PHOSPHORIC ACIDS AND PHOSPHATES

1. Introduction

Phosphorus (qv), in the form of phosphate, is an element essential to all life and the use of natural phosphatic fertilizers (qv) such as bones, fish, and guano predates recorded history. The birth of the modern phosphate industry occurred in the mid-nineteenth century through the manufacture of phosphatic fertilizer. Sulfuric acid was used for decomposing bones and mineral phosphates to render the phosphate value in a more concentrated and available form. As the production of fertilizers grew more economical and higher purity phosphoric derived from elemental phosphorus became available, so did the volume and diversity of industrial applications of phosphoric acid and the phosphates. A few of the historically notable nonfertilizer developments include the use of monocalcium phosphate [7758-23-8] (MCP) in baking powder in 1886 (see BAKERY PROCESS, YEAST-RAISED PRODUCTS) and the commercial production of elemental phosphorus in 1890.

Most commercial applications of phosphorus-containing materials are based on phosphoric acid and phosphate salts. A multitude of applications exist, including use in detergents (see DETERGENCY), animal feed supplements (see FEEDS AND FEED ADDITIVES, NONRUMINANT FEEDS), DENTIFRICS (qv), FERTILIZERS (qv), metal treating (see METALLIC COATINGS, SURVEY), water softening, leavening agents, and fire retardants (see FLAME RETARDANTS: AN OVERVIEW). On a weight basis, fertilizers remain the single largest application. The manufacture and uses of phosphoric acid and phosphate salts for most applications are usually dependent on the purity of the acid or salt. The chemistry and commercial technology of technical- and food-grade phosphoric acid and the inorganic phosphates is discussed herein. Wet-process phosphoric acid and fertilizer phosphates are discussed elsewhere (see FERTILIZERS).

Phosphoric acids and the phosphates may be defined as derivatives of phosphorus oxides where the phosphorus atom is in the +5 oxidation state. These are compounds formed in the $M_2O{-}P_2O_5$ system, where M represents one cation equivalent, eg, H^+, Na^+, 0.5 Ca^{2+}, etc. The molecular formula of the phosphorus(V) oxide [1314-56-3] is actually P_4O_{10}, but this oxide is commonly referred to in terms of its empirical formula, P_2O_5. Structurally, four phosphorus−oxygen (P−O) linkages are arranged in an approximate tetrahedral configuration about the phosphorus atom in the phosphate anion. Compounds containing discrete, monomeric $PO^{3-}{}_4$ ions are known as orthophosphates or simply as phosphates.

Orthophosphoric acid [7664-38-2], H_3PO_4, can be considered the building block from which other phosphoric acids and the phosphate salts are derived through the basic reactions of polymerization and/or neutralization. Polymerization occurs via dehydration, hence the polymers are known generally as condensed phosphates. Oxygen atoms shared between PO_4 tetrahedra lead to polymers built on a covalent backbone of P−O−P linkages. Phosphates containing even one P−O−P linkage are also included as condensed phosphates because these are considered to be molecularly dehydrated orthophosphate monomers. In a more specific consideration of the structure, linear P−O−P chains are termed polyphosphates, cyclic rings are known as metaphosphates, and branched polymeric materials and cage anions containing at least one triply linked phosphate monomeric unit are known as ultraphosphates. Structural studies of crystalline condensed phosphates have shown that each PO_4 group remains approximately tetrahedral. The O–P–O bond angles are 95–125°; P–O–P angles vary between 120–180°.

Traditionally, phosphates have been represented as stoichiometric combinations of oxides. It is common practice to speak of the phosphates in terms of oxide ratios; for example, phosphoric acid [7664-38-2], H_3PO_4, as $1.5\ H_2O{\cdot}0.5\ P_2O_5$; disodium phosphate [7558-79-4], Na_2HPO_4, as $Na_2O{\cdot}0.5H_2O{\cdot}0.5P_2O_5$; and sodium triphosphate [7601-54-9], $Na_5P_3O_{10}$, as $2.5\ Na_2O{\cdot}1.5P_2O_5$.

The oxide ratio, R, is defined as the mole ratio of M_2O to P_2O_5, where M represents one cation equivalent, metal or hydrogen, including the H_2O of composition, but not water of hydration. The oxide ratio determines the structural type for a pure phosphate compound. The structural designations, oxide ratios, and general formulas for the phosphate anions are shown in Table 1. If the oxide mole ratio is three, the substance is an orthophosphate, commonly known simply as phosphate. Linear polymers, known generally as polyphosphates, have the general formula, $M_{n+2}P_tP_nO_{3n+1}$. The R ranges from 1 to 2, depending on the chain length. An additional term, oligophosphates, is sometimes applied to polyphosphate chains of short or intermediate length. Common short-chain anions include the pyrophosphate, also called diphosphate, and tripolyphosphate (triphosphate). When the chain length, n, becomes large, the polyphosphate composition approaches that of the metaphosphate ring structures. Hence, it had been common practice in the phosphorus literature to designate polyphosphates having long chains as metaphosphates. These long-chain polyphosphates are sometimes also called pseudometaphosphates. The term metaphosphate should, however, be reserved for cyclic structures having an R of one and the exact composition, $(MPO_3)_n$, if a ratio of exact unity corresponds to the cyclic metaphosphates. When $0<R<1$, the substance contains branching phosphate groups and is called an ultraphosphate.

The ultraphosphates are situated between P_4O_{10} and the metaphosphates. These comparatively little-known, highly cross-linked polymers contain at least some of the phosphorus atoms as triply connected branching points. This structural feature is quite unstable toward hydrolysis. Ultraphosphates undergo rapid decomposition upon dissolution. In amorphous ultraphosphates, the cross-linking is presumably scattered randomly throughout the structural matrix; in contrast, crystalline ultraphosphates have a regular pattern.

Many of the terms describing phosphates are used loosely and interchangeably in the technical and trade literature. Herein the terminology most generally used in industry is employed, although cross reference to the most recent *Chemical Abstracts*-approved nomenclature is also given. However, the older naming system is favored. In addition, the phrase metaphosphate composition is used where long-chain structure is uncertain. The term metaphosphate is reserved for true ring systems, a convention that *Chemical Abstracts* follows.

2. Phosphoric Acids

2.1. Orthophosphoric Acid

Properties. Phosphoric acid is a tribasic acid, in which the first hydrogen ion is strongly ionizing, the second moderately weak, and the third very weak.

$$H_3PO_4 \overset{-H^+}{\rightleftharpoons} H_2PO^-{}_4 \overset{-H^+}{\rightleftharpoons} HPO_4^{2-} \overset{-H^+}{\rightleftharpoons} PO_4^{3-} \tag{1}$$

The titration curve of phosphoric acid in the presence of sodium hydroxide is shown in Figure 1. Three steps, corresponding to consecutive replacement of the three acidic hydrogens, and two inflection points, near $pH = 4.5$ and 9.0, are evident. Dissociation constants are $K_1 = 7.1 \times 10^{-3}$; $K_2 = 6.3 \times 10^{-8}$; and $K_3 = 4.4 \times 10^{-13}$. Both acidic and basic salts can be formed from phosphoric acid, and mixtures of mono- and dibasic salts of H_3PO_4 act as buffers near pH 7 (see HYDROGEN-ION ACTIVITY).

Phosphoric acid, aside from its acidic behavior, is relatively unreactive at room temperature. It is sometimes substituted for sulfuric acid because of its lack of oxidizing properties (see SULFURIC ACID AND SULFUR TRIOXIDE). The reduction of phosphoric acid by strong reducing agents, eg, H_2 or C, does not occur to any measurable degree below 350–400°C. At higher temperatures, the acid reacts with most metals and their oxides. Phosphoric acid is stronger than acetic, oxalic, silicic, and boric acids, but weaker than sulfuric, nitric, hydrochloric, and chromic acids.

A solid–liquid phase diagram of the phosphoric acid–water system is given in Figure 2 (1). The solid, crystalline phases in the phosphate region of the system are the anhydrous acid, H_3PO_4, and the hemihydrate [16271-20-8], $H_3PO_4 \cdot 0.5H_2O$. Pure, 100% phosphoric acid is a white, monoclinic crystalline solid that melts at 42.35°C; the hemihydrate has a melting point of 29.25°C. When anhydrous phosphoric acid is melted, reorganization occurs in the liquid phase according to the equilibrium

$$2\,H_3PO_4 \rightleftharpoons H_4P_2O_7 + H_2O \tag{2}$$

If the anhydrous acid is maintained in a molten state, the freezing point gradually falls to an equilibrium value of 34.6°C after several weeks; this corresponds to the presence of approximately 6 mol % pyrophosphoric acid [2466-09-3], $H_4P_2O_7$, also known as diphosphoric acid. Thus, sample history affects the melting point of phosphoric acid, which may explain the variation in values reported in the literature. Pure phosphoric acid supercools readily and typically can be stored without crystallization for long periods of time, at 10–20°C below the melting point. When cooled in liquid nitrogen or dry ice, phosphoric acid solidifies to a glass that crystallizes to H_3PO_4–III upon warming to −54°C. This, in turn, is converted reversibly at −6°C to H_3PO_4–I, which is stable at room temperature; H_3PO_4–II crystallizes from the melt between 8–15°C if careful temperature control is maintained.

Extensive hydrogen bonding takes place in phosphoric acid solutions. In concentrated (86% H_3PO_4) solutions, as well as in the crystal structures of the anhydrous acid and the hemihydrate, the tetrahedral H_3PO_4 groups are linked by hydrogen bonding. At lower (75% H_3PO_4) concentrations, the tetrahedra are hydrogen-bonded to the water lattice. Physical properties of phosphoric acid solutions of various concentrations are listed in Table 2; the vapor pressure of aqueous H_3PO_4 solutions at various temperatures is given in Table 3.

