THE CONDENSED PHOSPHATES

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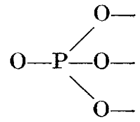
In this review it has seemed better to consider mainly the facts about the condensed phosphates of sodium because these are on the whole by far the best authenticated; and to select the facts which bear upon the covalent structures of the condensed phosphate anions. Another selection has been made in favour of properties with important practical applications. There is a substantial body of published work on the condensed phosphates of metals other than sodium, and much of it, especially where concerned with the heavy-metal metaphosphates, repays renewed study as a stimulus to further investigation; but as it stands it is very indefinite. Controversial matter in the literature concerns for the most part experimental technique rather than interpretation of facts in terms of general ideas. Other reviews present a more critical account of the discrepancies in published work. No attempt has here been made to give a balanced account of contradictory reports, and where the weight of evidence is not clear the point in question has usually been omitted. A few references are made to early literature for their historical interest or because they have remained unnoted by many subsequent authors.

Phosphoric anhydride is known in three polymeric crystalline forms and as a glass. X-Ray and electron-diffraction measurements have shown that a tetrahedral unit of four oxygen atoms attached to every phosphorus atom, as in (I), is a structural feature common to the oxide polymers and to crystalline ortho-, pyro-, and meta-phosphates. Acids, salts, and esters in which two or more PO_4 units are linked by sharing oxygen atoms form a numerous set of compounds designated as condensed phosphates. The set includes in principle compounds for which the atomic ratio P/O is in the range $2/5 \leqslant P/O \geqslant 2/7$, extending from $(P_2O_5)_n$ on the "acid" side of the sequence through the metaphosphates and polyphosphates as far as the pyrophosphates (diphosphates) on the "alkaline" side. Potentially, this field, even though it excludes the silicophosphates, borophosphates, and other heteropolyphosphates, is an extensive one, but little has yet been done to provide some of even the simplest physicochemical data. However, because of the scale of usage (in total probably more than 300,000 tons a year) of sodium pyrophosphate, the meta- and poly-phosphate glasses, and especially sodium triphosphate, interest in the systematic and preparative chemistry of the condensed phosphates is being stimulated, and the more highly polymerised phosphates are beginning to receive attention in their rôle of colloidal electrolytes.



(I.)

Literature.—The discovery of the condensed phosphates is credited to two Scotsmen, Thomas Clark (1827) and Thomas Graham (1833). As a matter of historical interest J. Berzelius [1] (1816) described the preparation of a pure specimen of disodium orthophosphate, showing that it formed a dodecahydrate, and his analysis of the product obtained by dehydrating this at red heat proved that it was $2Na_2O,P_2O_5$. It remained, however, for Clark [2] to demonstrate that the substance prepared by strongly heating disodium phosphate hydrate is a chemical individual not the same in its properties as disodium orthophosphate from which merely the water of crystallisation has been removed, and to recognise a difference of kind between the easily removable water and the last and much more tenaciously held water. Graham, " friend and fellow townsman " of Clark, published a notable memoir [3] entitled " Researches on the Arseniates, Phosphates, and Modifications of Phosphoric Acid " which deservedly has been read by generations of his successors; in this he established the constitutional relationship of ortho-, pyro-, and meta-phosphate, and demonstrated the existence of a crystalline, soluble variety and an insoluble variety as well as the soluble, glassy variety of sodium metaphosphate. Again, on a point of historical accuracy it should be recorded that there are earlier references to the preparation of sodium metaphosphate. Berzelius [1] described also the preparation of monosodium orthophosphate and mentions heating it to redness before analysing it for Na_2O and P_2O_5. Glassy sodium metaphosphate was described in some detail by J. L. Proust [4] who obtained it by heating $NaNH_4HPO_4$ and stated that the resulting transparent deliquescent and nearly neutral glass was a new salt equivalent to a union of ordinary sodium phosphate with the phosphoric acid left after the ammonia had been driven off.

An early paper, interesting because of its insight into the polymeric aspect of the structure of condensed phosphates and their hydrolytic instability in the presence of acids, is that of Th. Fleitmann and W. Henneberg,[5] who first suggested the generalised concept of condensed phosphates as including compounds intermediate between meta- and pyro-phosphates (*i.e.*, polyphosphates), and attempted to prepare $Na_6P_4O_{13}$ and $Na_4H_2P_4O_{13}$.

In a century of work following Graham's memoir there grew up an unfortunate state of confusion, apparent in the contradictory systems of nomenclature adopted for the polymetaphosphates. Most of the trouble arose from the inadequacy of the methods used to establish chemical individuality and to assign degrees of polymerisation. In recent years several helpful reviews of parts of the earlier literature have been made: H. Terrey,[6] " The Metaphosphates and Polyphosphates of Sodium "; K. Karbe and G. Jander,[7] " Die Metaphosphate "; O. T. Quimby,[8] " The Chemistry of Sodium Phosphates "; E. P. Partridge,[9] " The Peculiar Phosphates ". Mention may also be made of two modern experimental

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[1] *Ann. Physik*, 1816, **54**, 31.

[2] *Edinburgh J. Sci.*, 1827, **7**, 298.

[3] *Phil. Trans.*, 1833, **123**, 253.

[4] *Ann. Chim. Phys.*, 1820, **14**, 281.

[5] *Annalen*, 1848, **65**, 304.

[6] *Ann. Reports*, 1937, **34**, 115.

[7] *Koll. Beihefte*, 1942, **54**, 1.

[8] *Chem. Reviews*, 1947, **40**, 41.

[9] *Chem. Eng. News*, 1949, **27**, 214.

papers [10, 11] which have done much to clarify the phase equilibria of the system Na_2O–P_2O_5 in the range from $NaPO_3$ to $Na_4P_2O_7$, encountered when the melts are cooled.

Brief mention must be made of the discovery that certain organic derivatives of condensed phosphoric acids play an important part in the storage and release of energy in metabolic processes and in muscle action, which has brought into prominence the biochemical interest of the magnitude of the free-energy decrease accompanying hydrolysis of the condensed phosphate (pyrophosphate and triphosphate) portion of these substances. The so-called "high energy phosphate bonds" have been reviewed by F. Lipmann.[12]

Structural Formulæ.—In this Review it is explicitly assumed that when a 4-co-ordinated P atom is directly linked to H, C, N, or O or a combination of these elements, the P atom possesses an octet of shared electrons; and, as part of the same assumption, that in molecules or ions such that a transfer of electrical charge from the P atom is required to make the octet assumption possible ("formal positive charge" on the P atom) then to a substantial extent the charge distribution actually exists. Free use of this simplifying assumption is made in discussing structures from a unified point of view.

In an overwhelming proportion of all phosphorus compounds the phosphorus atom is 4-co-ordinated. Phosphorus atoms that are 3-co-ordinated and possess an unshared pair of valency electrons are very reactive when conditions are provided such that the unshared electrons can become shared as part of a tetrahedral 4-co-ordinated structure. For example, pure PCl_3 rapidly absorbs oxygen in the cold,* forming $POCl_3$, and trialkyl phosphites readily oxidise to trialkyl phosphates. Also the unshared pair of electrons of PCl_3 and $P(OR)_3$, with $R =$ alkyl, easily attack water so that the phosphorus atoms form a fourth bond:

$$:PCl_3 + 3H_2O = PHO(OH)_2 + 3HCl \qquad :P(OR)_3 + H_2O = PHO(OR)_2 + R\cdot OH$$

The reactions of P_4O_6 (II) with oxygen to form P_4O_{10} (III) or with water to form $PHO(OH)_2$ are similar. In the acids and anions $PO(OH)_3$,

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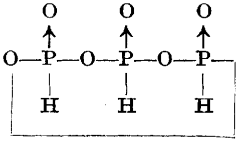
[10] E. P. Partridge, V. Hicks, and G. W. Smith, *J. Amer. Chem. Soc.*, 1941, **63**, 454.

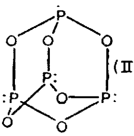
[11] G. W. Morey and E. Ingerson, *Amer. J. Sci.*, 1944, **242**, 1.

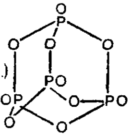
[12] *Advances in Enzymology*, 1941, **1**, 99; 1946, **6**, 231.

* Trialkylphosphines oxidise to the stable phosphine oxides. An interesting question is the nature of the white crystalline product of the reaction $PH_3 + O_2 = H_2 + PO_2H$ which is described by H. J. van der Stadt (*Z. physikal. Chem.*, 1893, **12**, 322) as occurring when the gases are mixed at low pressures. Van der Stadt regarded PO_2H as metaphosphorous acid because it reacts with water to form phosphorous acid. A monomeric structure seems impossible, and the crystalline character suggests a substance of low molecular weight such as a cyclic trimer



$PHO(OH)_2$, $PO(OH)_2{\cdot}PO(OH)_2$* and $PH_2O(OH)$ the 4-co-ordinate structure is certainly present, despite the internal charge separation which in the last three would in part be avoided if alternative structures involving octets with unshared electron pairs were the actual structures.


(II.)

(III.)


Compounds in which some of the oxygen atoms in $PO(OH)_3$ are replaced by the isoelectric groups CH_2 and NH, as in the alkane phosphonates and the amido- and imido-phosphates, and compounds in which the P–H of alkyl phosphites is replaced by P–Hal. further illustrate the stability of compounds containing 4-co-ordinated phosphorus atoms. The stability of 4-co-ordinated phosphorus exemplified is relative to tervalent phosphorus, *i.e.*, 3-co-ordinated phosphorus with an unshared electron pair, but there is also a wider body of chemical experience concerning the tendency of phosphorus to gain and retain the 4-co-ordinate condition, especially when oxy-phosphorus compounds stable at elevated temperatures are in question.

