that the P—O distances and also the oxygen valency angle in diphosphate, trimetaphosphate and the various forms of phosphorus(V) oxide do not in any way fall outside the range of values for the linear polyanions. The As—O distances in high-molecular polyarsenates are naturally greater than the P—O distances, but here too it is possible to differentiate clearly between the longer bonds to bridge oxygen atoms and the short ones to isolated oxygen atoms. The single O—As—O valency angle known at present agrees with that in the phosphates.

There are known several data for the lattice constants and usually also for the space groups of a large number of other condensed phosphates. These, however, will not be discussed here.

V. Cross-Linked or Ultra Phosphates

A. FORMATION THROUGH CRYSTALLINE ACID SALTS AS INTERMEDIATES

Ultraphosphates are defined as phosphates in which the ratio $Me^I:P$ is less than unity. The existence of such compounds, e.g. $Ag_2P_6O_{10}$, PbP_6O_{10} and $Ca_2P_6O_{17}$, was detected in the corresponding melts some time ago (*165*) and the compounds CaP_4O_{11} and $Ca_2P_6O_{17}$ were described as crystalline solid phases (*136*). In such compounds PO_4 tetrahedra must be present which are linked by three of their O atoms with neighboring P atoms (*349*).


(49)

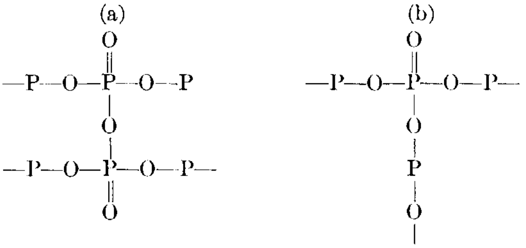
They are referred to as tertiary PO_4 tetrahedra (*272*, *318*). Since however, tertiary PO_4 tetrahedra are detected not only in phosphates with $Me^I:P < 1$ but also determine the chemical behavior of all compounds in which they occur, the term "cross-linked phosphate" has been proposed (*297*).

Unlike meta- and polyphosphates, cross-linked phosphates are unstable in aqueous solution; in accordance with theoretical predictions (*349*), they are readily hydrolyzed at the positions where cross linking occurs and form mixtures of polyphosphates and metaphosphates (*224*, *284*, *318*).

Cross-linked sodium phosphates with $Me^I:P < 1$ are obtained by melting together NaH_2PO_4 and P_4O_{10} (*339*) or NaH_2PO_4 and phosphoric acid at temperatures above about 350°C (*318*). Such melts, the viscosity of which shows a complicated dependence on the $Na_2O:H_2O$ ratio (*112*), solidify to glasses, and dissolve only slowly in water. The rate of solution is a minimum for a ratio $Na:P \sim 1:2$ (*339*).

At temperatures under ~350° mixtures of NaH_2PO_4 and H_3PO_4 first yield crystalline acid metaphosphates such as $Na_2H(P_3O_9)$ and $Na_2H_2(P_4O_{12})$, or high-molecular acid polyphosphates, $(Na_2H(PO_3)_3)_n$ (*107, 108*) or, with a high water vapor partial pressure in the atmosphere, $NaH_3P_2O_7$ also (*363*). The compound $Na_2H_2(P_4O_{12})$ contains a true tetrametaphosphate (*150*). The anionic chains of the acid polyphosphates correspond structurally with those of Maddrell's salts (*156*).

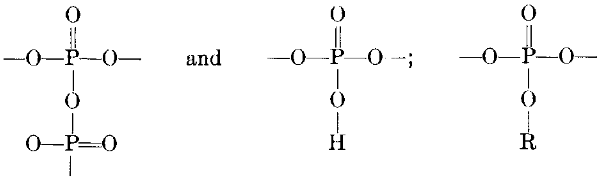
Two types of cross-linking may be detected in the glasses: first, that in which two polyphosphate chains are connected by an O atom between P atoms occupying a middle position (50a); second, those in which two chains are joined by an O atom connecting a P atom in the middle section of a chain with one at the end (50b). The first type on hydrolysis yields two strongly acidic OH groups situated in the middle of the chain whereas the second type gives one strongly and one weakly acidic (terminal) OH group. In melts, links of type a are favored initially and there are few of type b. The equilibrium shifts, however, with increasing duration of the melting time in favor of tetrahedra of type b (*364*).