Manufacture. Phosphoric acid, H_3PO_4, is the second largest volume mineral acid produced; sulfuric acid is the first. The greatest consumption of phosphoric acid is in the manufacture of phosphate salts, as opposed to direct use as acid. Markets are differentiated according to the purity of the acid.

Phosphoric acid is produced commercially by either the wet process or the thermal (furnace) process. Thermal acid, manufactured from elemental phosphorus, is more expensive and considerably purer than wet-process acid. Thermal acid is produced in much smaller quantities than wet-process acid, which is produced directly from phosphatic ores, and is characterized by relatively high production volume, low cost, and low purity. Wet-process acid is used primarily in the production of fertilizers and animal feed supplements. Wet-process acid may be purified for the manufacture of technical- and food-grade phosphate salts, usually employing a solvent extraction process. Wet-acid purification has been practiced extensively outside the United States and Canada, but was introduced to the United States in an ongoing commercial scale by Purified Acid Partners (a partnership between Texasgulf Inc. and Albright & Wilson Americas Inc.) and Olin Corp. in 1990, and by Rhone-Poulenc Basic Chemicals Co. in 1991. A comparative analysis of typical wet-process acid, purified wet acid, and thermal acid is given in Table 4. Both thermal and purified wet-process phosphoric acid (WPA) are used almost exclusively in various technical and food applications where fertilizer-grade wet acid is not suitable.

A process for a high quality technical acid that can be converted to food and pharmaceutical grade with a savings in cost has been reported (2).

Thermal Process. In the manufacture of phosphoric acid from elemental phosphorus, white (yellow) phosphorus is burned in excess air, the resulting phosphorus pentoxide is hydrated, heats of combustion and hydration are removed, and the phosphoric acid mist collected. Within limits, the concentration of the product acid is controlled by the quantity of water added and the cooling capabilities. Various process schemes deal with the problems of high combustion-zone temperatures, the reactivity of hot phosphorus pentoxide, the corrosive nature of hot phosphoric acid, and the difficulty of collecting fine phosphoric acid mist. The principal process types (Fig. 3) include the wetted-wall, water-cooled, or air-cooled combustion chamber, depending on the method used to protect the combustion chamber wall.

In wetted-wall units, the walls of a tall circular, slightly tapered combustion chamber are protected by a high volume curtain of cooled acid flowing down inside the wall. Phosphorus is atomized by compressed air or steam into the top of the chamber and burned in additional combustion air supplied by a forced or induced draft fan. Wetted-wall plants use 25–50% excess combustion air to reduce the tail-gas volume, resulting in flame temperatures in excess of 2000°C. The combustion chamber may be refractory lined or made of stainless steel. Acid sprays at the bottom of the chamber or in a subsequent, separate spraying chamber complete the hydration of phosphorus pentoxide. The sprays also cool the gas stream to below 100°C, thereby minimizing corrosion to the mist-collecting equipment (typically type 316 stainless steel).

When all acid is to be converted into sodium phosphate salt, a variation of the wetted-wall acid plant may be used (3). In this case, a relatively noncorrosive, neutral sodium phosphate solution is circulated in lieu of phosphoric acid. By operating this system at the solution boiling point, heats of combustion, hydration, and neutralization are removed via evaporative cooling, resulting in a more energy-efficient process. Phosphorus pentoxide absorption is rapid and over 95% is collected by the circulating stream. Alkali and makeup water are added through a tail-gas scrubber as dilute caustic soda, soda ash, or sodium sesquicarbonate solution adjusted to maintain the system material balance. They must have efficient phosphorus atomization and good control of combustion air and phosphorus feed rates to prevent formation of lower oxides of phosphorus.

In a development pioneered by the Tennessee Valley Authority (TVA), the phosphorus combustion was separated from the wetted-wall hydrator–absorber vessel in order to allow more time for complete combustion and increase the area available for heat transfer (4). Both vessels are constructed of extra low carbon type 316 stainless steel and are cooled by an external water jacket. A solid layer of combustion products deposits on the inner surfaces of the combustion chamber and serves as a self-repairing protective coating. This layer provides resistance to heat transfer and consequently the stainless steel wall remains near the jacket water temperature. Although the composition of the deposit varies with the amount of water introduced with the phosphorus and combustion air, it is known to be a mixture of different solid-phase forms (O and O′) of phosphorus pentoxide embedded in a glassy matrix (see PHOSPHOURS COMPOUNDS). These plants are quiet and clean, have high capacity, and are capable of producing both orthophosphoric acid and polyphosphoric acid [8017-16-1] at any strength up to about 117% H_3PO_4 (85% P_2O_5).

Air-cooled acid plants are characterized by a large refractory-lined combustion chamber from which waste heat is removed by radiation and convection. The combustion chamber is constructed of graphite or of carbon steel lined with a single layer of high alumina refractory brick. Refractory units operate at cooler temperatures because of the poorer heat transfer properties of brick compared to graphite. Corrosion of the carbon steel is, surprisingly, not a serious problem as long as the combustion gas stream and refractory stay well-above the dew point of the azeotropic (92% P_2O_5) phosphoric acid. Air-cooled plants normally operate with about 1–200% excess combustion air to reduce the flame temperature (1000–1700°C) and carry waste heat to the hydrator–absorber, where it is removed by evaporation of water.

Hot combustion gases are quenched and saturated with water in a spray chamber called a hydrator. An absorber bed of carbon or graphite rings may be mounted above the hydrator in the same structure to obtain more complete absorption of P_4O_{10} and to assure that the gas stream is cooled to about 100°C. Weak acid from mist collection is sprayed on the absorber bed, and product acid at 75–85% H_3PO_4 leaves the hydrator through a heat exchanger.

Burning phosphorus produces a persistent white cloud of phosphorus pentoxide and phosphoric acid droplets of such high obscuring power that this cloud is used as a standard military screening smoke (see CHEMICAL WARFARE). The opacity and persistence of the smoke results from the whiteness and small size of the particles, most of which are <3 μm in diameter and subject to appreciable Brownian motion. These particles are difficult to collect but an essentially haze-free stack effluent may be obtained to meet air quality regulations, which, for practical purposes, requires an effluent containing <ca 25 milligrams of P_2O_5 per dry standard cubic meter of stack gas.

Because P_2O_5 absorbs more rapidly in strong acid than in water, it is initially hydrated and absorbed in hot gas stream by direct contact with relatively strong acid. This is often followed by successive stages of scrubbing with progressively more dilute acid and, finally, with incoming makeup water. Many of the submicrometer-size droplets are induced to grow large enough for collection by conventional scrubbing techniques. Although this technique collects over 99% of the P_2O_5, it is usually inadequate to meet plume opacity regulations.

Electrostatic precipitators in phosphoric acid service are expensive to maintain and have been largely replaced by newer devices. High energy scrubbers such as the Venturi were used widely at one time, but are generally ineffective for phosphoric acid mist droplets under ca 1 μm. Neither precipitators nor Venturi scrubbers, as single-stage collectors, can reduce the P_2O_5 content of the stack to an acceptable level. Fine-mesh glass fiber or metal-mesh panels can be effective as final-stage collectors when operated at high pressure drop, but usually require a secondary coarse mesh pad to collect reentrained larger particles from the back side of the primary panel. A high efficiency fiber-bed mist eliminator, developed by Monsanto (5), is effective in eliminating mist droplets of <0.3 μm in diameter. By careful choice of fiber diameter, packing density, and bed depth, the gas flow through the tortuous passages is almost entirely in the laminar flow range, and Brownian movement causes impingement and coalescence of the droplets. Each fiber bed is in the form of a hollow cylinder having flow from outside to inside. Clean gas exits the cylinder top and liquid drains from the bottom. Multiple elements keep pressure drop low and, because collection efficiency is largely independent of pressure drop and inlet loading, the collector performs well under start-up and low operating rate conditions where high velocity devices are less efficient.

Elemental phosphorus from the electrothermal process is a distilled product of high purity and yields phosphoric acid pure enough for most industrial uses without any further treatment. The main impurity is ca 20–100 ppm arsenic present in the phosphorus as the element and in the phosphoric acid as arsenious acid. To remove the arsenic, the phosphoric acid destined for food, pharmaceutical, and some industrial-grade applications is treated with excess hydrogen sulfide, filtered, and blown with air to strip out excess H_2S. This treatment generally reduces the arsenic content of the phosphoric acid to less than 0.5 ppm. The small amount of filter cake is disposed of in approved chemical landfills.

The high heat of phosphorus combustion (3053 kJ/mol (730 kcal/mol) of P_4) is used in the evaporation of water from dilute phosphate solutions that require concentration before subsequent processing. A Progil process, for example, burns phosphorus in a wetted-wall tower in order to concentrate dilute sodium phosphate filtrate from wet-process acid purification (6). The concentration is effected both by evaporation of water and absorption of P_2O_5. Until 1973, the low cost of fuel and the considerable corrosion problems discouraged serious work on the utilization of waste heat for steam (qv) or electric power production (see POWER GENERATION). Rapidly escalating fuel costs, however, have changed this situation. Water-cooled stainless steel heat exchangers, located between the combustion chamber and the hydrator, can be operated below the dew point to recover heat and collect highly concentrated acid (7). Operating above a P_2O_5/H_2O mole ratio of 1.0, the condensed acid is noncorrosive. The heat exchangers may also be operated above the dew point (8).

Wet Process. Over 90% of the phosphoric acid produced, both in the United States and worldwide, is wet-process phosphoric acid used almost exclusively for agricultural application as both fertilizers and animal feed supplements. Although constituting a small proportion of the total wet-acid production, a significant amount of phosphoric acid for food and technical applications is made by purification of wet-process acid.