Against this background we may consider the hypothetical monomeric metaphosphate ion PO_3', and the relation of PO_3' and PO_4''' to NO_3' and NO_4'''. The high dissociation constant of nitric acid is attributable to the double positive formal charge on the nitrogen atom when it binds three oxygen atoms by six electrons. It is possible that the reason for the non-existence of NO_4''' is that steric interference of the four oxygen atoms would raise the internal energy of the structure too much. A simple calculation from the van der Waals radius of the oxygen atom with completed octet (1·32—1·40 A.), together with the C–O, N–O, P–O, S–O, and Cl–O atomic distances in crystals, certainly makes it appear that there must be some mutual lateral repulsion of the oxygen atoms even in the larger tetrahedral ions SiO_4'''', PO_4''', SO_4'', and ClO_4'; the de-stabilising action of lateral repulsion must be greater in NO_4''' than in PO_4''', and

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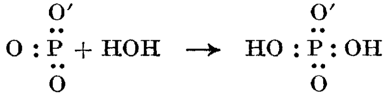
* The case for the P–P formula for hypophosphoric acid is now very strong. The "single" formula H_2PO_3 has an odd number of electrons, which is inconsistent with the diamagnetism of hypophosphates (F. Bell and S. Sugden, *J.*, 1933, 48). A "double" formula $H_4P_2O_6$ is consistent with the Raman spectrum (J. Gupta and A. K. Majumdar, *J. Indian Chem. Soc.*, 1942, **19**, 286) and the freezing-point lowering of aqueous solutions of hypophosphates (P. Nylén and O. Stelling, *Z. anorg. Chem.*, 1933, **212**, 16). Neither of the unsymmetrical formulæ $PO(OH)_2{\cdot}O{\cdot}PHO(OH)$ and $PO(OH)_2{\cdot}O{\cdot}P(OH)_2$ is easily reconcilable with the comparatively large fourth dissociation constant $pK_4 \approx 10$, since from both would be derived the same quadrivalent anion $''PO_3{\cdot}O{\cdot}PO_2''$, in which the right-hand portion is comparable with a hypothetical bivalent ion from monoethylphosphorous acid; but there seems to be no tendency for monoethylphosphorous acid to form a disodium salt (cf. P. Nylén, "Studien über organischen Phosphorverbindungen", Thesis, Uppsala, 1930, pp. 37, 151). On the other hand, the tetrabasicity of hypophosphoric acid, and the singleness of the X-ray absorption edge (Nylén and Stelling, *loc. cit.*) are consistent with the symmetrical formula $PO(OH)_2{\cdot}PO(OH)_2$. Recently (B. Raistrick and E. Hobbs, *Nature*, 1949, **164**, 113) confirmation of the symmetry of the hypophosphate anion has been obtained by X-ray structure work with diammonium hypophosphate.

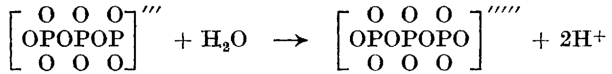
greater in NO_4''' than in NO_3'. Certainly, simple analogy with NO_3' is not a valid reason for expecting the existence of monomeric PO_3'.

If a monomeric variety of soluble sodium metaphosphate could by some means be prepared, the phosphorus atom would have a formal charge of + 2 and only six electrons in its valency shell—at least, reasoning from the high acid strength of nitric acid, such a structure would contribute considerably to the mesomeric structure. This would favour the addition of $H^{\bullet}$ and OH' during the process of dissolution :



$$O:\overset{\overset{O'}{\cdot\cdot}}{\underset{\underset{O}{\cdot\cdot}}{P}} + HOH \longrightarrow HO:\overset{\overset{O'}{\cdot\cdot}}{\underset{\underset{O}{\cdot\cdot}}{P}}:OH$$

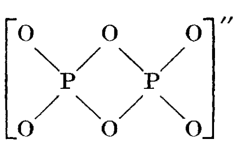
so that the monomeric metaphosphate would be rapidly hydrated to acidic orthophosphate, without the appearance of pyrophosphate intermediately. If the hydration of the hypothetical monomer were slow enough for observations to be made on its properties before hydration, it should be the salt of a monobasic acid about as strong as nitric acid. All the known varieties of sodium metaphosphate dissolve either in water or in dilute sulphuric acid, and in no case is the hydration or hydrolysis to orthophosphate immediate or very rapid, nor does the solution in any case have the properties expected for the monomer. So far as the dissolved state in water is concerned, it seems improbable that monomeric metaphosphate will ever be found. By the same reasoning it is unlikely that an *open polymetaphosphate chain structure* terminating in a 3-co-ordinate phosphorus atom will be found as an entity in aqueous solution ; if a structure such as (IV) exists in the solid state, on dissolution it would pass from the metaphosphate $(PO_3)_n$ to the polyphosphate $(PO_3)_{n-1}(PO_4)$ composition (V) :



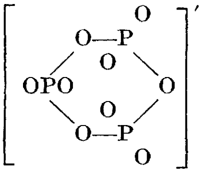
$$\left[\begin{matrix}O\;O\;O\\ OPOPOP\\ O\;O\;O\end{matrix}\right]''' + H_2O \longrightarrow \left[\begin{matrix}O\;O\;O\\ OPOPOPO\\ O\;O\;O\end{matrix}\right]''''' + 2H^+$$

(IV.) (V.)

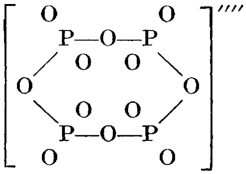
Cyclic metaphosphate structures with single rings of alternating phosphorus and oxygen atoms, *e.g.*, (VI)—(VIII), are true metaphosphates in



(VI.)



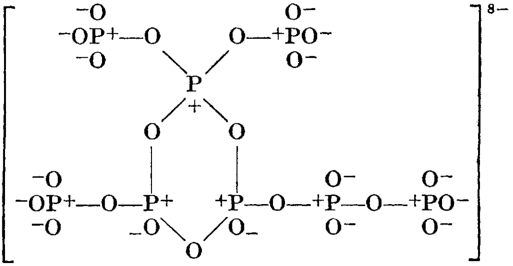
(VII.)



(VIII.)

the sense of having exactly the composition $(PO_3)_n^{n-}$. The trimetaphosphates (VII) and tetrametaphosphates (VIII) are known compounds, discussed later in this review. Several claims that dimetaphosphoric acid or its sodium salt has been obtained appear in the literature of the past twenty years but the evidence is very incomplete.

If the supposition made in this review about the immediate hydration of a terminal PO_3' group is correct, the only true metaphosphates which can persist in aqueous solution must be either purely cyclic or at least contain a closed ring as part of their structure. For example, a conceivable structure for an anion $(PO_3)_8{}^{8-}$ is (IX). In the structure written every


(IX.)

phosphorus atom is 4-co-ordinated with a formal charge of + 1, and every oxygen atom except those which join two phosphorus atoms has a formal charge of − 1. The formal charge on one of the phosphorus atoms of the ring is not balanced by a formal negative charge on an adjoining oxygen atom. This is a slight infringement of the microscopic neutrality principle, which, however, may not create a situation electrostatically too unfavourable for such an element of structure to exist. It is included here because of its interest in connection with the products of hydrolysis of metaphosphate glass, discussed later. In any case the corresponding formulation for the ion $(PO_3)_7{}^{7-}$ obtained by omitting one of the $(PO_3)''$ groups at the top of (IX) does not have this possible disability. The point which it is desired to make here is that chain-wise polymerisation, provided the chain starts or terminates on a closed ring, can be visualised as producing true metaphosphates in the sense of having the composition $(PO_3)_n{}^{n-}$, but which also have the terminal doubly charged groups characteristic of polyphosphates and pyrophosphates. The point is not merely formal, because some of the most interesting properties of condensed phosphates depend upon the distribution of (net) negative charge on the anion; for example, the important property of forming stable soluble complexes with calcium is most probably to be interpreted in terms of ion association, for which the distribution of the anionic charge plays a dominant part.

Polymorphism of Condensed Sodium Phosphates.—Polymorphism is frequent, both the kind which arises from different lattice arrangements of the same ions, and the kind which arises from different molecular structures of the condensed phosphate ions that form sub-units of the crystal structure. Typical of the first kind are the five forms [10] of $Na_4P_2O_7$ which appear in succession as the molten salt cools, the three forms [13] of anhydrous sodium trimetaphosphate and the two forms of anhydrous sodium triphosphate.[10]

Polymorphism which arises from structural, often polymeric, differences

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[13] R. W. Liddell, *J. Amer. Chem. Soc.*, 1949, **71**, 207.

in the anions is accompanied by notable differences in chemical properties which are retained in solution.