(50)

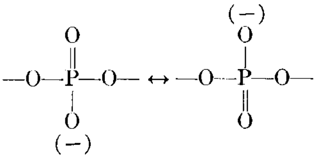
In the system (KH_2PO_4—H_3PO_4) high-molecular potassium polyphosphates are formed on heating, together with acid mono- and di-phosphate but only a little oligophosphate (*363*). But tertiary PO_4 tetrahedra occur not only in phosphates with Na:P < 1. They can also be detected in Graham's and Kurrol's salt with $M^I:P = 1$ (*224, 284, 285, 286*) and are also formed in melts of anhydrous trimetaphosphates, especially in a dry atmosphere (*364*). Their equilibrium concentration in the melt is about 2%.

The presence of cross-linked phosphates may be recognized by their ready hydrolysis, which leads to a rapid drop in the viscosity of the solution and a parallel decrease in its pH. Aqueous solutions of all cross-linked phosphates are hydrolyzed after twenty hours. In contrast to the hydrolysis of normal P—O—P bonds in meta- and polyphosphates, that of the cross-linking sites is practically independent of concentration, pH, ionic strength and the nature and concentration of added salts. It does, however, follow a first-order law, as for normal P—O—P bonds, and is strongly temperature dependent. Activation energies of 18.9 and 15.4 kcal/mole have been measured (*224, 286, 364*), values which are practically the same as those for polyphosphates in solutions at pH 1 (15.1 kcal). This should be attributable to the fact that in the groups



(51)

the P atoms are equally strongly polarized because of the equal negativity of phosphorus and hydrogen (*221*), and, in contrast to the grouping



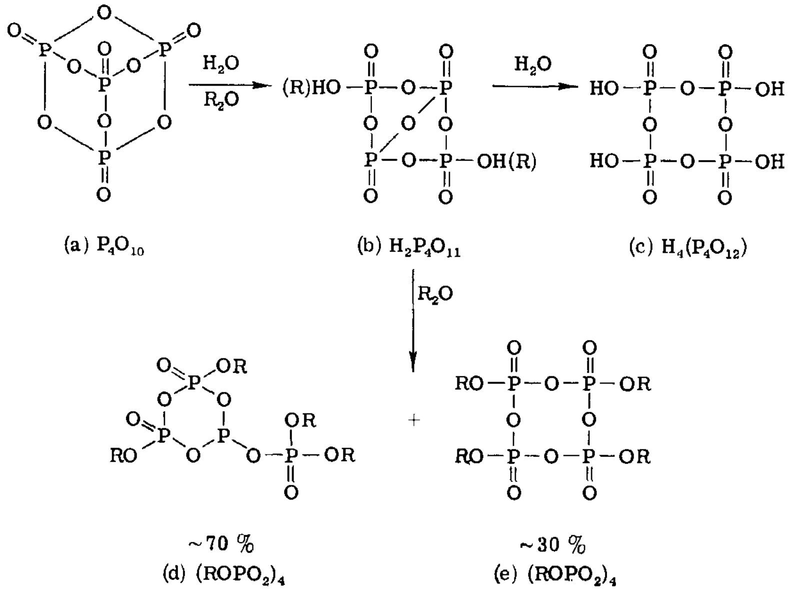
(52)

which occurs in the alkali polyphosphates, stabilization by mesomerism is hindered. Compounds with esterified POH groups (POR) behave similarly (*325*).

