$M_5^I[cyclo\text{-}P_5S_{10}]$ and $M_6^I[cyclo\text{-}P_6S_{12}]$ were obtained using red phosphorus, whereas white P_4 yielded $[NH_4]_4[cyclo\text{-}P_4S_8].2H_2O$ as shiny platelets. This unique $P_4S_8^{4-}$ anion is the first known homocycle of 4 tetracoordinated P atoms and X-ray studies reveal that the P atoms form a square with rather long P–P distances (228 pm).[117]

The new planar anion PS_3^- (cf. the nitrate ion, NO_3^-) has been isolated as its tetraphenylarsonium salt, mp 183°, following a surprising reaction of P_4S_{10} with KCN/H_2S in MeCN, in which the coproduct was the known dianion $[(NC)P(S)_2\text{–}S\text{–}P(S)_2(CN)]^{2-}$[118] The first sulfido heptaphosphane cluster anions, $[P_7(S)_3]^{3-}$ and $[HP_7(S)_2]^{2-}$ (cf. P_7^{3-}, p. 491), have also recently been characterized.[119]

Oxosulfides

When P_4O_{10} and P_4S_{10} are heated in appropriate proportions above 400°, $P_4O_6S_4$ is obtained as colourless hygroscopic crystals, mp 102°.

$$3P_4O_{10} + 2P_4S_{10} \longrightarrow 5P_4O_6S_4$$

The structure is shown in Fig. 12.15. The related compound $P_4O_4S_6$ is said to be formed by the reaction of H_2S with $POCl_3$ at 0° (A. Besson, 1897) but has not been recently investigated. An amorphous yellow material of composition $P_4O_4S_3$ is obtained when a solution of P_4S_3 in CS_2 or organic solvents is oxidized by dry air or oxygen. Other oxosulfides of uncertain authenticity such as $P_6O_{10}S_5$ have been reported but their structural integrity has not been established and they may be mixtures. However, the following series can be prepared by appropriate redistribution reactions: $P_4O_6S_n$ ($n = 1$–4), $P_4O_6Se_n$ ($n = 1$–3), P_4O_6SSe, $P_4O_7S_n$ ($n = 1$–3), P_4O_7Se, $P_4O_8S_n$ ($n = 1, 2$).[120] the crystal and molecular structures of $P_4O_6S_2$ and $P_4O_6S_3$ have recently been determined.[121] Two isomers each of $\beta\text{-}P_4S_2SeI_2$ and $\beta\text{-}P_4SSe_2I_2$, prepared by reaction of $P_4S_{3-n}Se_n$ with I_2 in CS_2 have been structurally identified by ^{31}P nmr spectroscopy.[122]

12.3.6 Oxoacids of phosphorus and their salts

The oxoacids of P are more numerous than those of any other element, and the number of oxoanions and oxo-salts is probably exceeded only by those of Si. Many are of great importance technologically and their derivatives are vitally involved in many biological processes (p. 528). Fortunately, the structural principles covering this extensive array of compounds are very simple and can be stated as follows:[†]

(i) All P atoms in the oxoacids and oxoanions are 4-coordinate and contain at least one P–O unit (1).

(1)

(ii) All P atoms in the oxoacids have at least one P–OH group (2a) and this often occurs in the anions also; all such groups are ionizable as proton donors (2b).

[117] H. FALIUS, W. KRAUSE and W. S. SHELDRICK, *Angew. Chem. Int. Edn. Engl.* **20**, 103–4 (1981).

[118] H. W. ROESKY, R. AHLRICHS and S. BRODE, *Angew. Chem. Int. Edn. Engl.* **25**, 82–3 (1986)

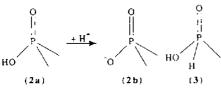[119] M. BAUDLER and A. FLORUSS, *Z. anorg. allg. Chem.* **620**, 2070–6 (1994).

[120] M. L. WALKER, D. E. PECKENPAUGH and J. L. MILLS, *Inorg. Chem.* **18**, 2792–6 (1979).

[121] F. FRICK and M. JANSEN, *Z. anorg. allg. Chem.* **619**, 281–6 (1993). See M. JANSEN and S. STROJEK, *Z. anorg. allg. Chem.* **621**, 479–83 (1995) for X-ray structures of P_4O_7S, i.e. $P_4O_6(O)_t(S)_t$.
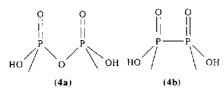
[122] P. LÖNNECKE and R. BLACHNIK, *Z. anorg. allg. Chem.* **619**, 1257–61 (1993). See also M. RUCK, *ibid.* **620**, 1832–6 (1994) R. BLACHNIK, A. HEPP, P. LÖNNECKE, J. A. DONKIN and B. W. TATTERSHALL, *ibid.* **620**, 1925–31 (1994).

[†] Heteropolyacids containing P fall outside this classification and are treated, together with the isopolyacids and their salts, on pp. 1010–16. Organic esters such as $P(OR)_3$ are also excluded.

(iii) Some species also have one (or more) P–H group (3); such directly bonded H atoms are not ionizable.

(2a)   (2b)   (3)

(iv) Catenation is by P–O–P links (4a) or via direct P–P bonds (4b); with the former both open chain ("linear") and cyclic species are known but only corner sharing of tetrahedra occurs, never edge- or face-sharing.

(4a)   (4b)

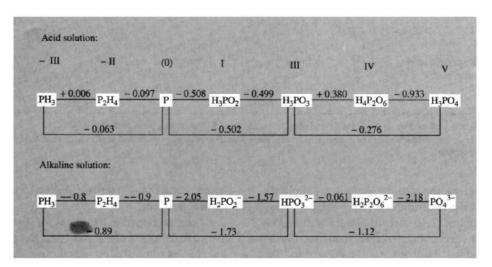(v) Peroxo compounds feature either $>$P–OOH groups or $>$POOP$<$ links.

It follows from these structural principles that each P atom is 5-covalent. However, the oxidation state of P is 5 only when it is directly bound to 4 O atoms; the oxidation state is reduced by 1 each time a P–OH is replaced by a P–P bond and by 2 each time a P–OH is replaced by

a P–H. Some examples of phosphorus oxoacids are listed in Table 12.7 together with their recommended and common names. It will be seen that the numerous structural types and the variability of oxidation state pose several problems of nomenclature which offer a rich source of confusion in the literature.

The oxoacids of P are clearly very different structurally from those of N (p. 459) and this difference is accentuated when the standard reduction potentials (p. 434) and oxidation-state diagrams (p. 437) for the two sets of compounds are compared. Some reduction potentials ($E°/V$) in acid solution are in Table 12.8[123] (p. 513) and these are shown schematically below, together with the corresponding data for alkaline solutions.

The alternative presentation as an oxidation state diagram is in Fig. 12.16 which shows the dramatic difference to N (p. 438).

The fact that the element readily dissolves in aqueous media with disproportionation into PH_3 and an oxoacid is immediately clear from the fact that P lies above the line joining PH_3 and either H_3PO_2 (hypophosphorous acid), H_3PO_3 (phosphorous acid) or H_3PO_4 (orthophosphoric acid). The reaction is even

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[123] G. MILAZZO and S. CAROLI, *Tables of Standard Electrode Potentials*, Wiley, New York, 1978, 421 pp. A. J. BARD, R. PARSONS and J. JORDAN, *Standard Potentials in Aqueous Solution*, Marcel Dekker, New York, 1985, 834 pp.

Phosphorus

Table 12.7 Some phosphorus oxoacids[a]

Formula/Name	Structure[a]	Formula/Name	Structure[a]
H_3PO_4 (Ortho)phosphoric acid		H_3PO_5 Peroxomonophosphoric acid	
$H_4P_2O_7$ Diphosphoric acid (pyrophosphoric acid)		$H_4P_2O_8$ Peroxodiphosphoric acid	
$H_5P_3O_{10}$ Triphosphoric acid		$H_4P_2O_6$ Hypophosphoric acid [diphosphoric(IV) acid]	
$H_{n+2}P_nO_{3n+1}$ Polyphosphoric acid (n up to 17 isolated)		$H_4P_2O_6$ Isohypophosphoric acid [diphosphoric(III,V) acid]	
$(HPO_3)_3$ *Cyclo*-trimetaphosphoric acid		H_3PO_3 (2)[b] Phosphonic acid (phosphorous acid)	
$(HPO_3)_4$ *Cyclo*-tetrametaphosphoric acid (anions known in both "boat" and "chair" forms)		$H_4P_2O_5$ (2)[b] Diphosphonic acid (diphosphorous or pyrophosphorous acid)	
$(HPO_3)_n$ Polymetaphosphoric acid (see text for salts)		H_3PO_2 (1)[b] Phosphinic acid (hypophosphorous acid)	

[a]Some acids are known only as their salts in which one or more —OH group has been replaced by O^-
[b]The number in parentheses after the formula indicates the maximum basicity, where this differs from the total number of H atoms in the formula.

more effective in alkaline solution. Similarly, $H_4P_2O_6$ disproportionates into H_3PO_3 and H_3PO_4. Figure 12.16 also illustrates that H_3PO_2 and H_3PO_3 are both effective reducing agents, being readily oxidized to H_3PO_4, but this latter compound (unlike HNO_3) is not an oxidizing agent.