Nomenclature of Condensed Sodium Phosphates.—Seven anhydrous crystalline forms of sodium metaphosphate are known with certainty, and various names have been given to them. The most recent system is that of Partridge,[9] who suggests that Roman numerals should be used as labels, starting with sodium trimetaphosphate as $NaPO_3$-I, because this is stable at its m.p. (628°) ; the polymorphic forms of this metaphosphate are labelled I′ and I″. Varieties of $(NaPO_3)_n$ prepared at lower temperatures by dehydrating NaH_2PO_4 are assigned numerals in sequence with the decreasing temperature of preparation. It is not claimed that this system is really less arbitrary than its several predecessors. Thus, a highly polymerised fibrous variety (Kurrol salt) which can only be prepared by crystallisation from the supercooled melt is labelled $NaPO_3$-IV, and the cyclic sodium tetrametaphosphate has not been accommodated in the scheme at all. In this review a Greek prefix will be used to indicate the degree of polymerisation where this is well established, *i.e.*, for sodium trimetaphosphate and tetrametaphosphate, and to these the Roman numeral designation will be added in parentheses ; otherwise Partridge's notation will be followed where he has assigned numerals, and the name most common in the literature will be added in parentheses. Knowledge of the polyphosphates has not yet developed to a point where the need for a systematic nomenclature is pressing ; apart from pyrophosphate, which might with advantage be called diphosphate, the only individual in this class actually isolated is the triphosphate. It is regrettable that this compound is so often burdened with the unnecessary name " tripolyphosphate ".

Sodium Trimetaphosphate, $Na_3P_3O_9$ ($NaPO_3$-I).—This is obtained almost exclusively when NaH_2PO_4 is heated to between 550° and 628° (m.p.). A considerable but very variable proportion of the metaphosphate obtained by dehydrating NaH_2PO_4 or $Na_2H_2P_2O_7$ at any temperature between about 250° and 500° usually consists of trimetaphosphate. All other varieties, including metaphosphate glass, are converted into the trimetaphosphate in the last 50° or so below the m.p. The conversion is so rapid near the m.p. that all varieties, including sodium Kurrol salt ($NaPO_3$-IV), appear to melt at the same temperature.

The two polymorphic forms of sodium trimetaphosphate, $NaPO_3$-I′ and $NaPO_3$-I″, are obtained [13] by controlled cooling of molten sodium metaphosphate ; they change into the stable form of $Na_3P_3O_9$ ($NaPO_3$-I) if cooled too slowly after crystallisation. The stable form is obtained as an opaque crystalline mass when prepared by direct solidification of the melt. All three forms of $Na_3P_3O_9$ are very soluble in water and can be recrystallised as $Na_3P_3O_9,6H_2O$, or above about 40° as $Na_3P_3O_9,H_2O$. The latter recrystallises as the anhydrous salt [identical with $Na_3P_3O_9$ ($NaPO_3$-I)] under its saturated solution at 60° in the course of a few days. Isothermal dehydration of the hexahydrate in vacuum at room temperature removes over 90% of the water of crystallisation without destroying the metaphosphate, but at higher temperatures or under conditions less favourable to the rapid removal of water vapour the dehydration is accompanied by extensive conversion into acidic ortho- and pyro-phosphate.[14]

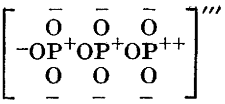
The cyclic trimeric formula VII was first proposed by C. G. Lindbom.[15] The evidence now available in its support is cogent.

(1) The physicochemical properties and the reproducible metathetical changes are those of a *molecularly homogeneous* salt of a moderately strong acid. The solutions show none of the irreversible solubility and the viscous effects characteristic of the crystalline varieties $NaPO_3$-II (Maddrell salt), $NaPO_3$-III, and $NaPO_3$-IV (Kurrol salt).

(2) Molecular-weight determinations by freezing-point lowering in sodium sulphate decahydrate [16] gave 307—313 ($Na_3P_3O_9 = 306$). In water as solvent, allowing for the effect of ionic strength upon the f.p. lowering, the molecular weight was found [17] to agree better with the supposition of a tervalent anion than with any alternative.

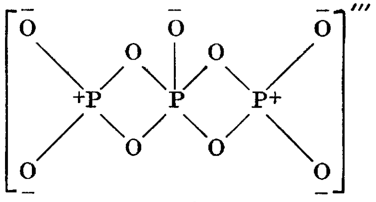
(3) Recent measurements [18] of the conductance of dilute solutions of sodium trimetaphosphate ($NaPO_3$-I) show that the salt is uni-tervalent. Older work [19] using the Ostwald empirical rule gave the same result.

(4) The titration curve of sodium trimetaphosphate [20] with hydrochloric acid and sodium hydroxide is practically indistinguishable from the titration curve of sodium chloride at the same equivalent concentration. It follows that the structure of $H_3P_3O_9$ does not include the feature responsible for the small value of the ratio K_3/K_2 ($\approx 2 \times 10^{-5}$) in pyrophosphoric acid. This feature is the dissociation of a proton from an $O(PO_2)OH'$ group already carrying a single negative charge. Thus in trimetaphosphoric acid all three protons come from different OPO_3H groups. This is consistent with the cyclic structure (VII), but two other trimeric structures would also have one hydrogen atom associated with each phosphorus atom. Written in terms of the formal charges involved, these are (X) and (XI).



$$\left[\begin{array}{c} \overset{-}{O}\quad\overset{-}{O}\quad\overset{-}{O} \\ -OP^{+}OP^{+}OP^{++} \\ \underset{-}{O}\quad\underset{-}{O}\quad\underset{-}{O} \end{array}\right]'''$$

(X.)



(XI.)

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[14] This review is written in the light not only of published work but also of a decade of experimental work by the research department of Albright and Wilson Ltd. Unpublished work, previously reported verbally at meetings of the Society of Chemical Industry, includes experiments by A. G. Taylor, J. E. Such, D. R. Peck, R. H. Tomlinson, and F. J. Harris, and is acknowledged by ref. (14) in the text.

[15] *Ber.*, 1875, **8**, 122.

[16] P. Bonneman-Bémia, *Ann. Chim.*, 1941, **16**, 395.

[17] P. Nylén, *Z. anorg. Chem.*, 1937, **229**, 30.

[18] C. W. Davies and C. B. Monk, *J.*, 1949, 413.

[19] A. Wiesler, *Z. anorg. Chem.*, 1901, **28**, 187.

[20] H. Rudy and H. Schloesser, *Ber.*, 1940, **73**, 484 ; W. D. Treadwell and F. Leutwyler, *Helv. Chim. Acta*, 1938, **21**, 1450.

Structure (X) is unacceptable as a description of the trimetaphosphate anion in aqueous solution for reasons discussed in connection with the non-existence of monomeric metaphosphate in solution. In addition there would be difficulty in understanding the absolute magnitude of K_3; Davies and Monk [18] calculate an approximate value $K_3 \approx 10^{-2}$ at 25° by taking account of the deviation from Onsager's formula, of the slope of a plot of conductance against $\sqrt{\text{concn.}}$ for $H_3P_3O_9$. Thus K_3 for $H_3P_3O_9$ is almost as large as K_1 for $H_4P_2O_7$. But considered as a base the $''O_3PO$ group in structure (X) would be comparable with the pyrophosphate ion $''PO_3{\cdot}O{\cdot}PO_2(OH)$, so that the first proton bound by (X) would dissociate as weakly as the second proton bound by the pyrophosphate ion ($K_3 \approx 2 \times 10^{-7}$). The objections to structure (XI) are (*a*) the rarity of stable compounds in which there is reason to assume the existence of a 5-co-ordinate phosphorus atom, (*b*) the circumstance that the first proton to be bound would attach itself to the central PO_5^- group and, because of the absence of formal charge on the phosphorus atom, would be almost as weakly acidic as silicic acid.

(5) *X*-Ray crystallographic evidence is consistent with a cyclic trimeric anion in anhydrous sodium trimetaphosphate. An alternative possibility that the crystal contains monomeric $NaPO_3$ is not yet quite excluded but is extremely improbable even on crystallographic grounds alone.[21]

(6) Sodium trimetaphosphate ($NaPO_3$-I) forms a series of well-defined salts containing one atom of $Na^{\bullet}$ and one of $M^{\bullet\bullet}$, of which $NaBaP_3O_9,4H_2O$ is typical. It was the discovery of these double salts that originally led Fleitmann and Henneberg [5] to the conclusion that the soluble crystalline sodium metaphosphate which they obtained by slow cooling of a melt was trimeric.

Sodium trimetaphosphate has so far found no application; it conspicuously lacks the properties which underlie the industrial use of some other condensed phosphates. A reaction of some interest is its hydrolytic conversion into triphosphate, described later. The trimetaphosphates of metals other than sodium are in general fairly soluble.

Sodium Tetrametaphosphate.—This salt is thermally less stable, but in resistance to hydrolysis by alkali to polyphosphate somewhat more stable, than the trimetaphosphate, which in several respects it resembles. It is not and perhaps cannot be made by dehydration of NaH_2PO_4. A. Boullé [22] described as irreversible the transformations

$$Na_4P_4O_{12} \xrightarrow{440°} NaPO_3\text{-II (Maddrell salt)} \xrightarrow{550°} Na_3P_3O_9$$

Sodium tetrametaphosphate forms two hydrates $Na_4P_4O_{12},4H_2O$[14] and a hydrate $Na_4P_4O_{12},10H_2O$,[14] which have high and reproducible solubility between 0° and at least 80°. The decahydrate and the stable tetrahydrate establish definite equilibrium vapour-pressure relationships, and can be fully dehydrated without appreciable hydrolytic alteration of the metaphosphate anion, since recrystallisation of the dehydrated substance reconverts it into one or other of the hydrates.

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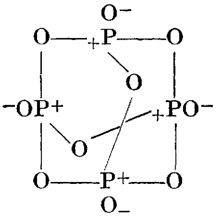
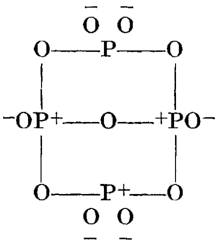
[21] B. Raistrick, Communication to Canadian Institute of Chemistry, Halifax, 1949.