Wet-process acid is manufactured by the digestion of phosphate rock (calcium phosphate) with sulfuric acid. Depending on availability, other acids such as hydrochloric may be used, but the sulfuric-based processes are by far the most prevalent. Phosphoric acid is separated from the resultant calcium sulfate slurry by filtration. To generate a filterable slurry and to enhance the P_2O_5 content of the acid, much of the acid filtrate is recycled to the reactor. Two main categories of the wet process exist, depending on whether the calcium sulfate is precipitated as the dihydrate or the hemihydrate. Operation at 70–80°C and $\sim$30% P_2O_5 in the liquid phase results in the precipitation of $CaSO_4{\cdot}2H_2O$ in a filterable form; 80–90°C and $\sim$40% P_2O_5 provide a filterable $CaSO_4{\cdot}0.5H_2O$. Operation outside these conditions generally results in poor filtration rates. A typical analysis of wet-process acid is given in Table 4. For more detailed discussion of the wet-process acid, see Fertilizers.

Purification. Process development for the purification of wet-process acid has taken place primarily outside North America where the cost differential between the sulfur used in manufacture of wet-process acid and the electricity needed for thermal acid has been large. Decline of the market for technical-grade phosphates in detergents, along with the escalating cost of electric power for elemental phosphorus production, has resulted in the closing of less efficient elemental phosphorus facilities and the introduction of wet-acid purification into the United States.

Chemical precipitation and solvent extraction are the main methods of purifying wet-process acid, although other techniques such as crystallization (9) and ion exchange (qv) have also been used. In the production of sodium phosphates, almost all wet-process acid impurities can be induced to precipitate as the acid is neutralized with sodium carbonate or sodium hydroxide. The main exception, sulfate, can be precipitated as calcium or barium sulfate. Most fluorine and silica can be removed with the sulfate filter cake as sodium fluorosilicate, Na_2SiF_6, by the addition of sodium ion and control of the Si/F ratio in the process.

In the double-neutralization process, Na_2SiF_6 is precipitated and removed by filtration at a pH of 3–4 (10). Upon raising the pH to 7–9, insoluble phosphates of Fe, Al, Ca, and Mg form and separate. Iron can be precipitated as hydrous ferric oxide, reducing the phosphate loss at the second filter cake. Both the fluorosilicate and metal phosphate filter residues tend to be voluminous cakes that shrink when dewatered; recovery of soluble phosphates trapped within the cakes is difficult.

The double-neutralization process was used in the production of high volume detergent-builder phosphates, such as sodium tripolyphosphate [7758-29-4] (STP), $Na_5P_3O_{10}$, and tetrasodium pyrophosphate [7722-88-5] (TSPP), $Na_4P_2O_7$, because the phosphate precursor solutions occur at pH 7–9. More acidic salts, however, require back-neutralization with pure phosphoric acid, whereas more basic salts may require an additional filtration to eliminate discoloration caused by remaining traces of ferric oxide that precipitate at higher pH. The double-neutralization process is no longer practiced in the United States. More flexibility, better purity, and good economics are provided by modern solvent extraction–purification technology.

Solvent extraction–purification of wet-process phosphoric acid is based on preferential extraction of H_3PO_4 by an organic solvent vs the cationic impurities present in the acid. Because selectivity of acid over anionic impurities is usually not sufficient, precipitation or evaporation steps are included in the purification process for removal. Crude wet-process acid is typically concentrated and clarified prior to extraction to remove post-precipitated sludge and improve partition of the acid into the solvent. Concentration also partially eliminates fluoride by evaporation of HF and/or SiF_4. Chemical precipitation of sulfate (as Ba or Ca salts), fluorosilicates (as Na salt), and arsenic (as sulfides) may also be used as a prepurification step preceding solvent extraction.

Modern commercial wet-acid purification processes (see Fig. 4) are based on solvents such as C_4 to C_8 alcohols, ethers, ketones, amines, and phosphate esters (11–13). Organic-phase extraction of phosphoric acid is accomplished in one or more extraction columns or, less frequently, in a series of countercurrent mixer–settlers. Generally, 60–75% of the feed acid P_2O_5 content is extracted into the organic phase as H_3PO_4. The residual phosphoric acid phase (raffinate), containing 25–40% of the original P_2O_5 value, is typically used for fertilizer manufacture such as triple superphosphate. For this reason, wet-acid purification units are almost always located within or next to fertilizer complexes.

The P_2O_5 value in the raffinate is largely in the form of phosphate salts of the metallic impurities which cannot be extracted directly. Higher levels of extraction may result in sludge precipitation in the settlers and the raffinate stream. Higher yields of purified acid may be achieved, however, by the addition of the stronger sulfuric acid for neutralizing the metallic impurities and freeing the residual P_2O_5 value as extractable phosphoric acid. Sulfuric acid may be added either during the extraction step (14), or the raffinate treated in a separate solvent extraction operation. These approaches may pose additional capital and/or energy requirements for phosphoric acid recovery without high levels of sulfate.

The purified acid is recovered from the loaded organic stream by contacting with water in another countercurrent extraction step. In place of water, an aqueous alkali can be used to recover a purified phosphate salt solution. A small portion of the purified acid is typically used in a backwashing operation to contact the loaded organic phase and to improve the purity of the extract phase prior to recovery of the purified acid. Depending on the miscibility of the solvent with the acid, the purified acid and the raffinate may be stripped of residual solvent which is recycled to the extraction loop. The purified acid can be treated for removal of residual organic impurities, stripped of fluoride to low (10 ppm) levels, and concentrated to the desired P_2O_5 level. Many variations of this basic scheme have been developed to improve the extraction of phosphate and rejection of impurities to the raffinate stream, and numerous patents have been granted on solvent extraction processes.

2.2. Condensed Phosphoric Acids. At equilibrium, the specific composition of a concentrated phosphoric acid is a function of its P_2O_5 content. Phosphoric acid solutions up to a concentration equivalent of about 94% H_3PO_4 (68% P_2O_5) contain H_3PO_4 as the only phosphoric acid species present. At higher concentrations, the orthophosphoric acid undergoes condensation (polymerization by dehydration) to yield a mixture of phosphoric acid species (Table 5), often referred to generically as polyphosphoric or superphosphoric acid, $H_2O/P_2O_5 = \sim 3$, or ultraphosphoric acid, $H_2O/P_2O_5 = \sim 1$. At the theoretical P_2O_5 concentration for orthophosphoric acid of 72.4%, the solution is actually a mixture containing 13% pyrophosphoric acid and about 1% free water. Because the pyrophosphoric acid present is the result of an equilibrium state dependent on the P_2O_5 content of the solution, pure orthophosphoric acid can be obtained because of a shift in equilibrium back to H_3PO_4 upon crystallization.

The only clearly defined crystalline compositions are three forms of phosphoric acid and hemihydrate, pyrophosphoric acid, and crystalline P_4O_{10}. The phosphoric acids obtained in highly concentrated solutions or by mixing phosphoric acid with phosphorus pentoxide are members of a continuous series of amorphous (excluding $H_4P_2O_7$) condensed phosphoric acid mixtures. Mixtures having more than 86% P_2O_5 contain some cyclic metaphosphoric acids [10343-62-1].

Phosphoric acids have one strongly acidic hydrogen for each phosphorus atom of the chain ($pK = \sim 1-2$). At each end of the straight chains, a weakly acidic hydrogen is also present. For long chains, pK is ~ 7.2 for the first of these; 8.2 for the second. The titration curves show inflection points near pH 4.5, 7.5, and 10. Dissociation of pyrophosphoric acid has $K_1 = 10^{-1}$, $K_2 = 1.5 \times 10^{-2}$, $K_3 = 2.7 \times 10^{-7}$, and $K_4 = 2.4 \times 10^{-10}$:

$$H_4P_2O_7 \overset{H^+}{\rightleftharpoons} H_3P_2O^{-}{}_7 \overset{H^+}{\rightleftharpoons} H_2P_2O^{2-}{}_7 \overset{H^+}{\rightleftharpoons} HP_2O^{3-}{}_7 \overset{H^+}{\rightleftharpoons} P_2O_7^{4-} \qquad (3)$$

The condensed phosphoric acids are hygroscopic and exhibit a variety of physical forms at room temperature. The material appears oily at 72–82 wt % P_2O_5; viscous and gummy at 82–90 wt % P_2O_5; and is a mixture of glassy and crystalline material at 90 wt %.

Upon boiling dilute phosphoric acid or a collection of P_4O_{10} in a limited amount of water, an azeotropic mixture is obtained. Its composition varies from 91.1–92.4% P_2O_5 as the pressure of the system increases from 6.6–13.3 kPa to 101.3 kPa (50–100 to 760 mm Hg). The boiling point and composition of vapor over the boiling acid are given in Figure 5 (16). The boiling point increases slowly up to compositions containing 60–70% P_2O_5, and rises rapidly thereafter. The composition of the vapor above boiling phosphoric acid becomes progressively richer in P_2O_5 up to the azeotrope, when both liquid and vapor have an identical composition.

Commercial condensed phosphoric acids are mixtures of linear polyphosphoric acids made by the thermal process either directly or as a by-product of heat recovery. Wet-process acid may also be concentrated to $\sim$70% P_2O_5 by evaporation. Linear phosphoric acids are strongly hygroscopic and undergo viscosity changes and hydrolysis to less complex forms when exposed to moist air. Upon dissolution in excess water, hydrolytic degradation to phosphoric acid occurs; the hydrolysis rate is highly temperature-dependent. At 25°C, the half-life for the formation of phosphoric acid from the condensed forms is several days, whereas at 100°C the half-life is a matter of minutes.