A comprehensive treatment of the oxoacids and oxoanions of P is inappropriate but selected examples have been chosen to illustrate
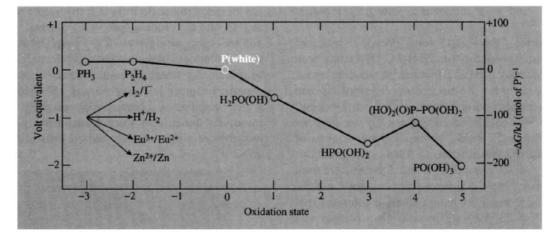
Figure 12.16　Oxidation state diagram for phosphorus. (Note that all the oxoacids have a phosphorus covalency of 5.)

interesting points of stereochemistry, reaction chemistry or technological applications. The treatment begins with the lower oxoacids and their salts (in which P has an oxidation state less than $+5$) and then considers phosphoric acid, phosphates and polyphosphates. The peroxoacids H_3PO_5 and $H_4P_2O_8$ and their salts will not be treated further[124] (except peripherally) nor will the peroxohydrates of orthophosphates, which are obtained from aqueous H_2O_2 solutions.[64]

Hypophosphorous acid and hypophosphites [H₂PO(OH) and H₂PO₂⁻]

The recommended names for these compounds (phosphinic acid and phosphinates) have not yet gained wide acceptance for inorganic compounds but are generally used for organophosphorus derivatives. Hypophosphites can be made by heating white phosphorus in aqueous alkali:

$$P_4 + 4OH^- + 4H_2O \xrightarrow[\text{[NaOH/Ca(OH)}_2\text{]}]{\text{warm}} 4H_2PO_2^- + 2H_2$$

Phosphite and phosphine are obtained as byproducts (p. 493) and the former can be removed via

[124] I. I. Creaser and J. O. Edwards, *Topics in Phosphorus Chemistry* **7**, 379–435 (1972).

its insoluble calcium salt:

$$P_4 + 4OH^- + 2H_2O \xrightarrow{2Ca^{2+}} Ca(HPO_3)_2 + 2PH_3$$

Table 12.8　Some reduction potentials in acid solution (pH 0)[a]

Reaction	$E°$/V
$P + 3H^+ + 3e^- \rightleftharpoons PH_3(g)$	-0.063
$P + 2H^- + 2e^- \rightleftharpoons \frac{1}{2}P_2H_4(g)$	-0.097
$\frac{1}{2}P_2H_4 + H^+ + e^- \rightleftharpoons PH_3$	$+0.006$
$H_3PO_2 + H^+ + e^- \rightleftharpoons P + 2H_2O$	-0.508
$H_3PO_3 + 3H^+ + 3e^- \rightleftharpoons P + 3H_2O$	-0.502
$H_3PO_4 + 5H^+ + 5e^- \rightleftharpoons P + 4H_2O$	-0.411
$H_3PO_3 + 2H^+ + 2e^- \rightleftharpoons H_3PO_2 + H_2O$	-0.499
$H_3PO_4 + 2H^+ + 2e^- \rightleftharpoons H_3PO_3 + H_2O$	-0.276
$H_3PO_4 + H^+ + e^- \rightleftharpoons \frac{1}{2}H_4P_2O_6 + H_2O$	-0.933
$\frac{1}{2}H_4P_2O_6 + H^+ + e^- \rightleftharpoons H_3PO_3$	$+0.380$

[a]P refers to white phosphorus. $\frac{1}{4}P_4(s)$.

Free hypophosphorous acid is obtained by acidifying aqueous solutions of hypophosphites but the pure acid cannot be isolated simply by evaporating such solutions because of its ready oxidation to phosphorous and phosphoric acids and disproportionation to phosphine and phosphorous acid (Fig. 12.16). Pure H_3PO_2 is obtained by continuous extraction from aqueous solutions into Et_2O; it forms white crystals mp

26.5° and is a monobasic acid pK_a 1.244 at 25°.[125]

During the past few decades hydrated sodium hypophosphite, $NaH_2PO_2.H_2O$, has been increasingly used as an industrial reducing agent, particularly for the electroless plating of Ni onto both metals and non-metals.[126] This developed from an accidental discovery by A. Brenner and Grace E. Riddel at the National Bureau of Standards, Washington, in 1944. Acid solutions ($E \sim -0.40$ V at pH 4–6 and $T > 90°$) are used to plate thick Ni layers on to other metals, but more highly reducing alkaline solutions (pH 7–10; T 25–50°) are used to plate plastics and other non-conducting materials:

$$HPO_3^{2-} + 2H_2O + 2e^- \rightleftharpoons H_2PO_2^- + 3OH^-;$$
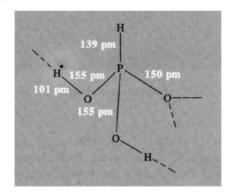
$$E \sim -1.57 \text{ V}$$

Typical plating solutions contain 10–30 g/l of nickel chloride or sulfate and 10–50 g/l NaH_2PO_2; with suitable pump capacities it is possible to plate up to 10 kg Ni per hour from such a bath (i.e. 45 m^2 surface to a thickness of 25 μm). Chemical plating is more expensive than normal electrolytic plating but is competitive when intricate shapes are being plated and is essential for non-conducting substrates. (See also the use of BH_4^- in this connection, p. 167.)

Phosphorous acid and phosphites
[HPO(OH)$_2$ and HPO$_3$$^{2-}$]

Again, the recommended names (phosphonic acid and phosphonates) have found more general acceptance for organic derivatives such as RPO_3^{2-}, and purely inorganic salts are still usually called phosphites. The free acid is readily made by direct hydrolysis of PCl_3 in cold CCl_4 solution:

$$PCl_3 + 3H_2O \longrightarrow HPO(OH)_2 + 3HCl$$

On an industrial scale PCl_3 is sprayed into steam at 190° and the product sparged of residual water and HCl using nitrogen at 165°. Phosphorous acid forms colourless, deliquescent crystals, mp 70.1°, in which the structural units shown form four essentially linear H bonds (O···H 155–160 pm) which stabilize a complex 3D network. The molecular dimensions were determined by low-temperature single-crystal neutron diffraction at 15 K.[127]

In aqueous solutions phosphorous acid is dibasic (pK_1 1.257, pK_2 6.7)[125] and forms two series of salts: phosphites and hydrogen phosphites (acid phosphites), e.g.

"normal": $[NH_4]_2[HPO_3].H_2O$, $Li_2[HPO_3]$, $Na_2[HPO_3].5H_2O$, $K_2[HPO_3]$
"acid": $[NH_4][HPO_2(OH)]$, $Li[HPO_2(OH)]$, $Na[HPO_2(OH)].2\frac{1}{2}H_2O$, $K[HPO_2(OH)]$ and $M[HPO_2(OH)]_2$ ($M = Mg$, Ca, Sr).

Dehydration of these acid phosphites by warming under reduced pressure leads to the corresponding pyrophosphites $M_2^I[HP(O)_2-O-P(O)_2H]$ and $M^{II}[HP(O)_2-O-P(O)_2H]$.

Organic derivatives fall into 4 classes $RPO(OH)_2$, $HPO(OR)_2$, $R'PO(OR)_2$ and the phosphite esters $P(OR)_3$; this latter class has no purely inorganic analogues, though it is, of course, closely related to PCl_3. Some preparative routes have already been indicated. Reactions with alcohols depend on conditions:

$$PCl_3 + 3ROH \longrightarrow HPO(OR)_2 + RCl + 2HCl$$

[125] J. W. LARSON and M. PIPPIN, *Polyhedron* **8**, 527–30 (1989).

[126] H. NIEDERPRÜM, *Angew. Chem. Int. Edn. Engl.* **14**, 614–20 (1975); G. A. KRULIK. *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 9, pp. 198–218, Wiley, New York, 1994.

[127] G. BECKER, H.-D. HAUSEN, O. MUNDT, W. SCHWARZ, C. T. WAGNER and T. VOGT. *Z. anorg. allg. Chem.* **591**, 17–31 (1990).

$$PCl_3 + 3ROH + 3R'_3N \longrightarrow P(OR)_3 + 3R'_3NHCl$$

Phenols give triaryl phosphites $P(OAr)_3$ directly at $\sim160°$ and these react with phosphorous acid to give diaryl phosphonates:

$$2P(OAr)_3 + HPO(OH)_2 \longrightarrow 3HPO(OAr)_2$$

Trimethyl phosphite $P(OMe)_3$ spontaneously isomerizes to methyl dimethylphosphonate $MePO(OMe)_2$, whereas other trialkyl phosphites undergo the Michaelis–Arbusov reaction with alkyl halides via a phosphonium intermediate:

$$P(OR)_3 + R'X \longrightarrow \{[R'P(OR)_3]X\}$$
$$\longrightarrow R'PO(OR)_2 + RX$$

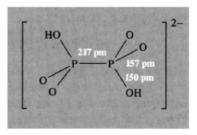Further discussion of these fascinating series of reactions falls outside our present scope.[2]

Hypophosphoric acid ($H_4P_2O_6$) and hypophosphates

There has been much confusion over the structure of these compounds but their diamagnetism has long ruled out a monomeric formulation, H_2PO_3. In fact, as shown in Table 12.7, isomeric forms are known: (a) hypophosphoric acid and hypophosphates in which both P atoms are identical and there is a direct P–P bond; (b) isohypophosphoric acid and isohypophosphates in which 1 P has a direct P–H bond

and the 2 different P atoms are joined by a P^{III}–O–P^V link.[23]

Hypophosphoric acid, $(HO)_2P(O)$–$P(O)(OH)_2$, is usually prepared by the controlled oxidation of red P with sodium chlorite solution at room temperature: the tetrasodium salt, $Na_4P_2O_6.10H_2O$, crystallizes at pH 10 and the disodium salt at pH 5.2:

$$2P + 2NaClO_2 + 8H_2O \longrightarrow Na_2H_2P_2O_6.6H_2O$$
$$+ 2HCl$$

Ion exchange on an acid column yields the crystalline "dihydrate" $H_4P_2O_6.2H_2O$ which is actually the hydroxonium salt of the dihydrogen hypophosphate anion $[H_3O]_2^+[(HO)P(O)_2$–$P(O)_2(OH)]^{2-}$; it is isostructural with the corresponding ammonium salt for which X-ray diffraction studies establish the staggered structure shown.