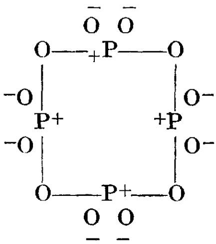
[22] *Ann. Chim.*, 1942, **17**, 213.

Until very recently all preparations of sodium tetrametaphosphate have been by the procedure adopted by Fleitmann and Henneberg [5] of forming the metaphosphate of bivalent copper or lead by heating the oxide with excess of phosphoric acid to 350—400°, then treating the insoluble heavy-metal phosphate with sodium sulphide solution and crystallising the sodium salt. Confirmatory and extensive investigations of this preparative method employing heavy-metal metaphosphates made at various temperatures have been published by Th. Fleitmann,[23] A. Glatzel,[24] G. Tammann,[25] and F. Warschauer.[26] (There is no doubt that these authors obtained other poly-metaphosphates besides the tetrametaphosphates, but it is questionable whether any other pure individuals were isolated.)

A more convenient preparation of tetrametaphosphate is directly from phosphoric anhydride. Such and Tomlinson [14] have shown that yields of $Na_4P_4O_{12},4H_2O$ exceeding 50% of the theoretically possible can be crystallised from the reaction product obtained by hydrating the volatile form, *i.e.*, P_4O_{10}, with $Na_2CO_3,10H_2O$ or a cold suspension of $NaHCO_3$. This result is easily visualised by considering the symmetrical tetrahedral structure [27] of the P_4O_{10} molecule. All the anhydride P–O–P linkages in (III) are equivalent, so that the initial step in the hydration can have only one result. It appears that of the three possibilities for the reaction of a second molecule of water, the attack is preferentially upon the anhydride bridge in (XII), giving the cyclic tetrametaphosphate (VIII). [In (III), (XII), and (VIII) as written here the formal charges are shown.]


(III.)


(XII.)


(VIII.)

The anion of sodium tetrametaphosphate has not been structurally determined by *X*-ray crystallography,* but in all probability it has the tetrameric and cyclic structure (VIII), first suggested by Glatzel.[19] The evidence now available is similar to that listed for sodium trimetaphosphate ($NaPO_3$-I).

(1) The same general statement can be made as for the trimetaphosphate.

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[23] *Ann. Phys. Chem.*, 1849, **78**, 233 ; 338.
[24] Thesis, Würzburg, 1880.
[25] *J. pr. Chem.*, 1892, **45**, 417.
[26] *Z. anorg. Chem.*, 1903, **36**, 137.
[27] G. C. Hampson and A. J. Stosick, *J. Amer. Chem. Soc.*, 1938, **60**, 1814.

* In the crystalline state, the only metaphosphate whose structure has been worked out is $Al(PO_3)_3$ (L. Pauling and J. Sherman, *Z. Krist.*, 1937, **96**, 481). These authors interpret the results in terms of a lattice built up from $Al^{\cdot\cdot\cdot}$ ions and closed ring anions P_4O_{12}'''' consisting of four tetrahedral PO_4 groups joined through O atoms held in common between consecutive P atoms.

(2) Molecular-weight determinations cryoscopically in sodium sulphate decahydrate [16] gave 414 and 417 ($Na_4P_4O_{12} = 408$). In water, allowing for the ionic strength, the molecular weight was found [17] to be in better agreement with the supposition of a quadrivalent anion than any other.

(3) The slope of the plot of conductance against $\sqrt{\text{concn.}}$ for sodium tetrametaphosphate is somewhat greater than corresponds to Onsager's limiting slope for a uni-quadrivalent electrolyte, but the excess is explained by assuming some ion association to NaP_4O_{12}'''. Davies and Monk [18] summarise their analysis of their data : " The value of the dissociation constant (*i.e.*, of NaP_4O_{12}'''), the anion's (*i.e.*, P_4O_{12}'''') mobility and the slope of the conductivity curve all support the quadrivalency assumed for the anion." Older work [19] using the Ostwald empirical rule gave the same result.

(4) The titration curve [14] of repeatedly recrystallised sodium tetrametaphosphate is practically identical with that of a salt of a strong acid. The deduction that the tetrametaphosphate anion is cyclic is the same as that already stated for sodium trimetaphosphate ($NaPO_3$-I).

Mild alkaline hydrolysis of $Na_4P_4O_{12}$ gives mixtures containing pyrophosphate and orthophosphate, but also polyphosphates, doubtless both tetra- and tri-phosphate. At certain stages the hydrolysate possesses in a high degree the power to combine with bi- and multi-valent cations, forming soluble complexes. So far the isolation of pure sodium tetraphosphate $Na_6P_4O_{13}$ has not been achieved.

The tetrametaphosphates of several metals besides the alkali metals and ammonium are fairly soluble.

Insoluble Sodium Metaphosphates, $NaPO_3$-III and $NaPO_3$-II (Maddrell Salt).—The first identifiable product obtained by heating NaH_2PO_4 or its hydrates is the acid pyrophosphate $Na_2H_2P_2O_7$; in an open vessel the dehydration of NaH_2PO_4 proceeds slowly at temperatures (in the solid) not much above 150°, and rapidly above 200°. Further dehydration of the acid pyrophosphate, which for practical purposes becomes measurable at about 240°, is a complicated process. No known product intervenes between pyrophosphate and metaphosphate. Fleitmann and Henneberg [5] believed they had evidence that an acid polyphosphate $Na_4H_2P_4O_{13}$ is formed when $Na_2H_2P_2O_7$ is slowly heated at 220°, but this result is certainly not easy to confirm.

Continued heating at temperatures below the fusion point (628°) gives rise to three distinct varieties of sodium metaphosphate, of which one is $Na_3P_3O_9$ ($NaPO_3$-I) which, as already described, becomes the only product between about 550° and 628°. Below 550° the proportions of the three forms vary widely according to the time and temperature of heating, the partial pressure of water vapour round the solid, and the physical nature of the solid (hard cake obtained by partial fusion of the NaH_2PO_4 in the water initially liberated quickly, or thin layer of finely divided solid). The two varieties, $NaPO_3$-III and $NaPO_3$-II (Maddrell salt), are practically insoluble in water. Both have well-defined *X*-ray powder diagrams and are obviously crystalline when viewed under the polarising microscope.

Insoluble sodium (and potassium) metaphosphate was obtained by R. Maddrell [28] by heating phosphoric acid with sodium nitrate (or potassium chloride). Insoluble sodium metaphosphate is very often referred to in the literature as Maddrell salt, but with little reason.* It is convenient to refer to " insoluble sodium metaphosphates ", distinguishing between the low- and the high-temperature variety [$NaPO_3$-III and $NaPO_3$-II (Maddrell salt)]. The two compounds are physically and chemically very similar.

In the dehydration of $Na_2H_2P_2O_7$, the two insoluble varieties can be isolated as follows. At the lowest temperatures (250–280°) the low-temperature variety ($NaPO_3$-III) is obtained mixed with trimetaphosphate ($NaPO_3$-I) and unchanged pyrophosphate, and the last two are removed by washing. In the range 350–400° the product consists of the high-temperature, insoluble variety, $NaPO_3$-II (Maddrell salt), together with trimetaphosphate ($NaPO_3$-I), from which the latter can be removed by washing. Very careful adjustment of the conditions of heating can give directly a product containing over 96% of $NaPO_3$-II (Maddrell salt). $NaPO_3$-III is itself slowly but completely transformed into $NaPO_3$-II (Maddrell salt) at about 350°, and $NaPO_3$-II (Maddrell salt) is transformed into $NaPO_3$-I with barely measurable velocity just above 410°, rapidly at 500°. Neither change is reversed at lower temperatures.

Nothing is known about the molecular structure of either $NaPO_3$-III or $NaPO_3$-II (Maddrell salt). The following observation [14] indicates that they are salts of highly polymerised metaphosphoric acids. When the finely ground solids are warmed ($NaPO_3$-III) or boiled [$NaPO_3$-II (Maddrell salt)] in a decimolar solution of an ammonium or any alkali-metal salt other than sodium, the metaphosphate readily dissolves. Alcohol precipitates a highly hydrated metaphosphate which, after being washed to remove most of the added salt, redissolves in water to form a decimolar solution with viscosity about ten times greater than that of water. The excess viscosity is almost eliminated by addition of electrolytes. The metaphosphate in these colloidal solutions gives a titration curve with a single inflexion curve near pH 7. Taken in conjunction with the viscosity, this suggests that long-chain or large-ring anion structures are present in the solution. The average size of the units of the dissolved metaphosphate is probably much less than that of the solids because in the process of dissolving some hydrolytic degradation is unavoidable; continued heating of the solutions reduces their viscosity to that of water. In other respects (formation of stable complexes with bivalent cations; precipitation from acid solutions as the benzidine salt [29]) they behave like solutions of metaphosphate glass. The peculiar mechanism of dissolving, in which alkali-metal ions other than

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[28] *Annalen*, 1847, **61**, 63; *Phil. Mag.*, 1847, **30**, 322.

[29] C. J. Munter, Communication to American Chemical Society, 1936, Pittsburgh meeting.

* Maddrell only contributed two brief but discordant descriptions of a single experiment; the substance obtainable in very small yield by repeating Maddrell's preparation has the same *X*-ray powder diagram as $NaPO_3$-II prepared by dehydrating NaH_2PO_4 at 300°, as had already been done by Graham.[3]

sodium are active, is presumably in some way connected with the highly polymerised state of the metaphosphate, and related to the base-exchange which is observed when $NaPO_3$-II (Maddrell salt) is acted on by concentrated solutions of non-sodium salts.