B. Phosphorus(V) Oxide

It has been known for a long time (*48, 49, 143, 149, 314*) that when phosphoric acid is dehydrated thermally or phosphorus(V) oxide is dissolved in phosphoric acid, the final products are acids containing more P_2O_5, than high-molecular polyphosphoric acids with the approximate composition $(HPO_3)_x$(= 88.74% P_2O_5). Starting from crystalline monophosphoric acid the final product, after heating and after passing through the whole series of polyphosphoric acids, is the azeotropic acid boiling at 869°C and having a P_2O_5 content of 92.1% at 735 mm of mercury (*292*). Such acids solidify to transparent glasses which dissolve only slowly. When introduced into water they decrepitate, as Berzelius observed, and break up into fibrous fragments. These compounds contain cross-linked acids (*112, 314*).

The theoretical endproduct of the dehydration of phosphoric acid is phosphorus(V) oxide, which has three crystalline forms with known structures (*65, 66, 128, 180*) and two amorphous forms (*135*). All of them contain only tertiary PO_4 tetrahedra and represent the nonacidic final product of the series of cross-linked or ultra phosphates. Only the readily volatile hexagonal crystalline form has been studied in any detail chemically. This form consists of P_4O_{10} molecules with four PO_4 tetrahedra joined together (47) [Formula (53)]. When this form of the oxide is treated with water or alkali—the other forms are only slowly attacked by water—hydrolysis proceeds via an intermediate product $H_2P_4O_{11}$ (b), which has not yet been isolated, to tetrameta phosphoric acid or its salts (c). This is indeed the easiest way of preparing the latter (*11, 12, 49, 50, 238, 244, 267, 321*). In addition, small amounts of amorphous high-molecular products are usually formed which dissolve only slowly; these products require further investigation.



(a) P_4O_{10} (b) $H_2P_4O_{11}$ (c) $H_4(P_4O_{12})$

~70 % (d) $(ROPO_2)_4$ ~30 % (e) $(ROPO_2)_4$

(53)

If H_4O_{10} is treated with ethers, very hygroscopic esters with the composition $(ROPO_2)_x$ are formed, which give on careful hydrolysis a mixture of free phosphoric acid, its esters and esters of pyrophosphoric acid. The products are formed in the following molecular proportions (*237, 325*).

TABLE XVII
HYDROLYSIS PRODUCTS OF THE ESTERS $(ROPO_2)_x$ MADE BY TREATING P_4O_{10} WITH ETHYL- AND ISOPROPYL-ETHER

Phosphate	$(C_2H_5OPO_2)_x$	$(i\text{-}C_3H_7OPO_2)_x$
H_3PO_4	0.92	0.92
RH_2PO_4	2.00	2.00
R_2HPO_4	0.85	0.93
$R_2H_2P_2O_7$	0.51	0.83

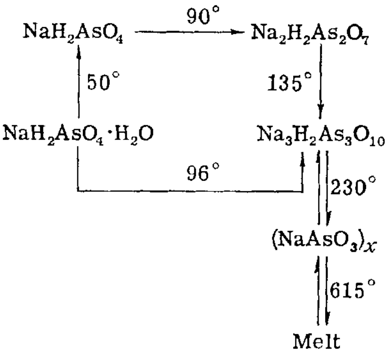
It is concluded from these results, which show the ratio of free phosphoric acid to dialkyl phosphoric acid to be close to 1:1, that the ester taken originally is a mixture of about 70% of the iso-tetrameta phosphoric ester (d) and 30% of tetrameta phosphoric acid ester (e). In recent work using nmr to study the esters these conclusions have been held to be inadmissable, though the method itself does not give unequivocal results (*207*). The preparative results are also not explained (*344*).