Pyrophosphoric (diphosphoric) acid, $H_4P_2O_7$, is the only condensed phosphoric acid definitely obtainable in crystalline form. It has a theoretical P_2O_5 content of 79.8%. However, liquid polyphosphoric acid of such content shows by analysis only 42.5% $H_4P_2O_7$; the remainder is phosphoric acid and various other condensed acids. Pyrophosphoric acid crystallizes in two anhydrous forms. The metastable form, $H_2P_2O_7$–I, which has an mp of 54.3°C, is usually obtained; the stable form, $H_2P_2O_7$–II, has an mp of 71.5°C. Pure pyrophosphoric acid solutions are best obtained by ion exchange from the sodium salt. Acid salts are well known.

Traditionally, the term metaphosphoric acid has been used rather freely to describe amorphous mixtures of polyphosphoric acids, especially the azeotropic forms which are also called polymetaphosphoric acids. Commercial forms of polyphosphoric acid are still occasionally referred to in this manner. The term is also used to describe a reagent for the precipitation of protein that contains up to 18% Na_2O in addition to P_2O_5 and H_2O. Technically, the term metaphosphoric acid [10343-62-1] should be reserved for ring-structured acids. Two cyclic acids are reasonably well-defined, tri- and tetrametaphosphoric acids, $H_3P_3O_9$ and $H_4P_4O_{12}$, respectively. Tetrametaphosphoric acid is the main product resulting from the hydrolysis of phosphorus pentoxide and an excess of water in organic medium. Trimetaphosphoric acid can be prepared by ion exchange of its sodium salt, a commercially available material. The cyclic metaphosphoric acids are strong acids having a single, strong inflection in their pH titration curves.

Uses. Owing to extensive use in fertilizers, wet-process phosphoric acid is the largest source of phosphoric acid in the United States, accounting for more than 85% of total worse acid demand (17). The remaining phosphoric acid is technical- and food-grade acid supplied by the furnace process or purified wet-process acid. Most of this relatively pure material is marketed in the various forms of phosphate salts. Technical- and food-grade phosphoric acid is used in a variety of applications, including metal treatment, refractories (qv), catalysts, foods, and beverages (see FOOD ADDITIVES).

Cleaners. Phosphoric acid is used in several acidic hard-surface (tile, porcelain, metal) cleaning and sanitizing formulations, as well as an acid cleaner for food processing equipment.

Metal Treatment. After rolling, the oxide scale on sheet steel is removed by acid treatment (pickling) (see METAL SURFACE TREATMENT). Phosphoric acid, a good pickling agent, leaves the steel coated with a thin film of iron phosphates. This process improves rust resistance but presents a problem if the steel is to be electroplated.

Phosphoric acid–nitric acid baths are used for chemical polishing (bright dipping) of aluminum prior to anodizing. The mixture selectively attacks the metal surface protrusions, resulting in an overall leveling effect. Some copper and brass are also chemically polished with phosphoric acid. Aluminum, steel (including stainless), and other metals are electropolished in relatively high (50–80%) concentration phosphoric acid baths containing sulfuric and chromic acids as well as other additives.

Iron, zinc, or manganese phosphate coatings are applied to steel-, zinc-, aluminum-, magnesium-, and tin-plated articles to reduce corrosion of the base metal and improve paint adhesion. Such coatings, called phosphate conversion coatings, contain crystalline salts of the metal being treated and the metal ions added to the coating solution. The base metal is attacked by free phosphoric acid. As acid is consumed at the interface, local pH rises, and phosphate salts are precipitated on the base metal, affording the mixed-metal phosphate surface coatings. The zinc phosphate [7779-90-0], $Zn_3(PO_4)_2$, coating offers superior paint adhesion, whereas the manganese phosphate provides excellent corrosion resistance (see CORROSION AND CORROSION CONTROL).

Food Additives. Phosphoric acid in dilute solution is nontoxic and has a pleasingly sour taste similar to common food acids such as citric and acetic, but without the fruity flavor of the organic acids. For this reason, it is used widely in cola beverages (see CARBONATED BEVERAGES) as a tart flavoring agent (see FLAVORS). Other food applications include its use as a general protein acidulant, buffering agent in jam and jelly preparation, nutrient and buffer in antibiotic manufacture, acid cleaner for dairy equipment, and purification reagent in sugar refining.

Refractories. Phosphoric acid is used as a bonding agent in various refractory products, particularly alumina, but also magnesia, zirconia, and carbon refractories. Phosphate-bonded refractories typically show improved green strength, load-bearing properties, high temperature stability, and good abrasion resistance.

Condensed Phosphoric Acid. The largest use of polyphosphoric (superphosphoric) acid is as an intermediate in the production of high quality liquid fertilizers. The TVA pioneered the development of electric-furnace superphosphoric acid for this application. However, wet-process superphosphoric acid prepared by evaporation of water from wet-process phosphoric acid has almost completely replaced furnace-grade acid in fertilizer manufacture.

Catalysts. Catalytic applications of phosphoric acid, particularly in the form of condensed thermal polyphosphoric acids, make use of its acidic, nonoxidizing, and dehydrating properties. Condensed acids of 82–84% P_2O_5 content are employed as catalysts in the petroleum and chemical industries for alkylation, dehydrogenation, polymerization, and isomerization reactions, including the production of adiponitrile from adipic acid, and the manufacture of cumene, ethylbenzene, gasoline, and plasticizer alcohols. The acid is typically supported on diatomaceous earth or other porous materials (see SUPPORTED CATALYSTS; DIATOMITE). The catalytic activity of polyphosphoric acids depends largely on their HYDROGEN-ION ACTIVITY (qv). Dehydration to even higher polyphosphoric acids, with a resulting decrease in strong acidity, begins to occur at around 230°C; hence, most reactions using polyphosphoric acid catalysts are carried out below this temperature. In addition, steam is often introduced together with the reactants to assure a supply of the more acidic shorter-chain length polyacids via hydrolysis of the more highly condensed acids. Polyphosphoric acid is also used as a dehydrating agent in dye and pigment production. Lesser amounts are used in the production of phosphate esters and agricultural chemicals.

Others. Miscellaneous uses for phosphoric acid are numerous, encompassing wood (qv) and fabric flameproofing, boiler cleaning, opacity control in glass manufacture, textile dyeing, rubber latex coagulation, lithographic engraving, and dental cements (see DENTAL MATERIALS), among others. Phosphoric acid-based formulations for the cleaning of exterior automotive plastic parts and semiconductors (18) have been developed.

3. Phosphates

3.1. Orthophosphates.

Orthophosphate salts are generally prepared by the partial or total neutralization of orthophosphoric acid. Phase equilibrium diagrams are particularly useful in identifying conditions for the preparation of particular phosphate salts. The solution properties of orthophosphate salts of monovalent cations are distinctly different from those of the polyvalent cations, the latter exhibiting incongruent solubility in most cases. The commercial phosphates include alkali metal, alkaline-earth, heavy metal, mixed metal, and ammonium salts of phosphoric acid. Sodium phosphates are the most important, followed by calcium, ammonium, and potassium salts.

Sodium Phosphates. Elementary chemical considerations might predict three simple sodium phosphates resulting from successive neutralization of the acidic protons of phosphoric acid; ie, monosodium dihydrogen phosphate [7558-80-7] (MSP) NaH_2PO_4; disodium monohydrogen phosphate [7558-79-4] (DSP) Na_2HPO_4; and trisodium phosphate [7601-54-9] (TSP), Na_3PO_4. The titration of phosphoric acid with sodium hydroxide shows pH inflections corresponding to two of these three well-known salts (see Fig. 1). The formation of the trisodium salt is too diffuse to be seen. The $Na_2O{-}P_2O_5{-}H_2O$ system, actually much more complex than the titration curve indicates, is shown in Figure 6 (19). There are double salts as well as several hydrate forms. Table 6 lists more of these compounds.

The solubility of a number of sodium orthophosphates is depicted in Figure 7. Some of the sodium phosphates dissolve or precipitate incongruently, affording a different Na_2O/P_2O_5 ratio in the solution phase from that of the solid phase. Sodium phosphates that precipitate are also a function of the temperature. As the temperature increases, the sodium phosphates that may precipitate from solution tend to be anhydrous or lower hydrates than those equilibrium sodium phosphate phases at lower temperature. Whereas most of the phases in Figure 7 represent congruently soluble sodium phosphates, solid phases appear or disappear upon changes in temperature.

Both mono- and disodium phosphates are prepared commercially by neutralization of phosphoric acid using sodium carbonate or hydroxide. Crystals of a specific hydrate can then be obtained by evaporation of the resultant solution within the temperature range over which the hydrate is stable. For the preparation of trisodium phosphate, sodium hydroxide must be used to reach the high end pH because CO_2 cannot be stripped readily from the solution above a pH of near 8.

The trisodium phosphate system is the most complex and the commercial product is generally of variable composition and often contains excess sodium hydroxide. It has long been recognized that the usual formula, $Na_3PO_4\cdot 12H_2O$, does not accurately represent the constitution of this salt. A better approximation is provided by the formula $4(Na_3PO_4\cdot 12H_2O)\cdot NaOH$, although the exact stoichiometry can vary below this level of sodium. Trisodium phosphate readily forms a variety of double salts with other sodium compounds, generally depicted as $4(Na_3PO_4\cdot 11H_2O)\cdot NaCl$, $5(Na_3PO_4\cdot 11H_2O)\cdot NaMnO_4$, and $4(Na_3PO_4\cdot 11H_2O)\cdot NaOCl$. The double salt of trisodium phosphate and sodium hypochlorite is a source of both alkalinity and active chlorine in disinfectant cleaners and automatic dishwashing formulations. This double salt is generally referred to as chlorinated trisodium phosphate [56802-99-4] (Cl-TSP), although this is a misnomer. It is assumed that Cl-TSP is a mixture of $4(Na_3PO_4\cdot 11H_2O)\cdot NaCl$ and $4(Na_3PO_4\cdot 11H_2O)\cdot NaOCl$ resulting from the chlorination of crystalline trisodium phosphate. However, Cl-TSP contains free sodium chloride and a mixture of phosphate salts. Commercial material approximates the formula $4(Na_3PO_4\cdot 11H_2O)\cdot NaOCl$, and has a typical chlorine content of ca 4%. The pH of a 1% solution is close to 12; water solubility at 25°C is approximately 20 wt %.