Insoluble Sodium Metaphosphate ($NaPO_3$-IV ; Kurrol salt).—Rapid cooling of molten sodium metaphosphate results in formation of a glass, very slow cooling gives sodium trimetaphosphate ($NaPO_3$-I). If the cooling is only moderately slow the result is sensitive to such factors as the rate of cooling at different stages between 630° and 500° (and almost certainly also the thermal history of the melt above 630°) ; the purity of the metaphosphate ; the nucleation, deliberate or accidental, of the supercooled melt. Whatever crystalline phases are formed during moderate cooling, substantial quantities of glass often accompany them. Occasionally, along with glass and trimetaphosphate, a small proportion of a brittle fibrous crystalline variety ($NaPO_3$-IV ; Kurrol salt) grows spontaneously and escapes complete transformation into trimetaphosphate. By nucleating the surface of the melt between 600° and 550° crystallisation of this variety is promoted. The most effective method is to seed with fragments of preformed $NaPO_3$-IV (Kurrol salt), which must be well washed to remove trimetaphosphate, since the latter has the higher crystallisation rate. Other finely divided solids can act as nuclei [14] for growth of $NaPO_3$-IV (Kurrol salt), including silica, carborundum, insoluble potassium metaphosphate, and $NaPO_3$-II (Maddrell salt). P. Pascal [30] described a preparation of $NaPO_3$-IV (Kurrol salt) by heating sodium methyl (and ethyl) hydrogen phosphate to low red heat, but attempts [14] to repeat this have over a wide temperature range given only mixtures of sodium trimetaphosphate ($NaPO_3$-I) and $NaPO_3$-II (Maddrell salt). A. G. Taylor [14] and H. Huber and K. Klumpner [31] noted that $NaPO_3$-IV (Kurrol salt) is more readily obtained if the ratio Na_2O/P_2O_5 is a little higher (A.G.T.) or lower (H. and K.) than unity. The explanation in both cases might be that the crystallisation of $Na_3P_3O_9$ is preferentially restrained. The ratio Na_2O/P_2O_5 in the fibrous crystals has not been examined.

The description of $NaPO_3$-IV (Kurrol salt) as insoluble needs qualification. In cold distilled water after some hours, much more quickly in hot water, the fibrous crystals swell and eventually give a viscous solution. A 1% solution may be compared with glycerol, but the solution is really a very weak gel. The viscosity and structure of the solution is sometimes retained for months, sometimes lost in the course of a week or so. The reason for this variable behaviour may be the presence of traces of impurities such as multivalent cations which catalyse (see p. 365) the hydrolytic fission of the macro-ions, or there may be size differences in the anions themselves. Different preparations of $NaPO_3$-IV (Kurrol salt), at least from a melt of the correct Na_2O/P_2O_5 ratio, give the same well-characterised *X*-ray powder diagram. The gel structure and viscosity of the colloidal solution is destroyed in a few minutes by boiling. The swelling and dissolving is very much accelerated by the presence of alkali-metal cations

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[30] *Bull. Soc. chim.*, 1924, **35**, 1119.

[31] *Z. anorg. Chem.*, 1943, **251**, 213.

other than sodium, whilst sodium salts greatly reduce the extent of swelling. The effect of foreign alkali-metal ions, which is evidently to be compared with their effect upon the other two insoluble varieties of sodium metaphosphate, was described by A. G. Taylor,[32] who showed also that insoluble potassium metaphosphate swells and dissolves in the presence of sodium or ammonium ions. It is remarkable that a finely ground mechanical mixture of any variety of " insoluble " potassium metaphosphate with any variety of " insoluble " sodium metaphosphate will go completely into solution on boiling for a short time, by reason of the reciprocal action of the initially very small concentrations of the dissolved salts.

A rough comparison of the time required at 60° for swelling and solution of $NaPO_3$-IV (Kurrol salt) in the presence of M/200 chlorides of univalent cations [14] puts the efficiency of the cations in the order

$$K^{\cdot} > Li^{\cdot} > NH_4^{\cdot} > Rb^{\cdot} = \text{Morpholine} > \text{Triethanolamine} > \text{Benzylamine}$$

The action is to a first approximation independent of the anion of the added salt. The mechanism is not obvious, but presumably it is related to a kind of base exchange which occurs when " insoluble " alkali-metal metaphosphates are immersed in more concentrated salt solutions. The effect of morpholine and triethanolamine salts was first observed by Huber and Klumpner.[31]

The discovery of $NaPO_3$-IV (Kurrol salt) was attributed by G. Tammann [33] to his collaborator, Kurrol. It is referred to by him [34] as having been obtained by the slow cooling of molten metaphosphate. Tammann also mentions other experiments attributed to Kurrol, whereby the yield of $NaPO_3$-IV (Kurrol salt) was improved by slow dehydration of NaH_2PO_4, apparently without fusion and crystallisation. The occasional spontaneous formation of a little of this fibrous variety from the melt has often been confirmed, but not the other procedure mentioned by Tammann.

The term " Kurrol salt " has been much used (in France and Germany especially) not only for $NaPO_3$-IV (Kurrol salt) but also for all the insoluble varieties of potassium metaphosphate, and for other alkali-metal metaphosphates. No criterion has been proposed by which a class of " Kurrol salts " can be characterised, except, by implication, the property of yielding viscous solutions. Since the other two " insoluble " varieties of sodium metaphosphate share this property, as also does sodium metaphosphate glass when prepared in a certain way, it would seem better to reserve the name (if used at all) for the fibrous sodium metaphosphate discovered by Kurrol.

What has already been said about the probable high molecular weight of $NaPO_3$-III and $NaPO_3$-II (Maddrell salt) applies also to $NaPO_3$-IV (Kurrol salt). The remarkable fibrous appearance of the latter is also found with KPO_3 under some conditions of crystallisation from the melt.

Sodium Metaphosphate Glass.—Molten sodium metaphosphate remains fluid at least down to 500° if cooled fairly quickly ; by rapid cooling con-

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[32] B.P. 543,218 (1941).

[33] *J. pr. Chem.*, 1892, **45**, 417.

[34] *Z. physikal. Chem.*, 1890, **6**, 140.

tinued down to below 200°, devitrification is avoided and a brittle transparent colourless glass is obtained, which softens and tends to devitrify if reheated above about 300°. This glass is sometimes called Graham's salt, and often, but only by custom and no longer implying a view about the degree of polymerisation, "sodium hexametaphosphate". It is hygroscopic and easily soluble, without definite limit, in water but not alcohol.

Molten sodium metaphosphate has a strong affinity for water. When any anhydrous crystalline sodium metaphosphate is fused in undried air the melt absorbs some water vapour (1% by weight is common). Much or all of this is retained on cooling if a glass is formed, but is suddenly and vigorously evolved if and when a large proportion of the supercooled melt crystallises to sodium trimetaphosphate ($NaPO_3$-I). The presence of this water affects the properties of the glass, and certainly some if not all of it is chemically combined. When pure $Na_3P_3O_9$ or $NaNH_4HPO_4$ is fused in air of ordinary humidity the glass obtained by quick cooling is slightly acid ($pH \approx 5{\cdot}7$ at 1% weight concentration in a solution freshly prepared in water of pH 7). The solution is not appreciably different in viscosity from water. If a shallow layer of the same melt is kept for a day at 700° in a stream of dry air before chilling, the solution has pH 6·5—7. The metaphosphate glass now dissolves by a process of swelling, and the solution is a very weak gel.

Solutions of metaphosphate glass (or the free acid obtained by ion exchange) titrate with strong acids and bases as the salt of a fairly strong acid, to a first approximation.[35] O. Samuelson,[36] working with undried metaphosphate glass, determined the small titration values to the phenolphthalein change point and interpreted them in terms of end-group titrations of long unbranched-chain polyphosphate anions. The calculated average molecular weights increased with the temperature from which the melt had been chilled, varying from 10,800 for 650° to 17,200 for 950°. Earlier authors also considered the diagnostic use that might be made of titration values between pH 4·5 and 9·5, but it may be remarked that interpretation of the titration values in terms of unbranched chains or with the aid of the assumption that a true metaphosphate $(NaPO_3)_n$ necessarily corresponds to an acid with no hydrogen titratable between pH 4 and pH 10 is open to the consideration that metaphosphate structures like (IX), which have a side chain attached to a closed ring, would behave like a linear polyphosphate in respect of the titration of the terminal groups [excepting, probably, the two at the top of (IX)].

The presence of acid polyphosphates in the glass could account for the steam evolved as sodium trimetaphosphate ($NaPO_3$-I) crystallises, as well as the pH observations already mentioned, and the conspicuous increase in colloidal character of the chilled metaphosphate from the dried melt. Measurements of the amount of steam evolved during crystallisation have not been made, but it would be interesting to compare it with the end-

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[35] E. P. Partridge, Dual Service News, Hall Laboratories, Pittsburgh, 1937; Glatzel, ref. (24); W. Teichert and K. Rinman, *Acta Chem. Scand.*, 1948, **2**, 225.

[36] *Svensk Kem. Tids.*, 1944, **56**, 343.

group titration and the initial pH of solutions of glass chilled from the same melt.