VI. Condensed Arsenates and Arsenatophosphates

A. CONDENSED SODIUM ARSENATES

The fact that $Na_2HAsO_4 \cdot 12H_2O$, like $Na_2HPO_4 \cdot 12H_2O$, loses its water of crystallization initially on thermal dehydration, but gives off its water of constitution only with difficulty, was described by Clark (*52*). He did not, however, recognize that a sodium pyroarsenate analogous to sodium pyrophosphate was formed in this process because only the starting material, the hydrogen monoarsenate, separated from the aqueous solution of his product. Analogous observations were made by Graham (*102*, *103*) in comparing the dehydration of $NaH_2AsO_4 \cdot H_2O$ and $NaH_2PO_4 \cdot H_2O$, when he discovered "metaphosphate." He did not recognize, however, the polyarsenate $(NaAsO_3)_x$, which is actually formed, as a new compound because it is reconverted to "orthoarsenate" on solution in water. Later Walden (*332*) unambiguously showed, in the course of electrical conductivity studies, that all condensed arsenates are unstable in aqueous solution and are immediately hydrolyzed to the monomeric starting material.

The course of the dehydration of $NaH_2AsO_4 \cdot H_2O$ is actually similar to that of $NaH_2PO_4 \cdot H_2O$ (*122*) (see Section II,A), though in a number of respects there are significant differences.



(54)

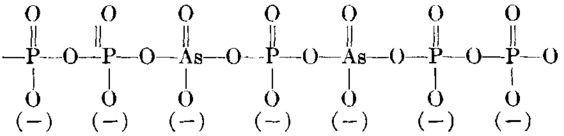
$NaH_2AsO_4 \cdot H_2O$ loses its water of crystallization at 50°C; at 90°C it goes over into the diacid pyroarsenate. At 135°C diacid triarsenate is formed, from which polyarsenate arises at 230°C. The latter melts at 615°. When the monohydrate is heated directly to 96°C there is a direct transition to triarsenate and the $Na_2H_2As_2O_7$ stage is missed. An analogous process never occurs in the dehydration of NaH_2PO_4.

All the condensed arsenates resulting in this way are hydrolyzed to orthoarsenate not only in aqueous solution but also on exposure to moist air. The acid triarsenate is an intermediate but not the pyroarsenate (*310*). Clearly the triarsenate is marked by special stability, for triarsenic acid, $H_5As_3O_{10}$, also occupies a special place in the series of hydration products form arsenic(V) oxide (*269*, *310*).

The final product of dehydration from NaH_2AsO_4, i.e., $(NaAsO_3)_x$ or, more correctly, $Na_xH_2As_xO_{3n+1}$, is a high-molecular polyarsenate and corresponds with Maddrell's salt. Both contain the same type of *Dreierketten* (see Fig. 9c) as anions (*78*, *174*). On quenching, the melts solidify to a glass which is analogous to Graham's salt. So far, an arsenic analog of sodium trimetaphosphate is unknown. For a discussion of the dehydration products of KH_2AsO_4 see Section VI,B,*2*.

B. POLYARSENATOPHOSPHATES

When mixtures of NaH_2PO_4 and NaH_2AsO_4 are melted, and the melts are quenched, glasses are formed consisting of polyarsenatophosphates with anions of the type,



$$—\underset{\underset{(-)}{O}}{\underset{|}{\overset{\overset{O}{\|}}{P}}}—O—\underset{\underset{(-)}{O}}{\underset{|}{\overset{\overset{O}{\|}}{P}}}—O—\underset{\underset{(-)}{O}}{\underset{|}{\overset{\overset{O}{\|}}{As}}}—O—\underset{\underset{(-)}{O}}{\underset{|}{\overset{\overset{O}{\|}}{P}}}—O—\underset{\underset{(-)}{O}}{\underset{|}{\overset{\overset{O}{\|}}{As}}}—O—\underset{\underset{(-)}{O}}{\underset{|}{\overset{\overset{O}{\|}}{P}}}—O—\underset{\underset{(-)}{O}}{\underset{|}{\overset{\overset{O}{\|}}{P}}}—O \qquad (55)$$