The anhydrous acid is obtained either by the vacuum dehydration of the dihydrate over P_4O_{10}

$H_4P_2O_6$ (hypophosphoric)

$H_4P_2O_6$ (isohypophosphoric) $H_4P_2O_7$ (pyrophosphoric) $H_4P_2O_5$ (pyrophosphorous)

or by the action of H_2S on the insoluble lead salt $Pb_2P_2O_6$. As implied above, the first proton on each $-PO(OH)_2$ unit is more readily removed than the second and the successive dissociation constants at 25° are pK_1 2.2, pK_2 2.8, pK_3 7.3, pK_4 10.0. Both $H_4P_2O_6$ and its dihydrate are stable at 0° in the absence of moisture. The acid begins to melt (with decomposition) at 73° but even at room temperature it undergoes rearrangement and disproportionation to give a mixture of isohypophosphoric, pyrophosphoric, and pyrophosphorous acids as represented schematically on the previous page.

Hypophosphoric acid is very stable towards alkali and does not decompose even when heated with 80% NaOH at 200°. However, in acid solution it is less stable and even at 25° hydrolyses at a rate dependent on pH (e.g. $t_{\frac{1}{2}}$ 180 days in 1 M HCl, $t_{\frac{1}{2}} < 1$ h in 4 M HCl):

$$(HO)_2P(O)-P(O)(OH)_2 + H_2O \xrightarrow{pH<0}$$

$$HP(O)(OH)_2 + P(O)(OH)_3$$

The presence of P–H groups amongst the products of these reactions was one of the earlier sources of confusion in the structures of hypophosphoric and isohypophosphoric acids.
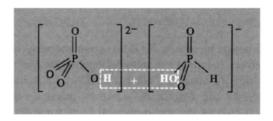
The structure of isohypophosphoric acid and its salts can be deduced from ^{31}P nmr which shows the presence of 2 different 4-coordinate P atoms, the absence of a P–P bond and the presence of a P–H group (also confirmed by Raman spectroscopy). It is made by the careful hydrolysis of PCl_3 with the stoichiometric amounts of phosphoric acid and water at 50°:

$$PCl_3 + H_3PO_4 + 2H_2O \xrightarrow{50°}$$

$$iso\text{-}[H_3(HP_2O_6)] + 3HCl$$

The trisodium salt is best made by careful dehydration of an equimolar mixture of hydrated disodium hydrogen phosphate and sodium hydrogen phosphite at 180°:

$$Na_2HPO_4.12H_2O + NaH_2PO_3.2\tfrac{1}{2}H_2O \xrightarrow{180°}$$

$$Na_3[HP_2O_6] + 15\tfrac{1}{2}H_2O$$

The structural relation between the reacting anions and the product is shown schematically below:

Other lower oxoacids of phosphorus

The possibility of P–H and P–P bonds in phosphorus oxoacids, coupled with the ease of polymerization via P–O–P linkages enables innumerable acids and their salts to be synthesized. Frequently mixtures are obtained and these can be separated by paper chromatography, paper electrophoresis, thin-layer chromatography, ion exchange or gel chromatography.[128] Much ingenuity has been expended in designing appropriate syntheses but no new principles emerge. A few examples are listed in Table 12.9 to illustrate both the range of compounds available and also the abbreviated notation, which proves to be more convenient than formal systematic nomenclature in this area. In this notation the sequence of P–P and P–O–P links is indicated and the oxidation state of each P is shown as a superscript numeral which enables the full formula (including P–H groups) to be deduced.

The phosphoric acids

This section deals with orthophosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$) and the polyphosphoric acids ($H_{n+2}P_nO_{3n+1}$). Several of these compounds can be isolated pure but their facile interconversion renders this area of phosphorus chemistry far more complex

[128] S. OHASHI, *Pure Appl. Chem.* **44**, 415–38 (1975).

Table 12.9 Some lower oxoacids of phosphorus (Superscript numerals in the abbreviated notation indicate oxidation states)

Formula (basicity)	Structure	Abbreviated notation	Formula (basicity)	Structure	Abbreviated notation
$H_4P_2O_4$ (2)		$\overset{2}{P}-\overset{2}{P}$	$H_5P_3O_9$ (5)		$\overset{5}{P}-O-\overset{4}{P}-\overset{4}{P}$
$H_4P_2O_5$ (3)		$\overset{2}{P}-\overset{4}{P}$	$H_6P_4O_{11}$ (6)		$\overset{4}{P}-\overset{4}{P}-O-\overset{4}{P}-\overset{4}{P}$
$H_4P_2O_6$ (3)		$\overset{3}{P}-O-\overset{5}{P}$	$H_4P_4O_{10}$ (10)		$(-\overset{4}{P}-\overset{4}{P}-O-)_2$ ring
$H_5P_3O_7$ (4)		$\overset{3}{P}-O-\overset{4}{P}-\overset{4}{P}$	$H_6P_6O_{12}$ (6)		$(-\overset{3}{P}-)_6$ ring
$H_5P_3O_8$ (5)		$\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$			

than might otherwise appear. The corresponding phosphate salts are discussed in subsequent sections as also are the cyclic metaphosphoric acids $(HPO_3)_n$, the polymetaphosphoric acids $(HPO_3)_n$, and their salts.

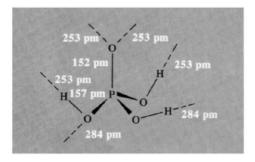Orthophosphoric acid is a remarkable substance: it can only be obtained pure in the crystalline state (mp 42.35°C) and when fused it slowly undergoes partial self-dehydration to diphosphoric acid:

$$2H_3PO_4 \rightleftharpoons H_2O + H_4P_2O_7$$

The sluggish equilibrium is obtained only after several weeks near the mp but is more rapid at higher temperatures. This process is accompanied by extremely rapid autoprotolysis (see below) which gives rise to several further (ionic) species in the melt. As the concentration of these various species builds up the mp slowly drops until at equilibrium it is 34.6°, corresponding to about 6.5 mole% of diphosphate.[129] Slow crystallization of stoichiometric molecular H_3PO_4 from this isocompositional melt gradually reverses the equilibria and the mp eventually rises again to the initial value. Crystalline H_3PO_4 has a hydrogen-bonded layer structure in which each $PO(OH)_3$ molecule is linked to 6 others by H bonds which are of two lengths, 253 and 284 pm. The shorter bonds link OH and O=P groups whereas the longer H bonds are between 2 OH groups on adjacent molecules.

Extensive H bonding persists on fusion and phosphoric acid is a viscous syrupy liquid that readily supercools. At 45°C (just above the mp) the viscosity is 76.5 centipoise (cP) and this increases to 177.7 cP at 25°. These values can be compared with 1.00 cP for H_2O at 20° and 24.5 cP for anhydrous H_2SO_4 at 25°. As shown in the Table[129] trideuterophosphoric acid has an even higher viscosity and deuteration also raises the mp and density.

Property	H_3PO_4	D_3PO_4
MP/°C	42.35	46.0
Density (25°C); supercooled/g cm^{-3}	1.8683	1.9083
η (25°C)/centipoise	177.5	231.8
κ/ohm^{-1} cm^{-1}	4.68×10^{-2}	2.82×10^{-2}

Property	$H_3PO_4 \cdot \frac{1}{2}H_2O$
MP/°C	29.30
Density (25°C); supercooled/g cm^{-3}	1.7548
η (25°C)/centipoise	70.64
κ/ohm^{-1} cm^{-1}	7.01×10^{-2}

Despite this enormous viscosity, fused H_3PO_4 (and D_3PO_4) conduct electricity extremely well and this has been shown to arise from extensive self-ionization (autoprotolysis) coupled with a proton-switch conduction mechanism for the $H_2PO_4^-$ ion:[129,130]

$$2H_3PO_4 \rightleftharpoons H_4PO_4^+ + H_2PO_4^- \qquad (1)$$

In addition, the diphosphate group is also deprotonated:

$$2H_3PO_4 \rightleftharpoons H_2O + H_4P_2O_7$$
$$\rightleftharpoons H_3O^+ + H_3P_2O_7^-$$
$$H_3P_2O_7^- + H_3PO_4 \rightleftharpoons H_4PO_4^+$$
$$+ H_2P_2O_7^{2-}$$

i.e.
$$3H_3PO_4 \rightleftharpoons H_3O^+ + H_4PO_4^+$$
$$+ H_2P_2O_7^{2-} \quad (2)$$

At equilibrium, the concentration of H_3O^+ and $H_2P_2O_7^{2-}$ are each ~0.28 molal and $H_2PO_4^-$ is ~0.26 molal, thereby implying a

[129] N. N. GREENWOOD and A. THOMPSON, *J. Chem. Soc.* 3485–92 and 3864–7 (1959).

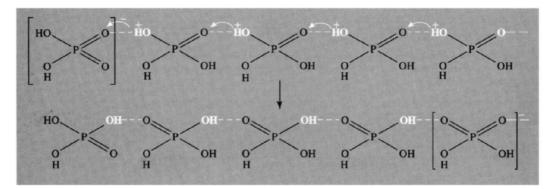[130] R. A. MUNSON, *J. Phys. Chem.* **68**, 3374–7 (1964).

Figure 12.17   Schematic representation of proton-switch conduction mechanism involving $[H_2PO_4]^-$ in molten phosphoric acid.

concentration of 0.54 molal for $H_4PO_4^+$. These values are about 20–30 times greater than the concentrations of ions in molten H_2SO_4, namely $[HSO_4^-]$ 0.0178 molal, $[H_3SO_4^+]$ 0.0135 molal and $[HS_2O_7^-]$ 0.0088 molal (see p. 711). Because of the very high viscosity of molten H_3PO_4 electrical conduction by normal ionic migration is negligible and the high conductivity is due almost entirely to a rapid proton-switch followed by a relatively slow reorientation involving the $H_2PO_4^-$ ion, H-bonded to the solvent structure (Fig. 12.17).[129] Note that the tetrahedral $H_4PO_4^+$ ion, i.e. $[P(OH)_4]^+$, like the NH_4^+ ion in liquid NH_3, does not contribute to the proton-switch conduction mechanism in H_3PO_4 because, having no dipole moment, it does not orient preferentially in the applied electric field; accordingly any proton switching will occur randomly in all directions independently of the applied field and therefore will not contribute to the electrical conduction.