Estimates by dialysis measurements of the average molecular weight of dissolved sodium metaphosphate glass (not from dried molten metaphosphate) have been made by Karbe and Jander [7] and by Teichert and Rinman.[35] The results are in reasonable agreement and indicate values in the range 1000—8000 increasing with the temperature from which the melt is chilled. Karbe and Jander's experiments are particularly interesting because of the wide temperature range (645° to 1280°) and the drastic chilling of the melts by pouring into partially frozen carbon tetrachloride. The ultracentrifuge has been applied [37] to study sedimentation in solutions of sodium metaphosphate glass, affording apparent molecular-weight values up to 13,000. Quimby [8] points out that the kinetic particle effective in sedimentation and dialysis might be an aggregate (micelle) of smaller polymerised units. Davies and Monk [18] determined conductivities of sodium metaphosphate glass, extending their measurements down to a concentration of 5×10^{-6}M.; the rapid decrease of equivalent conductivity between 5×10^{-6}M. and 5×10^{-3}M. is attributed to the anion having colloidal dimensions, but the authors, discussing Quimby's suggestion, point out that there is no evidence of micelle dissociation such as is found with typical micellar electrolytes. It is difficult to avoid the conclusion that true macro-ions are present in some circumstances, in view of the gel structure possessed by dilute solutions of $NaPO_3$-IV (Kurrol salt) and with dehydrated sodium metaphosphate glass.

Polyphosphates.—Only one series of polyphosphates has so far been isolated, the salts of triphosphoric acid with the anion structure (V). There is no reason to doubt that an indefinitely large number are capable of existence, and that in the future others will be isolated as chemical individuals. For example, a linear sodium tetraphosphate could no doubt be isolated by cautious hydrolysis of $Na_4P_4O_{12}$ in alkaline solution.

Sodium triphosphate, $Na_5P_3O_{10}$, has become an important commercial chemical because of excellent detergent effects when it is used as an auxiliary washing agent with soap or sulphonates.

F. Schwarz [38] observed that when a melt of composition $5Na_2O : 3P_2O_5$ is cooled slowly, small crystals of $Na_4P_2O_7$ form in the liquid; nevertheless, the compound $Na_5P_3O_{10}$ can be prepared in the form of a hydrate by dissolving and crystallising the cold mass. K. R. Andress and K. Wüst [39] confirmed this, and from *X*-ray powder diagrams deduced the existence of two crystal forms of sodium triphosphate. Partridge, Hicks, and Smith [10] and Morey and Ingerson [11] made a thorough investigation of the preparation of sodium triphosphate by the thermal method. No evidence was found of the formation as a pure phase of any other polyphosphate, from melts covering the whole range $Na_2O : P_2O_5$ from 1 : 1 to 2 : 1.

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[37] O. Lamm and H. Malmgren, *Z. anorg. Chem.*, 1940, **245**, 103; O. Lamm, *Chem. Abs.*, 1945, **39**, 3715.

[38] *Z. anorg. Chem.*, 1895, **9**, 249.

[39] *Ibid.*, 1938, **237**, 113.

The behaviour of a melt of composition $5Na_2O : 3P_2O_5$ on cooling is interesting. At about 860° crystals of $Na_4P_2O_7$ are present in the fluid system, and with further cooling there is formed a thick suspension of small crystals of $Na_4P_2O_7$ in a liquid increasingly rich in P_2O_5 relative to Na_2O, until at 622° the two-phase system contains approximately 44% of solid $Na_4P_2O_7$. At this temperature $Na_5P_3O_{10}$ appears as a third phase. Further removal of heat, if slow enough to maintain equilibrium, would result in isothermal conversion of the $Na_4P_2O_7$ into $Na_5P_3O_{10}$ with complete disappearance of the liquid phase. The reaction between the $Na_4P_2O_7$ crystals and the molten phase is slow ; a considerable amount of $Na_5P_3O_{10}$ is formed and the system becomes rigid in the form of an opaque vitreous mass containing, besides the high-temperature form usually denoted by $Na_5P_3O_{10}$-I, $Na_4P_2O_7$ and glassy material rich in P_2O_5. If further cooling to about 450° is slow enough, conversion into $Na_5P_3O_{10}$-I continues almost to completion. With still further cooling the solid mass breaks up into a fine powder, usually between 250° and 150°. It is probable that this spontaneous disintegration is caused by partial transformation into $Na_5P_3O_{10}$-II, the form stable at room temperature. Partridge, Hicks, and Smith [10] observed that a change to phase II in the *X*-ray powder diagram accompanies the disintegration, but it must be remarked that sometimes the disintegration occurs whilst the *X*-ray diagram remains predominantly that of $Na_5P_3O_{10}$-I.[14] Reversal of the polymorphic change occurs at 515° on the evidence of heating curves, but the temperature of reversible transformation is unknown. $Na_5P_3O_{10}$-I, when obtained by heating the disintegrated form of $Na_5P_3O_{10}$-II, does not readily revert to phase II on cooling again. This suggests that the polymorphic change is of the type in which the rate of propagation of the phase interface is high but the probability of spontaneous nucleus formation for phase II is low, a conclusion supported by observation of the transformation $\mathrm{I} \longrightarrow \mathrm{II}$ as it occurs in a large block of slowly cooled melt. When the phase I is in a finely divided form, growth of the second phase from each nucleus as it forms may be limited by the dimensions of the particle.

Sodium triphosphate is not usually manufactured by a process involving fusion and slow cooling, but by the reaction

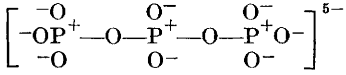
$$2Na_2HPO_4 + NaH_2PO_4 = Na_5P_3O_{10} + 2H_2O$$

The two orthophosphates are intimately mixed (*e.g.*, by rapid drying of the appropriate solution in a spray drier or on a rotating drum drier, or by heating the hydrated salts together so that they first fuse in their water of crystallisation) and the mixture is heated, usually in a rotary calciner. The polyphosphate product containing well over 90% of $Na_5P_3O_{10}$ is formed even at as low a temperature as 300°, and provided a temperature of about 400° is not exceeded, it is chiefly in the form $Na_5P_3O_{10}$-II. At 500—550° there is a considerable proportion of phase I.

The hydrate $Na_5P_3O_{10},6H_2O$, obtained when either form of $Na_5P_3O_{10}$ is exposed to the atmosphere or dissolved and crystallised, has a remarkably low dissociation pressure. If much of the water is pumped off in vacuum, even below 100° anhydrous triphosphate is not the product but a mixture containing ortho- and pyro-phosphate. At higher temperatures reconversion occurs into $Na_5P_3O_{10}$-I or -II according to the temperature. There is some evidence [16] that an octahydrate which readily passes into the hexahydrate can be obtained by vacuum evaporation below 20°. The solubility of $Na_5P_3O_{10},6H_2O$ is approximately 15% of $Na_5P_3O_{10}$ at 20°, and 16% at 40°. The phase I material is converted into hydrate almost immediately on contact with water, but the phase II can form a solution almost twofold supersaturated with respect to the stable hydrate, from which the latter crystallises comparatively slowly. The difference is practically important, phase I being unsuitable for use in some chemical plant because of separation of granular, slowly dissolving hexahydrate. Since phase I must potentially have a higher solubility than phase II with respect to which it is metastable, the explanation may be that local supersaturation with respect to the hydrate immediately round the particles of phase I is high enough to force spontaneous nucleation for crystallisation of the hydrate; or it may be that the lattice of phase I is itself able to initiate the growth of hydrate crystals. There is no evidence to support the suggestion that either phase I or phase II is a polymer of $Na_5P_3O_{10}$.

The most convenient method for the preparation of a pure specimen of $Na_5P_3O_{10},6H_2O$ is hydrolysis of $Na_3P_3O_9$. If a concentrated solution of the latter is mixed with an excess of sodium hydroxide solution, a large crop of $Na_5P_3O_{10},6H_2O$ crystallises after some hours.[40] Acids hydrolyse trimetaphosphate more rapidly than bases, but steps must then be taken to protect the triphosphate anion from further hydrolysis—*e.g.*, by having excess of $Zn^{\cdot\cdot}$ present in the acid solution, whereby the well-crystallised salt $NaZn_2P_3O_{10},9H_2O$ is precipitated.

The structural formula (XIII) for the anion of sodium triphosphate represents the substance well, within the limits of any single representation, for the following reasons:



$$\left[\begin{array}{ccccc} {}^{-}O & & O^{-} & & O^{-} \\ {}^{-}OP^{+} & —O— & P^{+} & —O— & P^{+}O^{-} \\ {}^{-}O & & O^{-} & & O^{-} \end{array}\right]^{5-}$$

(XIII.)

(1) It provides a natural explanation of the stepwise alkaline hydrolysis of cyclic trimetaphosphate through triphosphate to an equimolecular mixture of pyrophosphate and orthophosphate:

$$Na_3P_3O_9 \longrightarrow Na_5P_3O_{10} \longrightarrow Na_4P_2O_7 + Na_3PO_4$$

(2) Neither the anhydrous compound nor the hexahydrate is a "molecular compound" ($Na_3PO_4 + \frac{2}{3}Na_3P_3O_9$) or ($Na_4P_2O_7 + \frac{1}{3}Na_3P_3O_9$), this possibility being excluded [16] by comparison with the behaviour on crystallisation of solutions containing the relevant proportions of $Na_3P_3O_9$ with ortho- or pyro-phosphate, and by absence of precipitation reactions characteristic of the last two.

(3) Cryoscopic measurements in sodium sulphate decahydrate [16] gave 372 for the molecular weight ($Na_5P_3O_{10} = 368$).

[40] W. Faber, D.R.-P. 734,511 (1943); G. B. Hatch, U.S.P. 2,365,910 (1944).