Uses. The principal use of monosodium phosphate is as a water-soluble solid acid and pH buffer, primarily in acid-type cleaners. The double salt, $NaH_2PO_4\cdot H_3PO_4$, referred to as hemisodium orthophosphate or sodium hemiphosphate, is often generated *in situ* from monosodium phosphate and phosphoric acid in these types of formulations. Mixtures of mono- and disodium phosphates are used in textile processing, food manufacture, and other industries to control pH at 4–9. Monosodium phosphate is also used in boiler-water treatment, as a precipitant for polyvalent metal ions, and as an animal-feed supplement.

The single largest use for disodium phosphate is as an emulsifying aid for pasteurized process cheese. Its emulsification mechanism is not completely understood, but the phosphate interacts with the proteins such as casein to allow the proteins to function as emulsifiers and prevent separation of both fat and water in the cheese. A combination with insoluble sodium metaphosphate (IMP) also is used. Typical commercial mixtures contain 30–60% soluble phosphate and 40–70% IMP. Other food-related uses are in ham curing, starch processing, and as an ingredient in instant cereals and evaporated milk (see MILK AND MILK PRODUCTS). Disodium phosphate is also used in the preparation of certain ceramic glazes and enamels, in leather (qv) tanning, textile dyeing, pigment manufacture, water, sources and quality issues (qv) treatment, and detergents (see ENAMELS, PORCELAIN OR VITREOUS; PIGMENTS, INORGANIC; FIBERS).

Trisodium phosphate is strongly alkaline; many of its applications depend on this property. For example, many heavy-duty cleaning compositions contain trisodium phosphate as a primary alkalinity source. The crystalline dodecahydrate itself is marketed as a cleaning compound and paint remover. Traditionally, trisodium phosphate has been used in water softening to remove polyvalent metal ions by precipitation as insoluble phosphates. Because the hypochlorite complex of trisodium phosphate provides solutions that are strongly alkaline and contain active chlorine, it is used in disinfectant cleaners, scouring powders, and automatic dishwashing formulations.

Potassium Phosphates. The $K_2O{-}P_2O_5{-}H_2O$ system parallels the sodium system in many respects. In addition to the three simple phosphate salts obtained by successive replacement of the protons of phosphoric acid by potassium ions, the system contains a number of crystalline hydrates and double salts (Table 7). Monopotassium phosphate (MKP), known only as the anhydrous salt, is the least soluble of the potassium orthophosphates. Monopotassium phosphate has been studied extensively owing to its piezoelectric and ferroelectric properties (see FERROELECTRICS). At ordinary temperatures, KH_2PO_4 is so far above its Curie point as to give piezoelectric effects in which the emf is proportional to the distorting force. There is virtually no hysteresis.

Although the cost of the potassium phosphates is higher than the corresponding sodium salts, the former have applications utilizing their higher solubility and nutrient value. A widespread use for MKP is as a mineral nutrient for fermentation (qv) broths. In a similar vein, special liquid fertilizers contain KH_2PO_4 as a source of both potassium and phosphorus. Monopotassium phosphate is also used in various buffering systems and in paper (qv) processing. The piezoelectric effect of MKP has led to its use in sonar systems and other electronic applications.

Dipotassium phosphate (DKP) and tripotassium phosphate (TKP) are marketed both as solids and in 50% active solution. Most of the commercial output is used in conjunction with borates, nitrites, nitrates, and/or silicates as the corrosion inhibitor system in ethylene glycol antifreeze formulations (see ANTIFREEZES AND DEICING FLUIDS). The second largest use for DKP is as a buffer in coffee creamers to prevent casein protein coagulation and precipitation by coffee acids. Other uses of DKP include specialty fertilizers, paper-processing aids, and saline cathartics. Tripotassium phosphate is utilized in the polymerization of styrene–butadiene rubber to control the polymerization rate and latex stability. Other applications include rejuvenation of scrap rubber, hydrogen sulfide gas scrubbing, and liquid cleaners.

Ammonium Phosphates. Because ammonium hydroxide is a much weaker base than the common metal hydroxides, and because ammonia may escape as a gas at ambient temperatures, ammonium phosphates are comparatively unstable. For example, both triammonium phosphate [10361-65-6], $(NH_4)_3PO_4$, and the double salt [78436-08-5], $(NH_4)_3PO_4{\cdot}2(NH_4)_2HPO_4$, are unstable at room temperature and evolve ammonia (qv) to form diammonium phosphate [7783-28-0] (DAP), $(NH_4)_2HPO_4$. Even the commercial monoammonium phosphate [7722-76-1] (MAP) and DAP exhibit an ammonium vapor pressure both in the solid form and in solution. Although monoammonium phosphate is more stable than diammonium phosphate, which decomposes to ammonia and monoammonium phosphate at around 70°C, MAP also decomposes at high temperature, affording ammonia and polyphosphoric acid. The vapor pressure of a saturated solution of $(NH_4)H_2PO_4$ is expressed by the following, when t is between 292 and 363 K.

$$\log_{10}P_{\mathrm{kPa}} = -2240/t + 9.737 \tag{4}$$

When t is between 292 and 328 K, the vapor pressure over a saturated solution of $(NH_4)H_2PO_4$ is defined by

$$\log_{10}P_{\mathrm{kPa}} = -2240/t + 9.682 \qquad (5)$$

Monoammonium and diammonium phosphates are produced on a large scale as fertilizers. During the 1970s, these materials, produced from economical wet-process phosphoric acid, became the world's leading phosphate fertilizers.

Owing to the thermally unstable nature of ammonium phosphates, other applications are related to flame retarding and fire extinguishing. Monoammonium phosphate is a common fire-extinguishing ingredient in ABC-type dry-power extinguishers. The effectiveness of such extinguishers is closely related to their P_2O_5 content. Ammonium phosphates are used as flame retardants for cellulosic materials, including plywood, papers, and fabrics, to prevent afterglow in matches (qv) and to control forest fires. In flame retarding and fire extinguishing, the phosphoric acid generated during decomposition is thought to catalyze the decomposition of cellulose into a slow-burning char, as well as to smother the flame. Fire retardancy is second only to fertilizers in MAP consumption. Paper, wood, and cloth products not subject to washing are impregnated with an ammonium phosphate solution and dried. Such solutions are often made directly by sparging ammonia into phosphoric acid without crystallizing the solid salts. A high solubility of 140 g/100 g water at 25°C occurs at neutral pH, corresponding to an equimolar mixture of MAP and DAP. Neutral solutions of even higher P_2O_5 content are obtained from anhydrous ammonia and polyphosphoric acids in a short pipeline reactor. The product is cooled immediately to prevent hydrolysis of the polyphosphate.

Evolution of ammonia from a boiling dilute solution of diammonium phosphate gradually reduces the pH. This process is used commercially to control the precipitation of alkali-soluble–acid-insoluble colloidal dyes on wool. Other ammonium orthophosphate salts of interest are ammonium hemiphosphate [28537-48-6], $NH_4H_2PO_4{\cdot}H_3PO_4$, and its hydrate [28037-74-3], as well as the trihydrate [78436-07-4] of DAP.

Calcium Phosphates. The alkaline-earth phosphates are generally much less soluble than those of the alkali metals. Calcium phosphates include the most abundant natural form of phosphorus, ie, apatites, $Ca_{10}(PO_4)_6X_2$, where $X = OH$, F, Cl, etc. Apatite ores are the predominant basic raw material for the production of phosphorus and its derivatives. Calcium phosphates are the main component of bones and teeth. After sodium phosphates, the calcium salts are the next largest volume technical- and food-grade phosphates. Many commercial applications of the calcium phosphates depend on their low solubilities.

Several compounds of the $CaO{-}P_2O_5{-}H_2O$ system are given in Table 8. The common names for the mono-, di-, and tricalcium phosphates arise from the traditional double-oxide formulas, $CaO{\cdot}2H_2O{\cdot}P_2O_5$, $2CaO{\cdot}H_2O{\cdot}P_2O_5$, and $3CaO{\cdot}P_2O_5$, respectively. These terms are routinely used in industry. With the exception of the monocalcium salt, the calcium phosphates are all sparingly soluble.

Many orthophosphate salts, in particular those of polyvalent cations, exhibit incongruent solubility where disporportionation occurs in solution to yield a more basic orthophosphate salt and phosphoric acid. This hydrolytic disproportionation of orthophosphates should not be confused with the hydrolysis of the P−O−P linkage. Incongruent solubility behavior is readily detected by inspection of the aqueous phase diagram for the appropriate system. Hydrolytic disproportionation is probably one of the mechanisms related to the formation of bone and naturally occurring apatites.