Addition of the appropriate amount of water to anhydrous H_3PO_4, or crystallization from a concentrated aqueous solution of syrupy phosphoric acid, yields the hemihydrate $2H_3PO_4.H_2O$ as a congruently melting compound (mp 29.3°). The crystal structure[131] shows the presence of 2 similar H_3PO_4 molecules which, together with the H_2O molecule, are linked into

a three-dimensional H-bonded network: each of the nine O atoms participates in at least 1 relatively strong $O–H\cdots O$ bond (255–272 pm) and the interatomic distances $P=O$ (149 pm) and $P–OH$ (155 pm) are both slightly shorter than the corresponding distances in H_3PO_4. Hydrogen bonding persists in the molten compound, and the proton-switch conductivity is even higher than in the anhydrous acid (See Table on p. 518).

In dilute aqueous solutions H_3PO_4 behaves as a strong acid but only one of the hydrogens is readily ionizable, the second and third ionization constants decreasing successively by factors of $\sim 10^5$ (see p. 50). Thus, at 25°:

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-;$$
$$K_1 = 7.11 \times 10^{-3}; \quad pK_1 = 2.15$$
$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-};$$
$$K_2 = 6.31 \times 10^{-8}; \quad pK_2 = 7.20$$
$$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-};$$
$$K_3 = 4.22 \times 10^{-13}; \quad pK_3 = 12.37$$

Accordingly, the acid gives three series of salts, e.g. NaH_2PO_4, Na_2HPO_4, and Na_3PO_4 (p. 523). A typical titration curve in this system is shown in Fig. 12.18: there are three steps with two inflexions at pH 4.5 and 9.5. The first inflexion, corresponding to the formation of NaH_2PO_4, can be detected by an indicator such as methyl

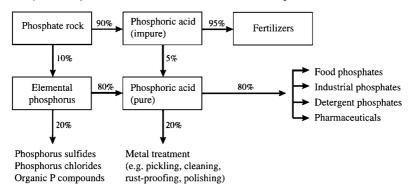[131] A. D. MIGHELL, J. P. SMITH, and W. E. BROWN, *Acta Cryst.* **B25**, 776 81 (1969).

Industrial production and uses of H_3PO_4[3-5,8,9,11,132]

Phosphoric acid[132] is manufactured on a vast scale and is produced in a wide variety of concentrations and purities. It is therefore convenient to express production figures in terms of the amount of contained P_4O_{10} (the figures based on the equivalent amount of contained anhydrous H_3PO_4 can be obtained by multiplying by the factor 1.380, though these may be misleading if they are taken to imply that it is the anhydrous acid that is being produced). World production capacity in 1986 exceeded 43 million tonnes of contained P_4O_{10} and was distributed as follows:

Production capacity of phosphoric acid (million tonnes/year of contained P_4O_{10})

Region	North America	USSR & East.Eur.	Africa	Western Europe	Asia and Australasia	Central/S. America	Middle East
"P_4O_{10}"/Mtpa	13.1	10.6	6.1	5.0	3.9	2.4	1.5

Production is still increasing steadily in many countries "Thermal" acid (made by oxidation of phosphorus in the presence of water vapour) is about 3 times as expensive as "wet" acid (made by treating rock phosphate with sulfuric acid). The present approximate pattern of production and uses is shown in the following scheme:
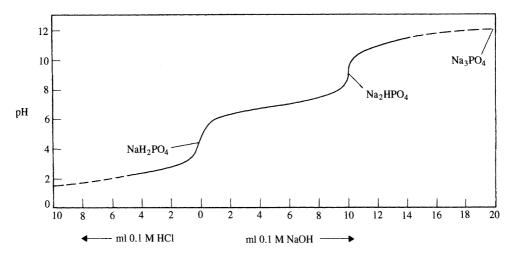

Many of these uses have already been discussed, or will be in later sections (pp. 524, 527).

Applications of phosphoric acid in metal treatment date from 1869 when a British patent was granted for the prevention of rusting of corset stays by damp air or perspiration. Improvements followed the incorporation of certain metal ions in the phosphatizing solution (notably Mn, Fe and Zn), and today corrosion resistance is imparted in this way to innumerable metal objects such as nuts, bolts, screws, tools, car-engine parts, gears, etc. In addition, car-bodies, refrigerators, washing machines and other electrical applicances with painted or enamelled surfaces all use phosphatized undercoatings to prevent the paint from blistering or peeling. The simple immersion process may take up to 2 h at 90°C but can be accelerated 25-fold by adding small amounts of oxidizing agent such as $NaNO_3$ and $Cu(NO_3)_2$. A zinc phosphatized coating is usually about $0.6\mu m$ thick (i.e. $2.2\,g\,m^{-2}$). Another important process is "bright dip" or chemical polishing of Al metal which has replaced chrome plating for car trims and other uses: the metal is immersed at 91–99°C in a solution containing 95 parts by weight of 85% H_3PO_4, 4 parts of 68% HNO_3, and 0.01% $Cu(NO_3)_2$, followed by electrolytic anodization to give the mirror-like surface a protective coating of transparent Al_2O_3.

Polyphosphoric acid supported on diatomaceous earth (p. 342) is a petrochemicals catalyst for the polymerization, alkylation, dehydrogenation, and low-temperature isomerization of hydrocarbons. Phosphoric acid is also used in the production of activated carbon (p. 274). In addition to its massive use in the fertilizer industry (p. 524) free phosphoric acid can be used as a stabilizer for clay soils: small additions of H_3PO_4 under moist conditions gradually leach out Al and Fe from the clay and these form polymeric phosphates which bind the clay particles together. An allied, though more refined use is in the setting of dental cements.

By far the greatest consumption of pure aqueous phosphoric acid is in the preparation of various salts for use in the food, detergent and tooth-paste industries (p. 524). When highly diluted the free acid is non-toxic and devoid of odour, and is extensively used to impart the sour or tart taste to many soft drinks ("carbonated beverages") such as the various colas (~0.05% H_3PO_4, pH 2.3), root beers (~0.01% H_3PO_4, pH 5.0), and sarsaparilla (~0.01% H_3PO_4, pH ~4.5).

[132]P. BECKER, *Phosphates and Phosphoric Acid*, Marcel Dekker, New York, 1988, 760 pp.

Oxoacids of phosphorus and their salts

Figure 12.18 Neutralization curve for aqueous orthophosphoric acid. For technical reasons the curve shown refers to $10\,cm^3$ of $0.1\,M$ NaH_2PO_4 titrated (to the left) with $0.1\,M$ aqueous HCl and (to the right) with $0.1\,M$ NaOH solutions. Extrapolations to points corresponding to $0.1\,M$ H_3PO_4 (pH 1.5) and $0.1\,M$ Na_3PO_4 (pH 12.0) are also shown.

orange (pK_i 3.5) and the second, corresponding to Na_2HPO_4, is indicated by the phenolphthalein end point (pK_i 9.5). The third equivalence point cannot be detected directly by means of a coloured indicator. Between the two inflexions the pH changes relatively slowly with addition of NaOH and this is an example of buffer action.[†] Indeed, one of the standard buffer solutions used in analytical chemistry comprises an equimolar mixture of Na_2HPO_4 and KH_2PO_4. Another important buffer, which has been designed to have a pH close to that of blood, consists of $0.030\,43\,M$ Na_2HPO_4 and $0.008\,695\,M$ KH_2PO_4, i.e. a mole ratio of 3.5:1 (pH 7.413 at 25°).

Concentrated H_3PO_4 is one of the major acids of the chemical industry and is manufactured on the multimillion-tonne scale for the production of phosphate fertilizers and for many other purposes (see Panel). Two main processes (the so-called "thermal" and "wet" processes) are used depending on the purity required. The "thermal" (or "furnace") process yields concentrated acid essentially free from impurities and is used in applications involving products destined for human consumption (see also p. 524); in this process a spray of molten phosphorus is burned in a mixture of air and steam in a stainless steel combustion chamber:

$$P_4 + 5O_2 \longrightarrow P_4O_{10} \xrightarrow{6H_2O} 4H_3PO_4$$

Acid of any concentration up to 84 wt% P_4O_{10} can be prepared by this method (72.42% P_4O_{10} corresponds to anhydrous H_3PO_4) but the usual commercial grades are 75–85% (expressed as anhydrous H_3PO_4). The hemihydrate (p. 518) corresponds to 91.58% H_3PO_4 (66.33% P_4O_{10}). The somewhat older "wet" (or "gypsum") process involves the treatment of rock phosphate (p. 476) with sulfuric acid, the idealized stoichiometry being:

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \longrightarrow 3H_3PO_4$$
$$+ 5CaSO_4.2H_2O + HF$$

[†] A buffer solution is one that resists changes in pH on dilution or on addition of acid or alkali. It consists of a solution of a weak acid (e.g. $H_2PO_4^-$) and its conjugate base (HPO_4^{2-}) and is most effective when the concentration of the two species are the same. For example at 25° an equimolar mixture of Na_2HPO_4 and KH_2PO_4 has pH 6.654 when each is $0.2\,M$ and pH 6.888 when each is $0.01\,M$. The central section of Fig. 12.18 shows the variation in pH of an equimolar buffer of Na_2HPO_4 and NaH_2PO_4 at a concentration of $0.033\,M$ (you should check this statement). Further discussion of buffer solutions is given in standard textbooks of volumetric analysis.
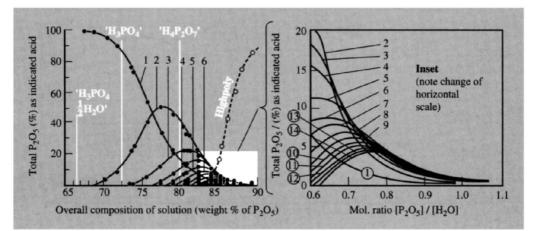
Figure 12.19   The composition of the strong phosphoric acids shown as the weight per cent of P_2O_5 present in the form of each acid plotted against the overall stoichiometric composition of the mixture. The overall stoichiometries corresponding to the three congruently melting species $H_3PO_4.\frac{1}{2}H_2O$, H_3PO_4 and $H_4P_2O_7$ are indicated. Compositions above 82 wt P_2O_5 are shown on an expanded scale in the inset using the mole ratio $[P_2O_5]/[H_2O]$ as the measure of stoichiometry. (For comparison, $H_4P_2O_7$ corresponds to a mole ratio of 0.500, $H_5P_3O_{10}$ to a ratio 0.600, $H_6P_4O_{13}$ to 0.667, etc.). In both diagrams the curves labelled 1,2,3, ... refer to ortho-, di-, tri- ... phosphoric acids, and "highpoly" refers to highly polymeric material hydrolysed from the column.