(4) The electrometric titration curve [41] of sodium triphosphate shows that the corresponding acid has for every three phosphorus atoms three rather strongly acidic protons and two much less strongly acidic; this is consistent with the formal charge distribution of the anion structure (XIII).

(5) Alternative formulation to (V) is not possible while retaining 4-co-ordinate phosphorus.

Complex-ion Formation.—Bi- and ter-valent metal ions are precipitated by alkali-metal polyphosphates and pyrophosphates, and in most instances the precipitates dissolve in excess of the reagent even when the system is very dilute. This manifestation of complex-ion formation is found also with the colloidal solutions obtained from $NaPO_3$-IV (Kurrol salt), $NaPO_3$-II (Maddrell salt), and $NaPO_3$-III by the action of non-sodium alkali-metal ions, and with analogous solutions obtained from other " insoluble " alkali-metal and ammonium polymetaphosphates, and with solutions of metaphosphate glasses and glasses of polyphosphate composition. The cyclic tri- and tetra-metaphosphate anions, particularly the former, form much less stable complexes with metal cations.

This marked tendency to form complexes has been recognised (especially with the pyrophosphate ion) for more than a century, but the composition of the complexes and the nature of the forces responsible for their stability in solution have been little studied. L. B. Rogers and C. A. Reynolds [42] demonstrated by conductimetric, electrometric, and polarographic measurements the formation in dilute solution (10^{-3}—10^{-4}M.) of the complex ions $(M^{\bullet\bullet}P_2O_7)''$ by Cd, Co, Cu, Pb, Mg, Ni, Zn, and of $(M^{\bullet\bullet\bullet}P_2O_7)'$ by Al and Fe.

Calcium and strontium ions, usually less prone to complex formation than the metals of variable valency, nevertheless show qualitatively the same behaviour as the latter when treated with a solution of sodium metaphosphate. This was observed by Tammann [25] for a polymetaphosphate thought to be hexametaphosphate but actually of unknown molecular weight. Tammann likened the complexes between metal ions and metaphosphate to such complex anions as $Fe(CN)_6''''$ and $PtCl_6''$. A significant feature, however, of the complex-anion formation by condensed phosphates is the generality of the phenomenon—most if not all bi- and ter-valent cations form rather stable complexes with all condensed phosphate anions except the cyclic tri- and tetra-metaphosphates (and with the last the interaction is considerable). The practical usefulness of the power to combine with $Ca^{\bullet\bullet}$ and $Mg^{\bullet\bullet}$ was not realised until R. E. Hall,[43] some forty years after Tammann's observations, saw in glassy sodium metaphosphate a means of softening natural waters without producing precipitates. From the time of this patent the calcium complexes with condensed phosphates have been studied mostly for their applications. Much of the work is only briefly described in patents or journals of applied science, although some experimental work has been more fully reported by H. Rudy, H. Schloesser, and R. Watzel [44] and by Rudy [45] and O. Stelling and G. Frang.[46]

[41] Rudy and Schloesser, ref. (20).

[42] *J. Amer. Chem. Soc.*, 1949, **71**, 2081.

[43] U.S.P. 1,956,515 (1934).

[44] *Angew. Chem.*, 1940, **53**, 525.

[45] *Ibid.*, 1941, **54**, 447.

[46] *Svensk Kem. Tids.*, 1941, **53**, 270.

The calcium complexes are sufficiently stable for rather insoluble salts such as $CaCO_3$, CaC_2O_4,H_2O, and calcium soaps to be dissolved by solutions of condensed phosphates of alkali metals. For example,[32] a solution containing 0·01634 mol./l. of $Na_5P_3O_{10}$ (held near to pH 9·5 by addition of a little sodium hydroxide) is in equilibrium with CaC_2O_4,H_2O at 25° when it has dissolved 0·00732 mol./l. The solubility product of CaC_2O_4,H_2O is $2{\cdot}3 \times 10^{-9}$, so the concentration of free Ca ion is about $3{\cdot}1 \times 10^{-7}$ mol./l. in the triphosphate solution, and only a fraction $4{\cdot}3 \times 10^{-5}$ of the total calcium is uncombined. It being assumed that the complex is CaP_3O_{10}''', the ionic equilibrium concentration product $[Ca^{\bullet\bullet}][P_3O_{10}{}^{5-}]/[CaP_3O_{10}''']$ equals $3{\cdot}9 \times 10^{-7}$ mol./l. When the highly condensed glassy metaphosphates, or solutions of $NaPO_3$-IV (Kurrol salt) or of $NaPO_3$-II (Maddrell salt) or $NaPO_3$-III, or analogous salts of other alkali metals, are used instead of $Na_5P_3O_{10}$, anionic complexes are produced in which one $Ca^{\bullet\bullet}$ ion is on the average associated with 5—6 PO_3' groups. The stability of the ion association involved is comparable with that of CaP_3O_{10}'''. When $Ca^{\bullet\bullet}$ is replaced by $Mg^{\bullet\bullet}$ or $Zn^{\bullet\bullet}$ (the latter is conveniently studied electrometrically as well as by solubility of ZnC_2O_4) the results are qualitatively similar. The complex formation is always manifested except when some extremely insoluble phase intervenes, as, for example, when the condensed phosphate employed itself forms a particularly insoluble salt with the bivalent metal, *e.g.*, barium pyrophosphate.

For the calcium complex with the cyclic tetrametaphosphate ion, assumed to be CaP_4O_{10}'', Taylor,[14] using calcium oxalate, and Davies and Monk,[18] using calcium iodate, found $K \approx 3 \times 10^{-5}$ and $1{\cdot}3 \times 10^{-5}$, respectively; the latter is probably the better value. For the cyclic trimetaphosphate complex assumed to be CaP_3O_9' these authors found 8×10^{-4} (by oxalate solubility) and $3{\cdot}3 \times 10^{-4}$ (by iodate solubility), and again Davies and Monk's value is probably the better.

It seems very probable that ion association as interpreted by the Bjerrum theory is a sufficient explanation of these complexes. The polymetaphosphates (other than the cyclic compounds) and the polyphosphates are flexible structures carrying a number of negative charges, and it may be supposed that the flexibility of the –O–P–O–P– chain allows a cation $M^{\bullet\bullet}$ to draw on to itself in an energetically favourable way the total negative charge of five or six $-OPO_3'$ groups. Terminal PO_4'' groups, so far as they are present, would be even more effective. Recalling that even for bivalent sulphates [47] such as $Ca^{\bullet\bullet}SO_4''$ and $Zn^{\bullet\bullet}SO_4''$ the dissociation constant $K \approx 5 \times 10^{-3}$ mol./l., it is qualitatively clear that when the effective negative charge is increased several fold (the $-O-PO_3'$ or PO_4'' groups being not seriously different in size from SO_4'') the appearance of values of K as low as 10^{-7} mol./l. is to be expected. Similarly, consideration of the dissociation constant [48] for the complex ion NaP_2O_7''', $K \approx 4{\cdot}5 \times 10^{-3}$, makes the stability of the complex pyrophosphate ions $M^{\bullet\bullet}P_2O_7''$ seem natural.

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[47] R. W. Money and C. W. Davies, *Trans. Faraday Soc.*, 1932, **28**, 609; C. W Davies, *J.*, 1938, 2093.

[48] C. B. Monk, *J.*, 1949, 423.

When a polymetaphosphate or a polyphosphate in which the proportion of terminal PO_4'' groups is small binds a cation, it is not to be expected that the pH of the solution (as long as it is above about 5) will have much effect upon the extent of formation of the complex, since competition by protons for the negative charge of the $-OPO_3'$ groups will be ineffective. With pyrophosphate, short-chain polyphosphates, or structures such as (IX), competition for the charge of the PO_4'' groups is to be looked for below about pH 10. In practice a large effect of pH is found with pyrophosphate, triphosphate, and the commercial glasses in which $Na_2O/P_2O_5 > 1$. On the other hand, using a metaphosphate glass prepared in dry air and having $Na_2O/P_2O_5 = 1{\cdot}00$, Taylor [14] has found electrometrically for the $Zn^{\bullet\bullet}$ complex that there is practically no effect on the ion association of pH in the range 4·9—7·7, and with the same metaphosphate dissolving calcium oxalate to equilibrium only a very slight effect of pH was found in the range 6·0—7·8. A solution of this glass gave a titration curve with a single inflexion at pH 7.

Consideration of the values of pK_3 and pK_4 for pyrophosphoric acid and pK_4 and pK_5 for triphosphoric acid, relative to K for the calcium complexes, shows that in the pH range 7—10 partial ejection of protons by $M^{\bullet\bullet}$ ions is to be expected, and in fact the pH of a sodium polyphosphate solution in this range falls when bivalent cations are added.

Hydrolytic Instability.—In aqueous solution all condensed phosphates, acids, salts, and esters, hydrolyse at the P–O–P linkages, complete stability being attained only with ultimate conversion into orthophosphate. The hydrolysis is acid–base catalysed. There is a large variation in the ratio of the velocity constants k_H/k_{OH} as the intramolecular environment of the P–O–P linkage is varied. For example,[14] with tetraethyl pyrophosphate hydrolysing to diethyl orthophosphate, $k_H/k_{OH} < 10^{-6}$ at 25°, whereas for sodium metaphosphate glass ($Na_2O/P_2O_5 = 1$) hydrolysing to a series of products including pyrophosphate and orthophosphate, $k_H/k_{OH} \gg 10^{+2}$ at 100°. Several papers have appeared in the past fifty years which provide fragmentary information on the rates of hydrolysis of condensed phosphoric acids and their salts, but scarcely a beginning has yet been made with quantitative measurements. The problem is complicated by the number of ionic species which have to be taken into account in the consecutive reactions even with a relatively simple substance such as $Na_5P_3O_{10}$, or with a definite metaphosphate such as $Na_4P_4O_{12}$, and analytical difficulties have so far prevented an effective study. The papers of R. N. Bell [49] and R. Watzel [50] contain rates of hydrolysis which are useful for practical applications.