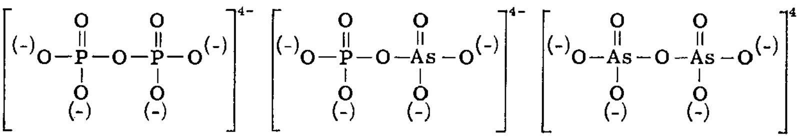
In these, AsO_4 tetrahedra are built into the polyphosphate chains (*309*). Since the P—O—As bond has much the same sensitivity to hydrolysis as the As—O—As bond, they are rapidly hydrolyzed in aqueous solution to monoarsenate and mixtures of polyphosphates, the mean chain length of which depends on the As:P ratio in the starting material (*74*). Contrary to an idea based originally on gravimetric analysis (*309*), the As atoms are not distributed regularly in the chain, but statistically (*308*). The observation that, after careful hydrolysis, the phosphate content is exclusively in the form of polyphosphates provides chemical proof of catenation in the polyarsenatophosphate anions. When arsenatophosphates with more than five P atoms per atom of As are hydrolyzed by hot water trimetaphosphates are formed, just as they are formed for all other high-molecular polyphosphates in solution (*316*).

When sodium arsenatophosphate glasses are tempered, substances with needle-like crystals are formed, and these crystals are also isomorphous with the polyarsenates and the high temperature form of Maddrell's salt. They contain anionic chains of the same structure as these, which is also evidence for the chain structure of the anions in polyarsenates and Maddrell's salt (*78*, *174*).

The number of phosphorus atoms per atom of arsenic entering into the chain appears to depend on the temperature of tempering. A maximum of 7 P atoms to 1 of As is observed for higher temperatures. When the phosphorus content of the melt is greater, the excess easily crystallizes as trimetaphosphate. Mixtures of lithium arsenate and phosphate show similar behavior. Thus when such melts or the glasses obtained by quenching them are tempered, two types of crystalline lithium arsenatophosphate are formed (*302*). The arsenic-rich monoclinic forms, containing five or more As atoms per atom of P, are isomorphous with the low temperature forms of lithium polyphosphate and lithium polyarsenate, which have the same anion chain type as diopside $[(Ca, Mg)SiO_3]_x$ (*138*) (see Fig. 9a). The arsenic-poor rhombic crystals with six or more atoms of phosphorus per atom of arsenic are isomorphous with the high temperature form of lithium polyphosphate, the structure of which is similar to that of Li_2SiO_3 (*264*).

1. *Di- and Tri-arsenatophosphates*

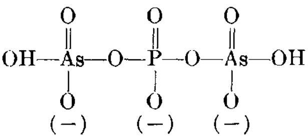
When mixed crystals of Na_2HPO_4 and Na_2HAsO_4 are heated, or a mixture of the two salts is melted, diarsenatophosphates are formed. The product contains the maximum possible amount of the anion type (b) and not a mixture of all the three forms which might be expected. Only when the original mixed crystal contains more atoms of P than of As does pure diphosphate (a) appear as well as (b). The presence of excess As likewise results in the formation of (c).



$$\left[{}^{(-)}O-\underset{\underset{(-)}{O}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{(-)}{O}}{\overset{\overset{O}{\|}}{P}}-O^{(-)}\right]^{4-}\quad\left[{}^{(-)}O-\underset{\underset{(-)}{O}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{(-)}{O}}{\overset{\overset{O}{\|}}{As}}-O^{(-)}\right]^{4-}\quad\left[{}^{(-)}O-\underset{\underset{(-)}{O}}{\overset{\overset{O}{\|}}{As}}-O-\underset{\underset{(-)}{O}}{\overset{\overset{O}{\|}}{As}}-O^{(-)}\right]^{4-}\qquad(56)$$

(a) (b) (c)