The gypsum is filtered off together with other insoluble matter such as silica, and the fluorine is removed as insoluble Na_2SiF_6. The dilute phosphoric acid so obtained (containing 35–70% H_3PO_4 depending on the plant used) is then concentrated by evaporation. It is usually dark green or brown in colour and contains many metal impurities (e.g. Na, Mg, Ca, Al, Fe, etc.) as well as residual sulfate and fluoride, but is suitable for the manufacture of phosphatic fertilizers, metallurgical applications, etc. (see Panel on p. 520).

Diphosphoric acid $H_4P_2O_7$ becomes an increasingly prevalent species as the system P_4O_{10}/H_2O becomes increasingly concentrated: indeed, the phase diagram shows that, in addition to the hemihydrate (mp 29.30°) and orthophosphoric acid (mp 42.35°) the only other congruently melting phase in the system is $H_4P_2O_7$. The compound is dimorphic with a metastable modification mp 54.3° and a stable form mp 71.5°, but in the molten state it comprises an isocompositional mixture of various polyphosphoric acids and their autoprotolysis

products. Equilibrium is reached only sluggishly and the actual constitution of the melt depends sensitively both on the precise stoichiometry and the temperature (Fig. 12.19)[133] For the nominal stoichiometry corresponding to $H_4P_2O_7$ typical concentrations of the species $H_{n+2}P_nO_{3n+1}$ from $n = 1$ (i.e. H_3PO_4) to $n = 8$ are as follows:

n	1	2	3	4	5	6	7	8
mole%	35.0	42.6	14.6	5.0	1.8	0.7	0.3	0.1

Thus, although $H_4P_2O_7$ is marginally the most abundant species present, there are substantial amounts of H_3PO_4, $H_5P_3O_{10}$, $H_6P_4O_{13}$ and higher polyphosphoric acids. Note that the table indicates mole% of each molecular species present whereas the graphs in Fig. 12.19 plot weight percentage of P_2O_5 present as each acid shown.

In dilute aqueous solution $H_4P_2O_7$ is a somewhat stronger acid than H_3PO_4: the 4 dissociation constants at 25° are: $K_1 \sim 10^{-1}$,

[133] R. F. JAMESON, *J. Chem. Soc.* 752-9 (1959).

Table 12.10 Factors affecting the rate of polyphosphate degradation

Factor	Effect on rate	Factor	Effect on rate
Temperature	10^5-10^6 faster from 0° to 100°	Complexing cations	Often much faster
pH	10^3-10^4 faster from base to acid	Concentration	Roughly proportional
Enzymes	Up to 10^5-10^6 faster	Ionic environment in solution	Several-fold change
Colloidal gels	Up to 10^4-10^5 faster		

$K_2 \sim 1.5 \times 10^{-2}$, K_3 2.7×10^{-7} and K_4 2.4×10^{-10}, and the corresponding negative logarithms are: $pK_1 \sim 1.0$, $pK_2 \sim 1.8$, pK_3 6.57 and pK_4 9.62. The P—O—P linkage is kinetically stable towards hydrolysis in dilute neutral solutions at room temperature and the reaction half-life can be of the order of years. Such hydrolytic breakdown of polyphosphate is of considerable importance in certain biological systems and has been much studied. Some factors which affect the rate of degradation of polyphosphates are shown in Table 12.10.

Orthophosphates [23,64]

Phosphoric acid forms several series of salts in which the acidic H atoms are successively replaced by various cations; there is considerable commercial application for many of these compounds.

Lithium orthophosphates are unimportant and differ from the other alkali metal phosphates in being insoluble. At least 10 crystalline hydrated or anhydrous sodium orthophosphates are known and these can be grouped into three series:

Na$_3$PO$_4$.nH$_2$O ($n = 0$, $\frac{1}{2}$, 6, 8, 12)
Na$_2$HPO$_4$.nH$_2$O ($n = 0$, 2, 7, 8, 12)
NaH$_2$PO$_4$.nH$_2$O ($n = 0$, 1, 2),
  NaH$_2$PO$_4$.H$_3$PO$_4$ [i.e. NaH$_5$(PO$_4$)$_2$]
  NaH$_2$PO$_4$.Na$_2$HPO$_4$ [i.e. Na$_3$H$_3$(PO$_4$)$_2$]
  and 2NaH$_2$PO$_4$.Na$_2$HPO$_4$.2H$_2$O

Likewise, there are at least 10 well-characterized potassium orthophosphates and several ammonium analogues. The presence of extensive H bonding in many of these compounds leads to considerable structural complexity and frequently confers important properties (see later). The mono- and di-sodium phosphates are prepared industrially by neutralization of aqueous H$_3$PO$_4$ with soda ash (anhydrous Na$_2$CO$_3$, p. 89). However, preparation of the trisodium salts requires the use of the more expensive NaOH to replace the third H atom. Careful control of concentration and temperature are needed to avoid the simultaneous formation of pyrophosphates (diphosphates). Some indication of the structural complexity can be gained from the compound Na$_3$PO$_4$.12H$_2$O which actually crystallizes with variable amounts of NaOH up to the limiting composition 4(Na$_3$PO$_4$.12H$_2$O).NaOH. The structure is built from octahedral [Na(H$_2$O)$_6$] units which join to form "hexagonal" rings of 6 octahedra which in turn form a continuous two-dimensional network of overall composition {Na(H$_2$O)$_4$}; between the sheets lie {PO$_4$} connected to them by H bonds.[134] Some industrial, domestic, and scientific applications of Na, K and NH$_4$ orthophosphates are given in the Panel.

Calcium orthophosphates are particularly important in fertilizer technology, in the chemistry of bones and teeth, and in innumerable industrial and domestic applications (see Panel). They are also the main source of phosphorus and phosphorus chemicals and occur in vast deposits as apatites and rock phosphate (p. 475). The main compounds occurring in the CaO–H$_2$O–P$_4$O$_{10}$ phase diagram are: Ca(H$_2$PO$_4$)$_2$, Ca(H$_2$PO$_4$)$_2$.H$_2$O, Ca(HPO$_4$).nH$_2$O ($n = 0$, $\frac{1}{2}$, 2), Ca$_3$(PO$_4$)$_2$, Ca$_2$PO$_4$(OH).2H$_2$O, Ca$_5$(PO$_4$)$_3$OH (i.e. apatite), Ca$_4$P$_2$O$_9$ [probably Ca$_3$(PO$_4$)$_2$.CaO] and Ca$_8$H$_2$(PO$_4$)$_6$.5H$_2$O.

In all of these alkali-metal and alkaline earth-metal orthophosphates there are discrete, approximately regular tetrahedral PO$_4$ units in

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[134] E. TILLMANNS and W. H. BAUR, *Inorg. Chem.* **9**, 1957–8 (1970).

Uses of Orthophosphates[9]

Phosphates are used in an astonishing variety of domestic and industrial applications but their ubiquitous presence and their substantial impact on everyday life is frequently overlooked. It will be convenient first to indicate the specific uses of individual compounds and the properties on which they are based, then to conclude with a brief summary of many different types of application and their interrelation. The most widely used compounds are the various phosphate salts of Na, K, NH_4 and Ca. The uses of di-, tri- and poly-phosphates are mentioned on pp. 527–29.

Na_3PO_4 is strongly alkaline in aqueous solution and is thus a valuable constituent of scouring powders, paint strippers and grease saponifiers. Its complex with NaOCl [$(Na_3PO_4.11H_2O)_4.NaOCl$], is also strongly alkaline (a 1% solution has pH 11.8) and, in addition, it releases active chlorine when wetted; this combination of scouring, bleaching and bacteriocidal action makes the adduct valuable in formulations of automatic dishwashing powders.

Na_2HPO_4 is widely used as a buffer component (p. 521). The use of the dihydrate (~2% concentration) as an emulsifier in the manufacture of pasteurized processed cheese was patented by J. L. Kraft in 1916 and is still used, together with insoluble sodium metaphosphate or the mixed phosphate $Na_{15}Al_3(PO_4)_8$, to process cheese on the multikilotonne scale daily. Despite much study, the reason why phosphate salts act as emulsifiers is still not well understood in detail. Na_2HPO_4 is also added (~0.1%) to evaporated milk to maintain the correct Ca/PO_4 balance and to prevent gelation of the milk powder to a mush. Its addition at the 5% level to brine (15–20% NaCl solution) for the pickling of ham makes the product more tender and juicy by preventing the exudation of juices during subsequent cooking. Another major use in the food industry is as a starch modifier: small additions enhance the ability to form stable cold-water gels (e.g. instant pudding mixes), and the addition of 1% to farinaceous products raises the pH to slightly above 7 and provides "quick-cooking" breakfast cereals.