Both monocalcium phosphate and dicalcium phosphate dissolve incongruently in water, disproportionating to more basic calcium phosphate and phosphoric acid. The extent of these reactions varies with the temperature and the amount of water. If water is added gradually to anhydrous monocalcium phosphate, equilibrium conditions first correspond to a mixture of the anhydrous salt and its monohydrate. After conversion to the monohydrate, further reaction affords dicalcium phosphate plus free phosphoric acid. Dicalcium phosphate decomposes in aqueous solution to the more basic hydroxyapatite and phosphoric acid via intermediate octacalcium phosphate. The complicated stepwise conversion of the acidic mono- and dicalcium phosphates to hydroxyapatite is summarized in equations 6–9. The kinetics are quite complex.

$$Ca(H_2PO_4)_2 + H_2O \longrightarrow Ca(H_2PO_4)_2 \cdot H_2O \qquad (6)$$

$$Ca(H_2PO_4)_2 \cdot H_2O \longrightarrow CaHPO_4 \cdot 2H_2O + H_3PO_4 \qquad (7)$$

$$8\ CaHPO_4 \cdot 2H_2O \longrightarrow Ca_8H_2(PO_4)_6 \cdot 5H_2O + 2\ H_3PO_4 + 11\ H_2O \qquad (8)$$

$$5\ Ca_8H_2(PO_4)_6 \cdot 5H_2O \longrightarrow 4\ Ca_{10}(PO_4)_6(OH)_2 + 6\ H_3PO_4 + 17\ H_2O \qquad (9)$$

Because monocalcium phosphate is incongruently soluble, it is typically contaminated with various amounts (6−10%) of dicalcium phosphate and free phosphoric acid resulting from in-process disproportionation of the monocalcium salt. Free phosphoric acid may render the product hygroscopic, and absorbed water plus acid catalyzes further decomposition to additional free acid and dicalcium phosphate. For this reason, industrial monocalcium phosphate may contain some dicalcium phosphate resulting from excess lime addition and then aged to ensure the removal of residual free phosphoric acid.

For many years, the hygroscopic nature of anhydrous monocalcium phosphate limited its commercial applications. However, the addition of small amounts of K^+, Na^+, and Al^{3+} ions to the crystallization mother liquor followed by heating to >200°C results in a mixed metal−polyphosphate coating on the calcium phosphate (22). This glassy coating protects the calcium phosphate from moisture and greatly improves its handling properties and performance in several applications, most notably as a leavening agent.

Crystalline $CaHPO_4{\cdot}2H_2O$ loses both water molecules in a single step at moderately elevated temperature or upon storage to yield the anhydrous salt. The presence of free moisture accelerates this dehydration, which results in anhydrous dicalcium phosphate, often as a hard mass. Addition of a few percent of tetrasodium pyrophosphate or trimagnesium phosphate, $Mg_3(PO_4)_2$, stabilizes the dihydrate. The mechanism, however, is not well understood. Nonetheless, these materials are used widely to stabilize $CaHPO_4{\cdot}2H_2O$, particularly for toothpaste applications.

Tricalcium phosphate, $Ca_3(PO_4)_2$, is formed under high temperatures and is unstable toward reaction with moisture below 100°C. The high temperature mineral whitlockite [64418-26-4], although often described as β-tricalcium phosphate, is not pure. Whitlockite contains small amounts of iron and magnesium. Commercial tricalcium phosphate prepared by the reaction of phosphoric acid and a hydrated lime slurry consists of amorphous or poorly crystalline basic calcium phosphates close to the hydroxyapatite composition and has a Ca/P ratio of approximately 3:2. Because this mole ratio can vary widely (1.3–2.0), free lime, calcium hydroxide, and dicalcium phosphate may be present in variable proportion. The highly insoluble basic calcium phosphates precipitate as fine particles, mostly less than a few micrometers in diameter. The surface area of precipitated hydroxyapatite is approximately 100 m^2/g.

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, may be regarded as the parent member of a whole series of structurally related calcium phosphates that can be represented by the formula $M_{10}(ZO_4)_6X_2$, where M is a metal or H_3O^+; Z is P, As, Si, Ga, S, or Cr; and X is OH, F, Cl, Br, 1/2 CO_3, etc. The apatite compounds all exhibit the same type of hexagonal crystal structure. Included are a series of naturally occurring minerals, synthetic salts, and precipitated hydroxyapatites. Highly substituted apatites such as Francolite, $Ca_{10}(PO_4)_{6-x}(CO_3)_x(F,OH)_{2+x}$, are the principal component of phosphate rock used for the production of both wet-process and furnace-process phosphoric acid.

Uses. Commercial monocalcium phosphate is available as both the anhydrous and the monohydrate salts. Most uses are based on acidic properties. Monocalcium phosphate is used to control acidity in powdered drink mixes, as an ingredient in effervescent tablets, as a plastics stabilizer, and in ceramics. Its single largest application is as a leavening agent in bread, cake mixes, and self-rising flour.

The leavening process involves the introduction and expansion of a gas at a controlled rate in a batter or dough system during cooking to afford a light, open texture to the product. Typically, either yeast (see YEASTS) or chemical leavening is employed. Chemical leavening involves the reaction of a dry acid with sodium bicarbonate to release carbon dioxide during batter or dough preparation and cooking. Various chemical leavening acids are available, many of which are phosphate salts, to provide different rates of CO_2 evolution. The phosphate also buffers the pH of the system and interacts with flour proteins to control elasticity and viscosity of the dough (see BAKERY PROCESSES, YEAST-RAISED PRODUCTS). Calcium phosphate cements can be used as a bone filler (23).

The main use for dicalcium phosphate on a tonnage basis is as an animal feed supplement (see FEEDS AND FEED ADDITIVES, NONRUMINANT FEEDS), for which it is produced from defluorinated wet-process phosphoric acid. Food-grade dicalcium phosphate is used as a dental polishing agent in toothpastes. This application accounts for the majority of food- and technical-grade production of dicalcium phosphate. The dihydrate is most generally used for this purpose, although anhydrous $CaHPO_4$ is used in special formulations where more abrasive properties are desired. Dicalcium phosphate also is used as a leavening agent, animal-food mineral supplement, plastics stabilizer, and in the manufacture of glass, medicines, and phosphors.

Commercial tricalcium phosphate is an effective flow conditioner for food products such as sugar and salt. The product is also used as a whitening agent in the manufacture of ceramics, as a mordant in dyeing, and as a polishing agent.

Considerable research on apatites occurred in the 1980s and 1990s by the desire for biocompatible bone and tooth enamel replacements (see BIOMATERIALS, PROSTHETICS, AND BIOMEDICAL DEVICES).

Other Orthophosphates. In many instances, magnesium orthophosphates exhibit different properties than the analogous calcium phosphates. Monomagnesium phosphate [13092-66-5], $Mg(H_2PO_4)_2$, and the di- [15609-80-0] and tetrahydrates [15609-87-7] are somewhat more soluble than the monocalcium phosphates. Unlike dicalcium phosphate dihydrate, dimagnesium phosphate trihydrate [7782-75-4], $MgHPO_4 \cdot 3H_2O$, is not incongruently soluble. In the thermal dehydration of dimagnesium phosphate trihydrate, both the hydrate and water and the water of constitution are removed at nearly the same temperature ($\sim$140–160°C), generating magnesium pyrophosphate and making the preparation of anhydrous (amorphous) $MgHPO_4$ in pure form difficult. The more basic magnesium phosphate phases have not been as deeply investigated as for the calcium system. Ammonium magnesium phosphate [7785-21-9], NH_4MgPO_4, is used for gravimetric phosphate analysis because of its insolubility in water. It can also be used as a cement in tooth and bone fillers and as a bone cement (24).

Aluminum acid phosphates readily form complex polymers when heated above 400°C. Solutions are used as binders in cements and in high temperature bonding of refractories. Aluminum and phosphate ions undergo considerable association in solution. Alumina–phosphoric acid solutions having an Al_2O_3/P_2O_5 mole ratio of 1.0–1.5 produce highly viscous fluids that, when dried, yield amorphous solids which can be redispersed in water to give solutions stable under acidic conditions. Monoaluminum phosphate [13530-30-2], $Al(H_2PO_4)_3$, in phosphoric acid solution is employed to surface-treat the steel plates in electrical transformers. Aluminum phosphate [7784-30-7], $AlPO_4$, is a highly insoluble, hard, and unreactive material with a high melting point ($>$1800°C) which is used as a refractory material (see REFRACTORIES).

A large number of crystalline phosphates contain two or more cations, and many phosphate minerals are mixed metal salts. Mixed-sodium–aluminum phosphates are utilized in some food applications, eg, $NaAl_3H_{14}(PO_4)_8 \cdot 4H_2O$ and $Na_3Al_2H_{15}(PO_4)_8$. These salts are prepared by crystallization of a concentrated solution containing the proper $Na_2O/Al_2O_3/P_2O_5$ ratio. The acid sodium aluminum phosphates are used as heat-activated leavening acids, generally in conjunction with the faster-reacting monocalcium phosphate for double-acting baking powders. The sodium aluminum phosphates are of particular interest in flavor-sensitive systems because of their neutral taste. The basic sodium aluminum phosphate [16073-43-1], $Na_{15}Al_3(PO_4)_8$, is used as a food emulsification aid, particularly in processed cheeses (Table 9).

Iron phosphates are generally similar to aluminum phosphates. The two varieties of $Fe(H_2PO_4)_3$ are isomorphous with the two forms of $Al(H_2PO_4)_3$. Both varieties of $Fe(H_2PO_4)_3$ are highly hygroscopic and hydrolyze to $FeH_3(PO_4)_2 \cdot 2.5H_2O$ and an acidic solution. Commercial applications of the iron phosphates are quite limited but include catalysts, mineral supplements, and specialty glass manufacture.

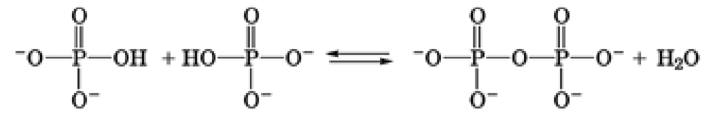
Zinc phosphate, $Zn_3(PO_4)_2$, forms the basis of a group of dental cements. Chromium and zinc phosphates are utilized in some metal-treating applications to provide corrosion protection and improved paint adhesion. Cobalt(II) phosphate octahydrate [10294-50-5], $Co_3(PO_4)_2{\cdot}8H_2O$, is a lavender-colored substance used as a pigment in certain paints and ceramics. Copper phosphates exhibit bioactivity and are used as insecticides and fungicides. Zinc, lead, and silver phosphates are utilized in the production of specialty glasses. The phosphate salts of heavy metals such as Pb, Cr, and Cu, are extremely water insoluble.