In alkaline solutions (pH > 11) the pyrophosphate and triphosphate anions, particularly the former, are very much more resistant to hydrolysis than P_4O_{12}'''', P_3O_9''', and the anions of more complex metaphosphates and polyphosphates. This may be due, in part at any rate, to the strength of the electric field in the proximity of the terminal double charge which

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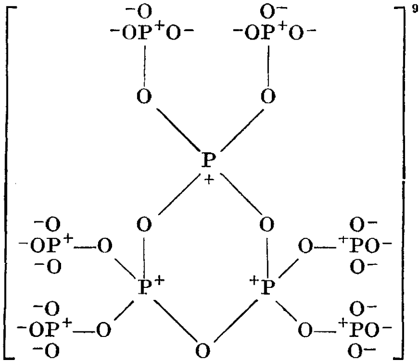
[49] *Ind. Eng. Chem.*, 1947, **39**, 136.

[50] *Die Chemie*, 1942, **55**, 356.

repels the OH' ion. It is not unexpected to find that the reduction of the local negative field of a portion of the anion resulting from association with $M^{\cdot\cdot}$ to form an ion pair considerably accelerates hydrolysis by OH'. For example,[14] addition of 5×10^{-4} mol. of $MgSO_4$ to 1 litre of a solution containing $7{\cdot}8 \times 10^{-2}$ mol. of potassium polymetaphosphate (calculated as KPO_3) dissolved in dilute sodium carbonate increased the rate of hydrolysis at 100° nearly ten-fold. Presumably, so long as there is sufficient metaphosphate left to re-associate bivalent cation liberated by the hydrolysis, the de-stabilising action continues. On the other hand, small additions of $Mg^{\cdot\cdot}$ or $Ca^{\cdot\cdot}$ would not be expected to accelerate hydrolysis in acid solution, when the hydrolytic catalyst is $H_3O^{\cdot}$. In confirmation, addition of 5×10^{-4} mol. of $CaCl_2$ to 1 litre of a solution containing $7{\cdot}8 \times 10^{-2}$ mol. of KPO_3 dissolved in dilute NaH_2PO_4 did not alter the rate of hydrolysis.

The nature and the molecular-weight distribution of the intermediate species produced during hydrolysis of the more highly condensed polymetaphosphates, *e.g.*, $NaPO_3$-IV (Kurrol salt), is an interesting matter awaiting investigation. Bell[49] found that when a metaphosphate glass with $Na_2O/P_2O_5 = 1$ is allowed to hydrolyse in dilute solution at 70° or 100°, the products are orthophosphate and trimetaphosphate in the molecular proportions 6 to 1, and concluded that part of the polymetaphosphate is hydrolysed, part depolymerised. It is difficult to see a possible mechanism for depolymerisation in aqueous solution except hydrolytic fission of P–O–P linkages, and difficult to see how the cyclic trimetaphosphate structure can arise during hydrolysis unless pre-existent as part of a more complex structure. The structure (XIV) represents a hypothetical anion



(XIV.)

$(PO_3)_9^{9-}$ which might be expected to hydrolyse comparatively readily to $6NaH_2PO_4 + Na_3P_3O_9$. The metaphosphate glass used by Bell presumably had a titration curve with a single inflexion at pH 7. In structure (XIV) each P^+ atom in the ring is linked to two OPO_3'' groups ; if this structure is to represent the dissolved metaphosphate, it is necessary to suppose that the formal positive charges on the three P^+ atoms involved is sufficient to raise to a pK of about 4 the acidity of the first hydrogen atom bound. In the undissociated acid, one of each pair of phosphate groups attached to the ring becomes $O(PO)(OH)_2$ and the other becomes $O(PO_2)OH$. The infringement of the rule of microscopic neutrality has already been referred to in connection with structure (IX); there does not seem to be any reason to reject (XIV) as impossible.

Surface Effects.—It is not surprising that condensed phosphates are strongly adsorbed on many surfaces, in view of the multiple negative charges carried by a single kinetic unit. Some resulting phenomena are both interesting and practically important.

At concentrations in the range 0·1—1·0% by weight, polymetaphosphates (other than the cyclic tetra- and tri-metaphosphates) and polyphosphates, and to some extent pyrophosphates, exert a strong dispersive effect upon suspensions of finely divided solids, such as clay. The rapidly growing use of condensed phosphates, especially sodium triphosphate, in conjunction with synthetic detergents for washing is partly attributable to this property.

The growth of crystalline precipitates from some supersaturated salt solutions is delayed or indefinitely prevented by very low concentrations of condensed phosphates. Calcite is a notable example much studied because of its application to the treatment of raw water to reduce scale deposition. The effect was apparently first noticed by R. F. Reitemeier and A. D. Ayers [51] in 1935, and first described by L. Rosenstein.[52] Concentrations of glassy metaphosphate as low as $1{\cdot}5 \times 10^{-5}$M. (in terms of $NaPO_3$) will inhibit precipitation of calcite in solutions very supersaturated with respect to $CaCO_3$, initially containing 10^{-3} mol. of $Ca(HCO_3)_2$ per litre, to which excess of ammonia is added, or from which carbon dioxide is withdrawn by boiling or by bubbling air. All soluble condensed phosphates except the cyclic tri- and tetra-metaphosphates, but including pyrophosphates, are effective inhibitors for calcite precipitation. As pointed out by G. B. Hatch and O. Rice,[53] it is probable that nuclei of calcite become covered by adsorbed metaphosphate and further growth is prevented. Other suggestions have been disproved by appropriate measurements on the solutions: the calcium carbonate does not go into a colloidal state stabilised by the metaphosphate; [54] the activity of $Ca^{\bullet\bullet}$ in the supersaturated solution is not appreciably reduced [51] by the minute concentration of metaphosphate; the phenomenon does not depend [55] upon any effect of the metaphosphate upon the rate of the conversion of $HCO_3^- \rightarrow CO_3^=$.

A study of the special case of calcium carbonate precipitation as affected by metaphosphate and pyrophosphate has been made.[54, 55] It was found that the inhibitory effect at about 10^{-5}M. is " a highly specific characteristic of the inorganic salts containing phosphorus in the pentavalent form ". The authors suggested as a possible explanation : " Since complex formation

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[51] *J. Amer. Chem. Soc.*, 1947, **69**, 2759.

[52] U.S.P. 2,038,316 (1936), re-issue 1937, 1938.

[53] *Ind. Eng. Chem.*, 1939, **31**, 51.

[54] T. F. Buehrer and R. F. Reitemeier, *J. Physical Chem.*, 1940, **44**, 552.

[55] R. F. Reitemeier and T. F. Buehrer, *ibid.*, p. 535.

occurs to a negligible extent, we must conclude that the action is largely an indirect one, involving either a stable electrostatic attraction between calcium and metaphosphate ion or a marked decrease in the activity of calcium ion due to the presence of the metaphosphate." The second alternative was later eliminated by Reitemeier and Ayers.[51] There has been some discussion as to the stage in the precipitation most affected by the condensed phosphate, whether it is the " nucleus " stage, or the subsequent growth of crystals of calcite. B. Raistrick [56] has drawn attention to the fact that the size of the repeating unit in a polymetaphosphate chain, relative to the spacing of the Ca$^{\cdot\cdot}$ ions in a layer of the calcite lattice, is such that the chain can lie without strain on top of the latter so that consecutive centres of negative charge occupy positions centrally above adjoining triangles of doubly charged Ca$^{\cdot\cdot}$ ions ; it is suggested that this favourable coincidence causes very strong adsorption. Buehrer and Reitemeier [54] found only 1 atom of P to 300 atoms of Ca in calcite precipitated in the presence of glassy sodium metaphosphate at a concentration just below the " threshold " value of $1{\cdot}5 \times 10^{-5}$M-$NaPO_3$, above which precipitation is virtually stopped ; the crystals are retarded in growth and distorted, but give the characteristic *X*-ray powder diagram of calcite. In connection with this absence of appreciable solid-solution formation, Raistrick [56] points out that when a layer of *singly charged* metaphosphate groups covers a layer of Ca$^{\cdot\cdot}$ ions, there will be a rough approximation to electrical neutrality just outside the adsorbed metaphosphate, since the double positive charge of the Ca$^{\cdot\cdot}$ ions is offset by their greater distance. This also makes it easier to understand the growth inhibition, since there will be no strong electrostatic force to retain a new layer of Ca$^{\cdot\cdot}$ outside the adsorbed metaphosphate.

It must be remarked that Reitemeier and Ayers [51] have shown that glassy metaphosphate at $1{\cdot}5 \times 10^{-5}$M. concentration (with respect to $NaPO_3$) will also stabilise a supersaturated solution of calcium sulphate against crystallisation as dihydrate ; this, and also the fact that pyrophosphate in alkaline solution is no less effective than glassy metaphosphate (although the adsorbable anion is then carrying a double charge at each end), are points requiring further explanation.

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[56] Faraday Society, Bristol Discussion on Crystal Growth, 1949.