NaH_2PO_4 is a solid water-soluble acid, and this property finds use (with $NaHCO_3$) in effervescent laxative tablets and in the pH adjustment of boiler waters. It is also used as a mild phosphatizing agent for steel surfaces and as a constituent in the undercoat for metal paints.
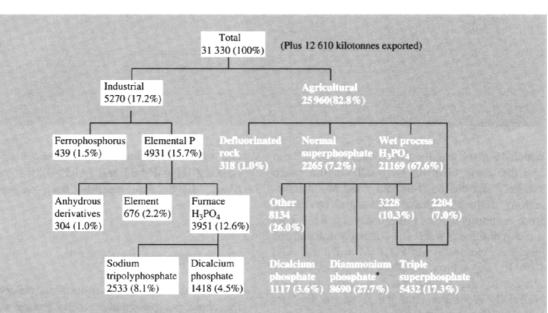
K_3PO_4 (like Na_3PO_4) is strongly alkaline in aqueous solution and is used to absorb H_2S from gas streams; the solution can be regenerated simply by heating. K_3PO_4 is also used as a regulating electrolyte to control the stability of synthetic latex during the polymerization of styrenebutadiene rubbers. The buffering action of K_2HPO_4 has already been mentioned (p. 521) and this is the reason for its addition as a corrosion inhibitor to car-radiator coolants which otherwise tend to become acidic due to slow oxidation of the glycol antifreeze. KH_2PO_4 is a piezoelectric (p. 57) and finds use in submarine sonar systems. For many applications, however, the cheaper sodium salts are preferred unless there is a specific advantage for the potassium salt; one example is the specialist balanced commercial fertilizer formulation [$KH_2PO_4.(NH_4)_2HPO_4$] which contains 10.5%, N, 53% P_2O_5 and 17.2% K_2O (i.e. N–P–K 10–53–17).

$(NH_4)_2HPO_4$ and $(NH_4)H_2PO_4$ can be used interchangeably as specialist fertilizers and nutrients in fermentation broths; though expensive, their high concentration of active ingredients ameliorate this, particularly in localities where transportation costs are high. Indeed, $(NH_4)_2HPO_4$ in granulated or liquid form consumes more phosphate rock than any other single end-product (over 8 million tonnes pa in the USA alone in 1974). Ammonium phosphates are also much used as flame retardants for cellulosic materials, about 3–5% gain in dry weight being the optimum treatment. Their action probably depends on their ready dissociation into NH_3 and H_3PO_4 on heating; the H_3PO_4 then catalyses the decomposition of cellulose to a slow-burning char (carbon) and this, together with the suppression of flammable volatiles, smothers the flame. As the ammonium phosphates are soluble, they are used mainly for curtains, theatre scenery and disposable paper dresses and costumes. The related compound urea phosphate ($NH_2CONH_2.H_3PO_4$) has also been used to flameproof cotton fabrics: the material is soaked in a concentrated aqueous solution, dried (15% weight gain) and cured at 160° to bond the retardant to the cellulose fibre. The advantage is that the retardant does not wash out, but the strength of the fabric is somewhat reduced by the process.

Calcium phosphates have a broad range of applications both in the food industry and as bulk fertilizers. The vast scale of the phosphate rock industry has already been indicated (p. 476) and this is further elaborated for the particular case of the USA in the Scheme on the page opposite (kilotonnes pa and %, 1974).

The crucial importance of Ca and PO_4 as nutrient supplements for the healthy growth of bones, teeth, muscle and nerve cells has long been recognized. The non-cellular bone structure of an average adult human consists of ~60% of some form of "tricalcium phosphate" [$Ca_5(PO_4)_3OH$]; teeth likewise comprise ~70% and average persons carry 3.5 kg of this material in their bodies. Phosphates in the body are replenished by a continuous cycle, and used P is carried by the blood to the kidneys and then excreted in urine, mainly as $Na(NH_4)HPO_4$. An average adult eliminates 3–4 g of PO_4 equivalent daily (cf. the discovery of P in urine by Brandt, p. 473).

Calcium phosphates are used in baking acids, toothpastes, mineral supplements and stock feeds. $Ca(H_2PO_4)_2$ was introduced as a leavening acid in the late nineteenth century (to replace "cream of tartar" $KHC_3H_4O_6$) but the monohydrate (introduced in the 1930s) finds more use today. "Straight baking powder", a mixture of $Ca(H_2PO_4)_2.H_2O$ and $NaHCO_3$ with some 40% starch coating, tends to produce CO_2 too quickly during dough mixing and so "combination baking

Panel continues

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                              Total
                          31 330 (100%)      (Plus 12 610 kilotonnes exported)


              Industrial                        Agricultural
              5270 (17.2%)                      25 960 (82.8%)


  Ferrophosphorus   Elemental P      Defluorinated   Normal          Wet process
  439 (1.5%)        4931 (15.7%)     rock            superphosphate  H₃PO₄
                                     318 (1.0%)      2265 (7.2%)     21169 (67.6%)


  Anhydrous     Element     Furnace       Other                  3228        2204
  derivatives   676 (2.2%)  H₃PO₄         8134                   (10.3%)     (7.0%)
  304 (1.0%)                3951 (12.6%)  (26.0%)