Mixed crystals of NaH_2PO_4 and NaH_2AsO_4 yield symmetrical triarsenatophosphates with the constitution shown, analogous to acid sodium triarsenate, only if the As:P ratio in the mixed crystal is >2. If the As:P

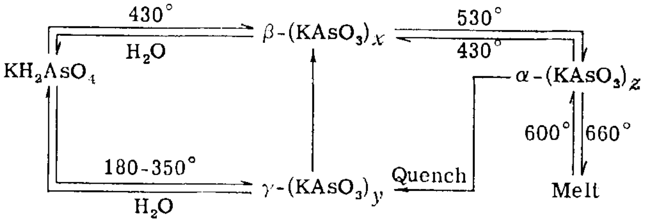


$$OH-\underset{\underset{(-)}{O}}{\overset{\overset{O}{\|}}{As}}-O-\underset{\underset{(-)}{O}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{(-)}{O}}{\overset{\overset{O}{\|}}{As}}-OH \qquad (57)$$

ratio is ≤2, acid diarsenatophosphate is first formed and this goes over directly to high-molecular polyarsenatophosphate at higher temperatures (*315*). Thus the (As . . . P) distribution in low-molecular polyarsenatophosphates is no longer statistical but favors the formation of P—O—As bonds. This has recently been confirmed by Raman spectroscopy (*35*).

2. Potassium Polyarsenates and Arsenatophosphates

While the polyarsenates and arsenatophosphates of lithium and sodium are closely related to the corresponding polyphosphates, the relationship is more complicated for the potassium compounds. The dehydration product of KH_2AsO_4 which is formed above about 180°C (*122*) has the analytical composition $(KAsO_3)_x$ and exists in three forms (*121, 298*).



(58)

The β-form occupies a special position. It may be obtained as a metastable form at room temperature, while transformation into the α-form on raising the temperature is retarded, and it cannot be converted directly into the γ-form.

Three crystalline forms of potassium polyphosphate also exist (*22, 29*)

$$(KPO_3)_xC \overset{510°}{\rightleftharpoons} (KPO_3)_xB \overset{670°}{\rightleftharpoons} (KPO_3)_xA \overset{810°}{\rightleftharpoons} \text{melt} \qquad (59)$$

but there are sharp and reversible transitions without any delay. It is not possible to render the high temperature forms A or B metastable.

There is a series of arsenatophosphates corresponding with each of the three forms of condensed potassium arsenate and phosphate, the transition points and melting point of which vary systematically with composition (see Fig. 10). A chain structure for the α-form of potassium arsenate and arsenophosphate may be inferred from their isomorphism with $(KPO_3)_xB$. The γ-forms also contain high-molecular anionic chains for, when they are hydrolyzed, monoarsenate and polyphosphates with chain length up to $n = 6$ are formed, depending on their phosphorus content. No metaphosphate is produced, however.