The tertiary metal phosphates are of the general formula MPO_4, where M is B, Al, Ga, Fe, Mn, etc. The metal–oxygen bonds of these materials have considerable covalent character. The anhydrous salts are continuous three-dimensional networks analogous to the various polymorphic forms of silica. Of limited commercial interest are the aluminum, boron, and iron phosphates. Boron phosphate [13308-51-5], BPO_4, is produced by heating the reaction product of boric acid and phosphoric acid or by adding H_3BO_3 to H_3PO_4 at room temperature, followed by crystallization from a solution containing >48% P_2O_5. Boron phosphate has limited use as a catalyst support, in ceramics, and in refractories.

Many phosphates exhibit two- or three-dimensional structures (25). The titanium and zirconium phosphates, $M(HPO_4)_2{\cdot}nH_2O$, form inert, high temperature-stable ion-exchange agents possessing a layered structure. Both α-$Zr(HPO_4)_2{\cdot}H_2O$ and γ-$Zr(HPO_4)_2O$ are of particular interest. Proposed uses include high temperature processing of nuclear waste and kidney dialysis. Polar organics may also be intercalated between the layers, and reactions such as phosphate group exchange can be catalyzed. The Nasicon family of compounds, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, are three-dimensional sodium ion conductors that also have controllable, near-zero thermal expansion properties.

3.2. Condensed Phosphates. Condensed phosphates are derived by dehydration of acid orthophosphates. The resulting polymeric structures are based on a backbone of P–O–P linkages where PO_4 tetrahedra are joined by shared oxygen atoms. The range of materials within this classification is extremely broad, extending from the simple diphosphate, also known as pyrophosphate, to indefinitely long-chain polyphosphates and ultraphosphates (see Table 1). Both well-defined crystalline and amorphous materials occur among the condensed phosphates.

Pyrophosphates. The simplest linear condensed phosphates are pyrophosphates, which can be considered as the dehydration product of two orthophosphate groups. A water molecule is eliminated to form a P–O–P linkage in a reversible reaction.



$$^{-}O-\underset{O^-}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-OH + HO-\underset{O^-}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-O^- \rightleftharpoons {}^{-}O-\underset{O^-}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-O-\underset{O^-}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-O^- + H_2O \qquad (10)$$

Many pyrophosphates can be prepared by thermal treatment of the acid orthophosphates.

$$2\,MH_2PO_4 \xrightarrow{}_{\Delta} M_2H_2P_2O_7 + H_2O \qquad (11)$$

$$2\,M_2HPO_4 \xrightarrow{}_{\Delta} M_4P_2O_7 + H_2O \qquad (12)$$

Compositions having an oxide ratio, $R<2$, eg, in equation 11, can dehydrate to form more highly condensed phosphates beyond the pyrophosphate. Conditions must therefore be controlled to prevent complete dehydration. Insoluble pyrophosphates are obtained by treatment of a soluble salt of the desired cation using a sodium pyrophosphate solution.

Most crystalline pyrophosphate salts have a nonlinear configuration; the angle of the central P–O–P linkage varies with different cations. Most anhydrous pyrophosphates are thermally stable up to their melting points, although upon heating many undergo polymorphic phase changes in crystalline structure involving an alteration of the P–O–P angle.

A large number of pyrophosphate salts have been prepared (Table 10). In addition to individual metal salts, ammonium pyrophosphates and many mixed-metal pyrophosphates are known. Pyrophosphates of notable commercial importance include sodium, potassium, and calcium salts.

Sodium Pyrophosphates. Known pyrophosphate compounds in the $Na_2O-H_2O-P_2O_5$ system are given in Table 10. Commercially important sodium pyrophosphates include tetrasodium pyrophosphate (TSPP), $Na_4P_2O_7$, and disodium pyrophosphate, $Na_2H_2P_2O_7$, commonly referred to as sodium acid pyrophosphate (SAPP). These are prepared industrially by thermal dehydration of disodium and monosodium orthophosphate, respectively. Tetrasodium pyrophosphate exists in five crystalline modifications, only one of which is stable at room temperature.

$$Na_4P_2O_7(\mathrm{V}) \xrightleftharpoons{400^\circ\mathrm{C}} \mathrm{IV} \xrightleftharpoons{510^\circ\mathrm{C}} \mathrm{III} \xrightleftharpoons{520^\circ\mathrm{C}} \mathrm{II} \xrightleftharpoons{545^\circ\mathrm{C}} \mathrm{I} \xrightleftharpoons{985^\circ\mathrm{C}} \text{melt} \tag{13}$$

TSPP is readily crystallized from water as the decahydrate between −0.4° and 79°C, and as the anhydrous salt above 79°C. The solubility of tetrasodium pyrophosphate is illustrated in Figure 8. The pH of a 1% solution is 10.2. TSPP is quite stable in alkaline medium but hydrolyzes rapidly to orthophosphate under acid conditions.

Tetrasodium pyrophosphate is a builder in detergent and cleaning formulations. Food applications include consistency control in buttermilk (thinning), chocolate milk (thickening), and instant puddings. Thinning action results from neutralization of lactic acid that agglomerates butterfat; thickening results from the formation of calcium pyrophosphate gels. Tetrasodium pyrophosphate is widely used as an effective deflocculant, eg, in kaolin clays, drilling muds, dyes, and inks. TSPP stabilizes hydrogen peroxide through chelation of heavy-metal ion impurities that catalyze peroxide decomposition. TSPP is used as an anticalculus agent in toothpastes and mouthwashes (see Dentifrices). A primary component of calculus is a calcium scale and TSPP is thought to function by complexing soluble calcium ion and inhibiting crystallization from the tooth plaque (26).

The solubility of $Na_2H_2P_2O_7$ is also illustrated in Figure 8. The hexahydrate, $Na_2H_2P_2O_7{\cdot}6H_2O$, is the solid form in equilibrium with solution up to near 27°C, whereupon the anhydrous form is obtained above this temperature. Commercial $Na_2H_2P_2O_7$ typically contains small amounts of added potassium, calcium, and aluminum to reduce the rate of reaction with sodium bicarbonate in leavening, the largest application of SAPP. More reactive forms of SAPP are particularly suited for making doughnuts, whereas the slower reacting grades are used in refrigerated canned dough products such as biscuits. However, SAPP sometimes imparts an astringent aftertaste to certain baked goods. SAPP is also used to eliminate darkening of cut potatoes to prevent the formation of highly colored iron–tannin complexes. The pyrophosphate chelates the iron as a colorless iron pyrophosphate. Other applications are in acid-cleaning formulations and in electroplating.

Potassium Pyrophosphates. Tetrapotassium pyrophosphate (TKPP), $K_4P_2O_7$, is easily prepared by thermal dehydration of K_2HPO_4. TKPP is highly soluble in water, 187.4 g/100 g H_2O at 25°C. In a saturated solution, the equilibrium solid is $K_4P_2O_7{\cdot}3H_2O$. Potassium pyrophosphates are typically quite hygroscopic. Tetrapotassium pyrophosphate has been used as a highly soluble detergent builder because it permits easy formulation in liquid detergent systems. It is also used in water treatment and dentifrices (27). Unlike TKPP or SAPP, dipotassium dihydrogen pyrophosphate, $K_2H_2P_2O_7$, is difficult to prepare by thermal dehydration of KH_2PO_4 because the rate of conversion to the fully dehydrated metaphosphate composition, KPO_3, is fast.

Calcium Pyrophosphates. As is typical of the pyrophosphate salts of multiple-charged or heavy-metal ions, the calcium pyrophosphates are extremely insoluble in water. Calcium pyrophosphate exists in three polymorphic modifications, each of which is metastable at room temperature. These are formed progressively upon thermal dehydration of calcium hydrogen phosphate dihydrate as shown below. Conversion temperatures indicated are those obtained from thermal analyses (28,29). The presence of impurities and actual processing conditions can change these values considerably, as is true of commercial manufacture.

$$\begin{aligned}\mathrm{CaHPO_4{\cdot}2H_2O} \xrightarrow{135^\circ\mathrm{C}} \mathrm{CaHPO_4} \xrightarrow{360-450^\circ\mathrm{C}} \mathrm{Ca_2P_2O_{7\,amorphous}} \xrightarrow{530^\circ\mathrm{C}} \gamma-\mathrm{Ca_2P_2O_7} \xrightarrow{750^\circ\mathrm{C}} \\ \beta-\mathrm{Ca_2P_2O_7} \xrightarrow{1180^\circ\mathrm{C}} \alpha-\mathrm{Ca_2P_2O_7} \xrightarrow{1352^\circ\mathrm{C}} \text{melt} \qquad (14)\end{aligned}$$

The calcium pyrophosphates are utilized primarily as dental abrasives in fluoride-containing toothpastes. Typically, a mixture of β- and γ-$Ca_2P_2O_7$ achieves a balance of abrasivity and fluoride compatibility.

Tripolyphosphates. The most commercially important tripolyphosphate salt is sodium tripolyphosphate (STP), $Na_5P_3O_{10}$. Three distinct crystalline forms are known: two are anhydrous (STP-I and STP-II); the other is the hexahydrate [15091-98-2], $Na_5P_3O_{10}{\cdot}6H_2O$. Sodium tripolyphosphate anhydrous Form I is the high temperature, thermodynamically stable phase; sodium tripolyphosphate anhydrous Form II is the lower temperature form which can be readily converted to STP-I by heating to above 417±8°C, the transition temperature. However, the reverse reaction is extremely slow below 417°C. Both anhydrous forms of sodium tripolyphosphate are therefore stable enough to coexist at room temperature.