     Sodium          Dicalcium     Dicalcium     Diammonium    Triple
     tripolyphosphate phosphate    phosphate     phosphate*    superphosphate
     2533 (8.1%)     1418 (4.5%)   1117 (3.6%)   8690 (27.7%)  5432 (17.3%)
```

* Note that ammoniation of H_3PO_4 to give granulated or liquid ammonium phosphates consumes
more phosphate rock in the USA than any other single end product.

powder", which also incorporates a slow-acting acid such as $NaAl(SO_4)_2$, is preferred. Nearly 90% of all US household baking powders now use such combinations, e.g.:

$$Ca(H_2PO_4)_2.H_2O + 2NaHCO_3 \longrightarrow 2CO_2 + 3H_2O + \text{'}Na_2Ca(HPO_4)_2\text{'}$$

$$NaAl(SO_4)_2 + 3NaHCO_3 \xrightarrow{H_2O} 3CO_2 + Al(OH)_3 + 2Na_2SO_4$$

A typical powder contains 28% $NaHCO_3$, 10.7% $Ca(H_2PO_4)_2.H_2O$, 21.4% $NaAl(SO_4)_2$ and 39.9% starch and the scale of manufacture approaches 10^5 tonnes pa.

In toothpastes, $CaHPO_4.2H_2O$ was first used to replace chalk as a mild abrasive and polishing agent in the early 1930s. It is still widely used provided the toothpaste does not also contain fluoride, since this would precipitate as CaF_2 and effectively eliminate the desired anion. Some 25 000 tonnes of $CaHPO_4.H_2O$ are used in this way annually in the USA and the compound typically comprises 50% by weight of the paste. The first important fluoride toothpaste contained 39% of the diphosphate $Ca_2P_2O_7$ which is the most insoluble and inert of all calcium phosphates. It is made by careful dehydration of $CaHPO_4.2H_2O$ at 150° and then above 400°. It was first used in Procter and Gamble's "Crest" which also contained 0.4% SnF_2 and 1% $Sn_2P_2O_7$.

Synthetic $Ca_5(PO_4)_3OH$ is added to table salt (1–2%) to impart free-flowing properties and it is likewise added to granulated sugar, baking powders and even fertilizers. It is prepared by adding H_3PO_4 to a slurry of hydrated lime — this is the reverse order of addition to that used for making $Ca(H_2PO_4)_2$ and $CaHPO_4$ since the aim is to deprotonate all three OH groups. The compound is extremely insoluble and precipitates as very fine particles ($\sim$0.5–3 μm diameter).

The idea of converting insoluble "tricalcium phosphate" or phosphate rock into soluble "monocalcium phosphate" $Ca(H_2PO_2)_2$ dates back to the 1830s when J. von Liebig observed that acidulated bones made good fertilizer. The limited supply of bones (including those from old battlefields!) was soon replaced by Suffolk coprolites and apatites, though the vast North African deposits were still unknown. The phosphate fertilizer industry originated in England (Lawes, 1843); it grew rapidly as shown by the dramatic increase in world production of phosphate rock, which leapt from 500 tonnes in 1847 to 500 kilotonnes in 1880, 3.1 million tonnes in 1900, and now exceeds 150 Mt (p. 476). This unprecedented demand for phosphatic fertilizers is, of course, closely related to the demand for food from an exploding world population of humans which reached 1 billion (10^9) in 1830, 2 billion in 1930, 3 billion in 1960, 4 billion in 1974 and will be over 8 billion by the end of the century.

"Superphosphate" is now made by the (highly exothermic) addition of H_2SO_4 to fine-ground phosphate rock:

$$2Ca_5(PO_4)_3F + 7H_2SO_4 + H_2O \longrightarrow 7CaSO_4 + 3Ca(H_2PO_4)_2.H_2O + 2HF$$

Panel continues

The CaSO$_4$ or its hydrate (gypsum) acts only as an unwanted diluent. Its presence can be avoided by using H$_3$PO$_4$ instead of H$_2$SO$_4$ for the acidulation, thus giving rise to "triple superphosphate"

$$Ca_5(PO_4)_3F + 7H_3PO_4 + H_2O \longrightarrow 5Ca(H_2PO_4)_2.H_2O + HF$$

Commercial triple superphosphate contains almost 3 times the amount of available (soluble) P$_2$O$_5$ as ordinary superphosphate, hence its name (45–50 wt% vs. 18–20 wt%).

which P–O is usually in the range 153 ± 3 pm and the angle O–P–O is usually in the range $109 \pm 5°$. Extensive H-bonding and M–O interactions frequently induce substantial deviations from a purely ionic formulation (p. 81). This trend continues with the orthophosphates of tervalent elements M^{III}PO$_4$ (M = B, Al, Ga, Cr, Mn, Fe) which all adopt structures closely related to the polymorphs of silica (p. 342). NaBePO$_4$ is similar, and YPO$_4$ adopts the zircon (ZrSiO$_4$) structure. The most elaborate analogy so far revealed is for AlPO$_4$ which can adopt each of the 6 main polymorphs of silica as indicated in the scheme below. The analogy covers not only the structural relations between the phases but also the sequence of transformation temperatures (°C) and the fact that the α–β-transitions occur readily whilst the others are sluggish (p. 343). Similarly, the orthophosphates of B, Ga and Mn are known in the β-quartz and the α- and β-cristobalite forms whereas FePO$_4$ adopts either the α- or β-quartz structure. Numerous hydrated forms are also known. The Al–PO$_4$–H$_2$O system is used industrially as the basis for many adhesives, binders and cements.[135] Novel chain
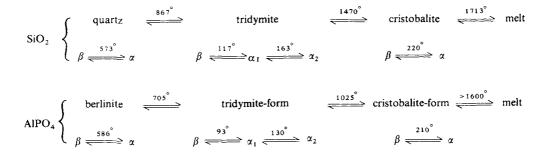
and sheet aluminium phosphate anions of composition [H$_2$AlP$_2$O$_8$] and [Al$_5$P$_4$O$_{16}$]$^{3-}$, respectively, have also recently been structurally characterized.[136]

Chain polyphosphates [(23,64)]

A rather different structure-motif is observed in the chain polyphosphates: these feature corner-shared {PO$_4$} tetrahedra as in the polyphosphoric acids (p. 522). The general formula for such anions is [P$_n$O$_{3n+1}$]$^{(n+2)-}$, of which the diphosphates, P$_2$O$_7$$^{4-}$, and tripolyphosphates, P$_3$O$_{10}$$^{5-}$, constitute the first two members. Chain polyphosphates have been isolated with n up to 10 and with n "infinite", but those of intermediate chain length ($10 < n < 50$) can only be obtained as glassy or amorphous mixtures. As the chain length increases, the ratio $(3n + 1)/n$ approaches 3.00 and the formula approaches that of the polymetaphosphates [PO$_3$$^{-}$]$_\infty$.

Diphosphates (pyrophosphates) are usually prepared by thermal condensation of dihydrogen

[135] J. H. Morris, P. G. Perkins, A. E. A. Rose and W. E. Smith, *Chem. Soc. Revs.* **6**, 173–94 (1977).

[136] J .M. Thomas *et al., J. Chem. Soc., Chem. Commun.,* 1170–2 (1992), 929–31 and 1266–8 (1992). See also R. Kniep, *Angew. Chem. Int. Edn. Engl.* **25**, 525–34 (1986).

SiO$_2$
quartz $\overset{867°}{\rightleftharpoons}$ tridymite $\overset{1470°}{\rightleftharpoons}$ cristobalite $\overset{1713°}{\rightleftharpoons}$ melt
$\beta \overset{573°}{\rightleftharpoons} \alpha$ $\beta \overset{117°}{\rightleftharpoons} \alpha_1 \overset{163°}{\rightleftharpoons} \alpha_2$ $\beta \overset{220°}{\rightleftharpoons} \alpha$

AlPO$_4$
berlinite $\overset{705°}{\rightleftharpoons}$ tridymite-form $\overset{1025°}{\rightleftharpoons}$ cristobalite-form $\overset{>1600°}{\rightleftharpoons}$ melt
$\beta \overset{586°}{\rightleftharpoons} \alpha$ $\beta \overset{93°}{\rightleftharpoons} \alpha_1 \overset{130°}{\rightleftharpoons} \alpha_2$ $\beta \overset{210°}{\rightleftharpoons} \alpha$

phosphates or hydrogen phosphates:

$$2MH_2PO_4 \xrightarrow{\Delta} M_2H_2P_2O_7 + H_2O$$

$$2M_2HPO_4 \xrightarrow{\Delta} M_4P_2O_7 + H_2O$$

They can also be prepared in specialized cases by (a) metathesis, (b) the action of H_3PO_4 on an oxide, (c) thermolysis of a metaphosphate, (d) thermolysis of an orthophosphate, or (e) reductive thermolysis, e.g.:

(a) $Na_4P_2O_7 + 4AgNO_3$

$$\longrightarrow Ag_4P_2O_7\downarrow + 4NaNO_3$$

(b) $2H_3PO_4 + PbO_2 \longrightarrow PbP_2O_7\downarrow + 3H_2O$

(c) $4Cr(PO_3)_3 \xrightarrow{\Delta} Cr_4(P_2O_7)_3 + 3P_2O_5$

(d) $2Hg_3(PO_4)_2 \xrightarrow{\Delta} 2Hg_2P_2O_7 + 2Hg + O_2$

(e) $2FePO_4 + H_2 \longrightarrow Fe_2P_2O_7 + H_2O$

Many diphosphates of formula $M^{IV}P_2O_7$, M_2^{II}-P_2O_7 and hydrated $M_4^{I}P_2O_7$ are known and there has been considerable interest in the relative orientation of the two linked {PO_4} groups and in the P–O–P angle between them.[137] For small cations the 2 {PO_4} are approximately staggered whereas for larger cations they tend to be nearly eclipsed. The P–O–P angle is large and variable, ranging from 130° in $Na_4P_2O_7.10H_2O$ to 156° in α-$Mg_2P_2O_7$. The apparent colinearity in the higher-temperature (β) form of many diphosphates, which was previously ascribed to a P–O–P angle of 180°, is now generally attributed to positional disorder. Bridging P–O distances are invariably longer than terminal P–O distances, typical values (for $Na_4P_2O_7.10H_2O$) being P–O_μ 161 pm, P–O_t 152 pm. Note that bridging can also be via a peroxo group as in ammonium peroxodiphosphate[138] which features the zig-zag anion $[O_3P–O–O–PO_3]^{4-}$ with P–O_μ 165.8 pm, P–O_t 150.8 pm and O–O

150.1 pm (cf. 145.3 pm in H_2O_2 and 148–150 pm in $S_2O_5^{2-}$).

As diphosphoric acid is tetrabasic, four series of salts are possible though not all are always known, even for simple cations. The most studied are those of Na, K, NH_4 and Ca, e.g.:

$Na_4P_2O_7.10H_2O$(mp 79.5°), $Na_4P_2O_7$(mp 985°)

$$Na_3HP_2O_7.9H_2O \xrightarrow{30-35°} Na_3HP_2O_7.H_2O$$

$$\xrightarrow{150°} Na_3HP_2O_7$$

$$Na_2H_2P_2O_7.6H_2O \xrightarrow{\sim27°} Na_2H_2P_2O_7$$

$NaH_3P_2O_7$(mp 185°)

Before the advent of synthetic detergents, $Na_4P_2O_7$ was much used as a dispersant for lime soap scum which formed in hard water, but it has since been replaced by the tripolyphosphate (see below). However, the ability of diphosphate ions to form a gel with soluble calcium salts has made $Na_4P_2O_7$ a useful ingredient for starch-type instant pudding which requires no cooking. The main application of $Na_2H_2P_2O_7$ is as a leavening acid in baking: it does not react with $NaHCO_3$ until heated, and so large batches of dough or batter can be made up and stored. $Ca_2P_2O_7$, because of its insolubility, inertness, and abrasive properties, is used as a toothpaste additive compatible with Sn^{II} and fluoride ions (see Panel on p. 525).