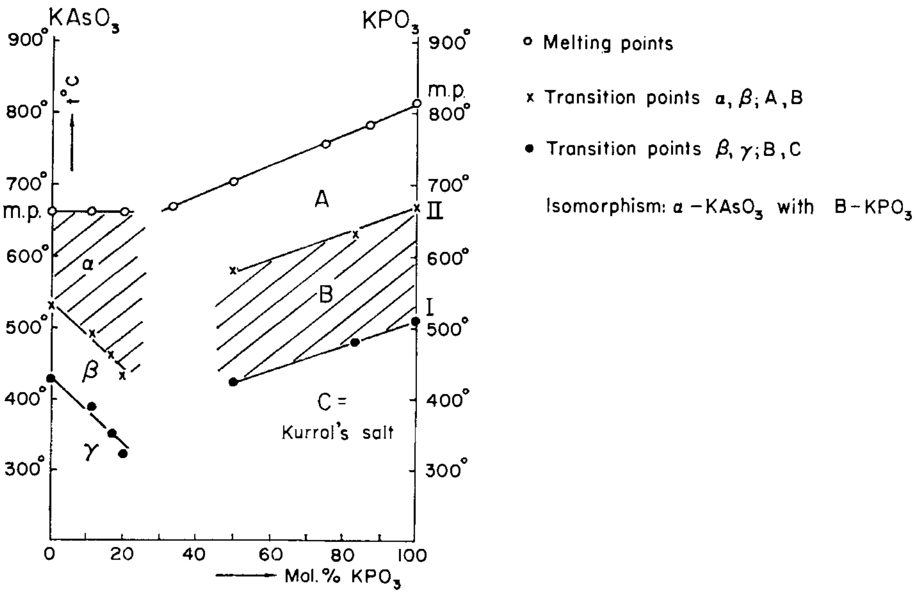
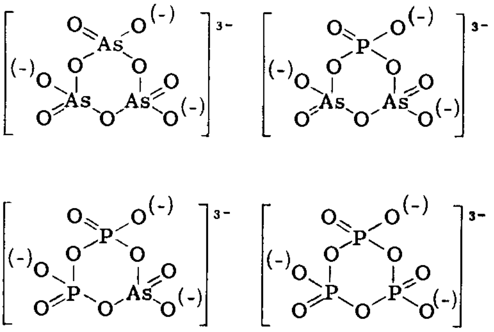


Fig. 10. Transition and melting points of potassium arsenatophosphates as a function of the P:As ratio.

3. *Potassium Trimeta-arsenatophosphate*

The β-form of the arsenatophosphate and β-$KAsO_3$ contain trimeric anionic rings. This follows from the isomorphism with the low temperature form of $K_3(P_3O_9)$, which is formed when KH_2PO_4 is treated with a mixture of acetic acid and acetic anhydride (*121*). It may also be concluded from the observation that in the hydrolysate of β-arsenatophosphate it is possible to detect, in addition to monoarsenate and a little trimetaphosphate, only mono- and diphosphate, but no tri- or higher polyphosphate (*121*). The β-forms of arsenatophosphates contain anions of the types:



(60)

Their proportions clearly depend on the As:P ratio in the starting material, and are found from the quantities of hydrolysis products, determined chromatographically. Assuming the reactivities of the arsenate and the phosphate in melts are the same it is possible to calculate the amounts of the products in a theoretical manner (*365*).

VII. Analysis of Condensed Phosphates

A. CLASSICAL METHODS

Since all condensed phosphates are ultimately degraded to monophosphate in hot solution, especially at low pH, the total phosphorus(V) content of a substance may readily be determined after hydrolysis either gravimetrically or titrimetrically (*109*). However, as soon as it is a question of estimating the content of separate components in mixtures of condensed phosphates insuperable difficulties are encountered if methods depending on precipitation, titration, or a combination of the two are used. Even a quantitative precipitation of monophosphate is impossible if polyphosphates with chain length of $n = 3$ or more are present in the solution. The precipitating cation and the compound to be precipitated by it are partly kept in solution by the polyphosphate; part of the polyphosphate is also carried down by the precipitate. Both of these effects depend in their extent in different ways on the nature and quantity of the substances present and the analysis gives a correct quantitative result only in isolated instances (*116*).

Provided only polyphosphates are present it is possible to determine titrimetrically: (1) the end-group content of mixtures; (2) the content of groups within the chain, after hydrolysis and by estimating the total phosphate content; (3) the monophosphate content after precipitation with silver nitrate (*347*). These methods are likewise of no use in presence of meta- and cross-linked phosphates.

Since most technical products always contain the same constituents in approximately the same amounts it has been possible to develop numerous empirical methods which, for the most part, involve a combined procedure based on precipitation and titrimetric determinations. These are of practical use for particular purposes, e.g., in comparative determinations, but have no claims to general validity (*4, 9, 68, 70, 71, 75, 87, 187, 236, 240, 352*).