Of the tripolyphosphates only the sodium salt need be mentioned. It was introduced in the mid-1940s as a "builder" for synthetic detergents, and its production for this purpose is now measured in megatonnes per annum (see Panel on the next page). On the industrial scale $Na_5P_3O_{10}$ is usually made by heating an intimate mixture of powdered Na_2HPO_4 and NaH_2PO_4 of the required stoichiometry under carefully controlled conditions:

$$2Na_2HPO_4 + NaH_2PO_4 \longrightarrow Na_5P_3O_{10} + 2H_2O$$

The low-temperature form (I) converts to the high-temperature form (II) above 417°C and both forms react with water to give the crystalline hexahydrate. All three materials contain the

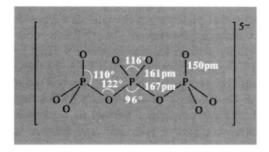[137] G. M. CLARK and R. MORLEY, *Chem. Soc. Revs.* **5**, 269–95 (1976).
[138] W. P. GRIFFITH, R. D. POWELL and A. C. SKAPSKI, *Polyhedron* **7**, 1305–10 (1988).

Uses of Sodium Tripolyphosphate

Many synthetic detergents contain 25–45% $Na_5P_3O_{10}$ though the amount is lower in the USA than in Europe because of the problems of eutrophication in some areas (p. 478). It acts mainly as a water softener, by chelating and sequestering the Mg^{2+} and Ca^{2+} in hard water. Indeed, the formation constants of its complexes with these ions are nearly one million-fold greater than with Na^+: ($NaP_3O_{10}^{4-}$ pK ~2.8; $MgP_3O_{10}^{3-}$ pK ~8.6; $CaP_3O_{10}^{3-}$ pK ~8.1). In addition, $Na_5P_3O_{10}$ increases the efficiency of the surfactant by lowering the critical micelle concentration, and by its ability to suspend and peptize dirt particles by building up a large negative charge on the particles by adsorption; it also furnishes a suitable alkalinity for cleansing action without irritating eyes or skin and it provides effective buffering action at these pHs. The dramatic growth of synthetic detergent powders during the 1950s was accompanied by an equally dramatic drop in the use of soap powders.[11]

$Na_5P_3O_{10}$ is also used as a dispersing agent in clay suspensions used in oil-well drilling. Again, addition of <1% $Na_5P_3O_{10}$ to the slurries used in manufacturing cement and bricks enables much less water to be used to attain workability, and thus less to be removed during the setting or calcining processes.

tripolyphosphate ion $P_3O_{10}^{5-}$ with a *trans*-configuration of adjacent tetrahedra and a twofold symmetry axis; forms (I) and (II) differ mainly in the coordination of the sodium ions and the slight differences in the dimensions of the ion in the three crystals are probably within experimental error. Typical values are:

The complicated solubility relations, rates of hydrolysis, self-disproportionation and interconversion with other phosphates depends sensitively on pH, concentration, temperature and the presence of impurities.[139] Though of great interest academically and of paramount importance industrially these aspects will not be further considered here.[11,23,64,140] Triphosphates such as adenosine triphosphate (ATP) are also of vital importance in living organisms (see text books on biochemistry, and also ref. 141).

The stoichiometric formula of a chain-polyphosphate can sometimes be an unreliable guide to its structure. for example, the crystalline compound "$CaNb_2P_6O_{21}$" has been shown by X-ray crystal structure analysis to contain equal numbers of oxide(2−), diphosphate(4−) and tetraphosphate(6−) anions, i.e. $CaNb_2O[P_2O_7][P_4O_{13}]$.[142] By contrast, $CsM_2P_5O_{16}$ (M = V, Fe) does contain the anticipated homologous *catena*-pentaphosphate $[P_nO_{3n+1}]^{(n+2)-}$ anion (p. 512) with $n = 5$.[143]

Long-chain polyphosphates, $M_{n+2}^IP_nO_{3n+1}$, approach the limiting composition M^IPO_3 as $n \to \infty$ and are sometimes called linear metaphosphates to distinguish them from the cyclic metaphosphates of the same composition (p. 529). Their history extends back over 150 y to the time when Thomas Graham described the formation of a glassy sodium polyphosphate mixture now known as Graham's salt. Various heat treatments converted this to crystalline compounds known as Kurrol's salt, Maddrell's salt, etc., and it is now appreciated, as a result of X-ray crystallographic studies, that these and many related substances all feature unbranched chains of corner-shared {PO₄} units which differ only in the mutual orientations and

[139] G. P. HAIGHT, T. W. HAMBLEY, P. HENDRY, G. A. LAWRANCE and A. M. SARGESON, *J. Chem. Soc., Chem. Commun.*, 488–91 (1985), and references cited therein

[140] E. J. GRIFFITH, *Pure Appl. Chem.* **44**, 173–200 (1975).

[141] I. S. KULAEV, *The Biochemistry of Inorganic Polyphosphates*, Wiley, Chichester, 1980, 225 pp.

[142] M.-T. AVERBUCH-POUCHOT, *Z. anorg. allg. Chem* **545**, 118–24 (1987).

[143] B. KLINKERT and M. JANSEN, *Z. anorg. allg. Chem.* **567**, 87–94 (1988).
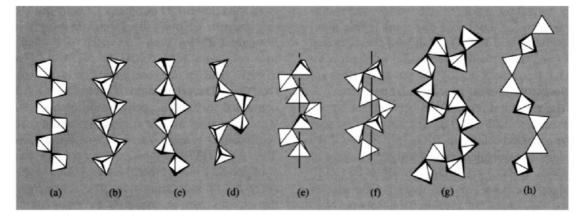
Figure 12.20   Types of polyphosphate chain configuration. The diagrams indicate the relative orientations of adjacent PO_4 tetrahedra, extended along the chain axes. (a) $(RbPO_3)_n$ and $(CsPO_3)_n$, (b) $(LiPO_3)_n$ low temp, and $(KPO_3)_n$, (c) $(NaPO_3)_n$ high-temperature Maddrell salt and $[Na_2H(PO_3)_3]_n$, (d) $[Ca(PO_3)_2]_n$ and $[Pb(PO_3)_2]_n$, (e) $(NaPO_3)_n$, Kurrol A and $(AgPO_3)_n$, (f) $(NaPO_3)_n$, Kurrol B, (g) $[CuNH_4(PO_3)_3]_n$ and isomorphous salts, (h) $[CuK_2(PO_3)_4]_n$ and isomorphous salts. Each crystalline form of Kurrol salt contains equal numbers of right-handed and left-handed spiralling chains.

repeat units of the constituent tetrahedra.[144] These, in turn, are dictated by the size and coordination requirements of the counter cations present (including H). Some examples are shown schematically in Fig. 12.20 and the geometric resemblance between these and many of the chain metasilicates (p. 350) should be noted. In most of these polyphosphates $P-O_\mu$ is 161 ± 5 pm, $P-O_t$ 150 ± 2 pm, $P-O_\mu-P$ $125-135°$ and O_t-P-O_t $115-120°$ (i.e. very similar to the dimensions and angles in the tripolyphosphate ion, p. 528).

The complex preparative interrelationships occurring in the sodium polyphosphate system are summarized in Fig. 12.21 (p. 531). Thus anhydrous NaH_2PO_4, when heated to 170° under conditions which allow the escape of water vapour, forms the diphosphate $Na_2H_2P_2O_7$, and further dehydration at 250° yields either Maddrell's salt (closed system) or the cyclic trimetaphosphate (water vapour pressure kept low). Maddrell's salt converts from the low-temperature to the high-temperature form above 300°, and above 400° reverts to the cyclic

trimetaphosphate. The high-temperature form can also be obtained (via Graham's and Kurrol's salts) by fusing the cyclic trimetaphosphate (mp 526°C) and then quenching it from 625° (or from 580° to give Kurrol's salt directly). All these linear polyphosphates of sodium revert to the cyclic trimetaphosphate on prolonged annealing at ~400°C.

Fuller treatments of the phase relations and structures of polyphosphates, and their uses as glasses, ceramics, refractories, cements, plasters and abrasives, are available.[144,145]

Cyclo-*polyphosphoric acids* and cyclo-*polyphosphates*[146]

These compounds were formerly called metaphosphoric acids and metaphosphates but the IUPAC *cyclo-* nomenclature is preferred as being structurally more informative. The only

[144] J. MALING and F. HANIC, *Topics in Phosphorus Chemistry* **10**, 341-502 (1980).

[145] A. E. R. WESTMAN, *Topics in Phosphorus Chemistry* **9**, 231-405, 1977. A comprehensive account with 963 references.

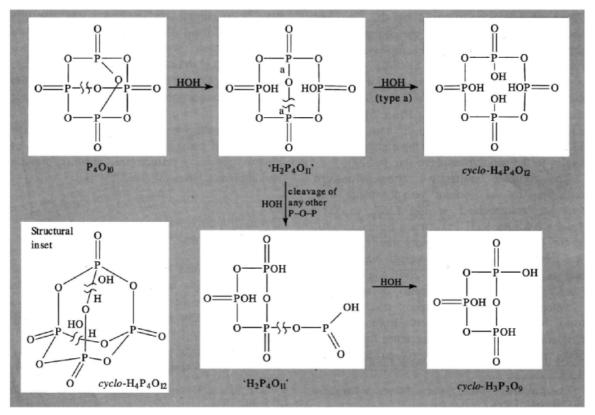[146] S. Y. KALLINEY, *Topics in Phosphorus Chemistry* **7**, 255-309, 1972.

two important acids in the series are *cyclo*-triphosphoric acid $H_3P_3O_9$ and *cyclo*-tetra-phosphoric acid $H_4P_4O_{12}$, but well-characterized salts are known with heterocyclic anions [*cyclo*-$(PO_3)_n]^n$ ($n = 3-8, 10$),[147] and larger rings are undoubtedly present in some mixtures.

The structural relationship between the *cyclo*-phosphates and P_4O_{10} (p. 504) is shown schematically below. In P_4O_{10} all 10 P-O(-P) bridges are equivalent and hydrolytic cleavage of any one leads to "$H_2P_4O_{11}$" in which P-O(-P) bridges are now of two types. Cleavage of "type a" leads to *cyclo*-tetraphosphoric acid or its salts (as shown in the upper line of the scheme), whereas cleavage of any of the other bridges leads to a *cyclo*-triphosphate ring with a pendant -OP(O)OH group which can subsequently be hydrolysed off to leave $(HPO_3)_3$

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[147] G. SCHÜLKE, M. T. AVERBUCH-POUCHOT and A. DURIF, *Z. anorg. allg. Chem.* **612**, 107-12 (1992).

or its salts (lower line of scheme). *Cyclo*-$(HPO_3)_4$ can, indeed, be made by careful hydrolysis of hexagonal P_4O_{10} with ice-water, and similar treatment with iced NaOH or $NaHCO_3$ gives a 75% yield of the corresponding salt *cyclo*-$(NaPO_3)_4$. The preparation of *cyclo*-$(NaPO_3)_3$ by controlled thermolytic dehydration of NaH_2PO_4 was mentioned in the preceding section and acidification yields *cyclo*-triphosphoric acid. The *cyclo*-$(PO_3)_3^{3-}$ anion adopts the chair configuration with dimensions as shown; *cyclo*-$(PO_3)_4^{4-}$ is also known in this configuration though this can be modified by changing the cation.

The crystal structure of the *cyclo*-hexaphosphate anion in $Na_6P_6O_{18}.6H_2O$ shows that all 6 P atoms are coplanar and that bond lengths are similar to those in the $P_3O_9^{3-}$ and $P_4O_{12}^{4-}$ anions. See ref. 147 for the structure of the hydrated *cyclo*-decaphosphate $K_{10}P_{10}O_{30}.4H_2O$. Higher *cyclo*-metaphosphates can be isolated by

P_4O_{10} '$H_2P_4O_{11}$'   *cyclo*-$H_4P_4O_{12}$

cleavage of any other P-O-P

Structural inset   *cyclo*-$H_4P_4O_{12}$ '$H_2P_4O_{11}$'   *cyclo*-$H_3P_3O_9$