B. DETERMINATION OF THE TWO FORMS OF THE TRIPHOSPHATE, $Na_5P_3O_{10}$(I) AND (II), IN THE PRESENCE OF ONE ANOTHER

One of the special methods mentioned above may be used in determining the two forms of sodium triphosphate, one of which ($Na_5P_3O_{10}$(I)) is undesirable in technical products (see Section IV,B,*2*), when they are present together. The ratio of the two in a mixture cannot be estimated in solution, since solutions of the two forms are identical. They differ, however, in their rates of hydration and therefore in the heat evolved on solution. This effect is applied in the so-called temperature increase test, which gives a measure of the content of form I in the sample under study (*189*). In addition the two forms, together with other components, may be detected and estimated by infrared spectroscopy (*58*) or by X-ray methods if the sample is crystalline (*59, 178, 238*). The isotope dilution method also gives reliable results for the determination of triphosphate in simple cases (*233*).

C. Paper Chromatography

For mixtures of metaphosphates and polyphosphates with $n = 1$–10 only paper chromatography of the alkali salts is dependable. These must be prepared when necessary from salts of other cations by ion exchange (*303, 305*). Paper chromatography was worked out for the condensed phosphates independently by Ebel (*81*) and Westmann and his co-workers (*355, 356*). With its aid, it became possible for the first time to make an exact analysis of mixtures of condensed phosphates, thereby obtaining insight into the relationships governing their formation and transformations; it also became possible to correct many false conclusions arising from earlier inadequate analytical methods. Later work brought improvements, especially in the number of components which could be separated, and in the development of the relationship governing the R_f values for the individual phosphates. This proved to be that the logarithm of the R_f value is a linear function of the chain length n (*117, 299*).

$$\log R_f = -an + b$$

Introduction of the technique of labeling the phosphate with radioactive P^{32} finally facilitated the quantitative determination of separate components, the quantities of which were previously determined colorimetrically after eluting the chromatogram spots with ammonia (*171, 192*).

Since the labeling technique was introduced, a large number of further publications on the paper chromatography of phosphates have appeared (*159*), but these papers will not be considered separately here. They serve to confirm what was already partly known, and they describe improvements in technique, thereby reducing the risk of hydrolysis of the condensed phosphates in the acid medium used in chromatography. They also show how the accuracy of quantitative analysis could be increased (*226*).

A detailed study of the influence of cations (*299*) on the R_f or P_k values of the separate phosphate components showed that the substances which migrate in the chromatogram are free acids or acid salts. The difference in the rate of migration of the individual phosphates depends on their decreasing degrees of dissociation as the chain length increases and the associated variation in the solubility of the migrating species in the chromatographic liquid. The pH value or the acid:base ratio of the chromatographic liquid is, in addition to the water, alcohol, and salt content, the determinative factor for the chromatography of this class of substance. Chromatography is particularly valuable for the certainty with which it differentiates metaphosphates from polyphosphates. The former migrate better in alkaline and the latter in an acid medium.

Highly condensed polyphosphates, which cannot be separated by paper chromatography may be separated into groups by paper electrophoresis (*255*). Paper chromatography allows the complete separation and quantitative determination of all condensed phosphates with n up to 10, but its use is limited to γ-quantities.

D. EXCHANGE CHROMATOGRAPHY

Separation by anion exchange has recently proved valuable in the separation and purification of polyphosphates with chain lengths between $n = 5$ and ~ 12. This is not possible by classical methods (*14*, *38*, *85*, *176*, *185*, *223*). Using gradient elution, this method has the advantages of ease of separation and the possibility of preparing some polyphosphates with chain length greater than $n = 4$ in milligram quantities. With this method, it is also possible to exclude almost completely any hydrolysis of the separate components of the phosphate mixture, even for small chain lengths (*105*, *164*, *357*, *358*).

The most recent proposal for analysis of condensed phosphates depends on the examination of nuclear magnetic resonance spectra (*43*, *343*).

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