The structures of STP-I and -II differ primarily in the ionic coordination of cations. In STP-II all sodium ions are octahedrally coordinated by oxygen, whereas in STP-I some sodium ions are surrounded by only four oxygen atoms. In STP-II a distinct sheet-like arrangement occurs. The faster hydration rates are attributed to these properties.

The hexahydrate is formed by the addition of anhydrous STP to water or by the hydrolysis of sodium trimetaphosphate [7785-84-4] (STMP), $(NaPO_3)_3$, in alkaline media. The hexahydrate is stable at room temperature but undergoes rapid hydrolytic degradation to pyro- and orthophosphate upon drying.

Sodium tripolyphosphate is produced by calcination of an intimate mixture of orthophosphate salts containing the correct overall Na/P mole ratio of 1.67. The proportions of the two anhydrous STP phases are controlled by the calcination conditions. Commercial STP typically contain a few percent of tetrasodium pyrophosphate and some trimetaphosphate. A small amount of unconverted orthophosphates and long-chain polyphosphates also may be present.

The two anhydrous forms of sodium tripolyphosphate can be differentiated by x-ray diffraction, or by infrared or Raman spectroscopy. For industrial purposes, the temperature rise (TR) test (30) is based on the faster hydration rate of STP-I in a water–glycerol mixture, where $\%\text{STP}-\text{I} = 4(\text{TR}-6)$. Low TR (LTR) STP has a TR value of 6–10 and is predominantly Form II STP. High TR (HTR) STP has a TR range of 10–20 and is a mixture of Forms I and II. Ultrahigh TR (UHTR) STP consists almost entirely of Form I STP and has a typical TR value of 25 or higher.

The solubility and hydration behavior of sodium tripolyphosphate are of particular importance in many of its industrial applications. At room temperature, $Na_5P_3O_{10}\cdot 6H_2O$ dissolves to an equivalent $Na_5P_3O_{10}$, of about 13 g/100 g solution. Both anhydrous forms are more soluble than the hexahydrate but each is unstable with respect to the hexahydrate. STP-I is the more rapidly hydrating form having a higher transient solubility than STP-II. Dissolution of STP-I is accompanied by rapid formation of crystalline hexahydrate, and the higher initial solubility drops almost immediately to that of $STP\cdot 6H_2O$. STP-II, on the other hand, dissolves less readily in water, but supersaturated solutions containing 35% or more STP-II can be formed from which the hexahydrate crystallizes slowly. Thus, for both forms of anhydrous STP, maximum solubility under a given set of conditions is determined by two opposing factors, the rate of the solution of anhydrous salt, and the rate of the crystallization of hexahydrate. The greater ease of STP-I hydration is attributed to the lower degree of coordination for the sodium ions in its crystalline structure. Phosphate impurities in STP affect the solubility and hydration behavior. For example, the presence of a small amount of glassy polyphosphate can stabilize supersaturated solutions of STP-II for several hours. STP may be hydrated during manufacture to ca 0.5–1% moisture to form some portion as the hexahydrate. The presence of seed hexahydrate crystals promotes rapid hydration and little tendency to supersaturate. STP particle size, order of addition, agitation, etc, can also affect properties such as the dissolution rate, clumping of solid, and the persistence of supersaturation.

The hydration rate of sodium tripolyphosphate to its stable hexahydrate, $Na_5P_3O_{10}\cdot 6H_2O$, directly affects detergent processing and product properties. The proportion of STP-I (fast-hydrating form) and STP-II (slow-hydrating form) in commercial sodium tripolyphosphate is controlled by the time–temperature profile during calcination. In most processes, a final product temperature of near 450°C results in a product containing about 30% STP-I, which is desired by detergent manufacturers. Addition of a small amount of water to the sodium tripolyphosphate furnishes hexahydrate seed crystals that minimize any induction period or variation in hydration in the detergent manufacturing process. Water is added during STP manufacture either after cooling and before milling, by atomizing water into special high intensity blenders, or by vapor-phase hydration.

The pH of a 1% solution of pure sodium tripolyphosphate is 9.9 and that of commercial samples may vary between 9.5 and 10.1. The pH of a given sample of solid STP drops slowly with age because of water adsorption and partial reversion to orthophosphate and pyrophosphate. The pH of solutions varies with concentration because the sodium ion is bound in the complex form $NaP_3O^{4-}{}_{10}$ at higher concentrations; maximum pH is reached at between 1–2% solution.

Anhydrous sodium tripolyphosphate is slow to hydrate in contact with the atmosphere under normal ambient conditions and generally remains free-flowing. If the relative humidity is below a critical relative humidity, which is different for both anhydrous forms of STP and dependent on temperature, hydration does not take place. For prolonged storage at room temperature, relative humidities above ca 60% in the air result in water absorption. For shorter periods, high levels of humidity can be tolerated. However, even at higher humidities, the amount of water absorbed is small. The heats evolved from vapor hydration of STP-I and -II have been estimated at 343 and 334 kJ/mol (82.0 and 79.9 kcal/mol), respectively (31).

Uses. Sodium tripolyphosphate was introduced in the 1940s as a builder for synthetic detergents. It was once the largest volume commercial product manufactured from technical-grade phosphoric acid but in the 1990s volumes are small compared to the nearly 1×10^9 kg produced in the United States alone in 1970. As a builder in cleaning formulations, sodium tripolyphosphate is used in household laundry products, automatic dishwashing formulations, car washes, and numerous industrial cleaners. STP provides many functions to improve the cleaning efficiency, including the sequestration of hardness ions, buffered alkalinity, deflocculation of dirt particles, and antiredeposition of soil.

Food-grade sodium tripolyphosphate is used for the curing of hams and bacon, where interaction with the meat protein allows for better moisture retention during cooking. Treatment with STP improves the quality of poultry and seafood products. Uses for technical-grade material include clay processing, water softening, textile processing, paper pulping, rubber and paint manufacture, drilling muds, and ore flotation.

Other Tripolyphosphates. Potassium tripolyphosphate [24315-83-1] (KTP), $K_5P_3O_{10}$, has a high aqueous solubility (near 180 g/100 g) and has been used in place of STP for liquid detergents. The potassium salt, however, is more expensive than STP. Sodium potassium tripolyphosphate (SKTP), $Na_3K_2P_3O_{10}$, is prepared by calcination of a feed liquor having the proper $Na_2O/K_2O/P_2O_5$ ratio or by reaction of sodium trimetaphosphate with KOH. For some detergent or food applications, SKTP may provide the optimum compromise between solubility and cost.

Long-Chain Polyphosphates and Metaphosphates. Polyphosphates larger than tetrapolyphosphate are difficult to obtain in pure form. These usually occur as amorphous glassy materials having a distribution of various chain lengths. As the chains become long, however, the properties of the individual chains become so similar that the mixtures behave much like pure compounds and occur as crystalline substances. The composition of long-chain polyphosphates approaches that of metaphosphate, $(MPO_3)_n$, and long-chain polyphosphates may commonly be referred to as metaphosphates, although this term should be reserved for cyclic anions of the exact $(PO^-{}_3)_n$ composition. Most polyphosphates are amorphous glasses, but several high molecular weight polyphosphates occur as crystalline substances. Both types are used commercially.

Thermal dehydration of monosodium phosphate gives rise to numerous condensed polyphosphates (Fig. 9). Structures are diverse and can be controlled by manipulating the conditions of dehydration, ie, temperature, water vapor, and tempering. Graham's salt is a water-soluble polyphosphate glass having a composition approximating $(NaPO_3)_{50}$. It is manufactured by heating NaH_2PO_4 to above 620°C and quenching rapidly. The melt solidifies into a glass consisting of about 90% high molecular weight polyphosphates. The remainder is a mixture of various cyclic metaphosphates. One example of a glassy phosphate has a Na_2O/P_2O_5 ratio of about 1.05–1.1, a molecular weight of 1500–2000, and a degree of polymerization of 15–20. Similar commercial materials of average chain lengths of 6–8, 12–14, and up to ~30 are available. The misnomer hexametaphosphate is often applied to the glassy polyphosphates of this type. Glassy polyphosphates are used in water treatment, owing to the ability of the polyphosphate anion to sequester hardness ions (Ca, Mg, Fe) and convert them into soluble complexes. Polyphosphates are effective thresholding agents, because ppm levels inhibit scale formation in water systems. Glassy polyphosphates act as dispersants on finely divided solids in clay processing, oil-well drilling muds, and pigment manufacture.

Several crystalline condensed phosphates may also be formed by the dehydration of monosodium phosphate (MSP). Maddrell's salt exists as Form II (high temperature Maddrell, $NaPO_3$-II, insoluble metaphosphate-II) and Form III (low temperature Maddrell, $NaPO_3$-III, insoluble metaphosphate-III). Both forms are highly polymerized and difficult (slow) to dissolve in water. Mixtures of the two forms are marketed as a dental abrasive for toothpaste formulations containing soluble fluoride. Maddrell's salt is also used with disodium phosphate as a cheese emulsifying aid.

The only true metaphosphate (ring structure) of significant commercial interest is sodium trimetaphosphate (STMP), $Na_3P_3O_9$. Because of the strain inherent in the small ring structure, STMP is more reactive toward nucleophiles than chain phosphates. In the presence of NaOH, for example, STMP forms sodium tripolyphosphate.

$$Na_3P_3O_9 + 2\,NaOH \longrightarrow Na_5P_3O_{10} + H_2O + 115\ \text{kJ/mol} \quad (27.5\ \text{kcal/mol}) \qquad (15)$$

This reaction is the basis for the Fluff detergent process (32). The heat evolved coupled with the hydration of the STP is sufficient to dry the reaction mass to yield a light density laundry detergent. Requiring a low capital investment, the Fluff process has found use in less-industrialized countries.

STMP reacts with other nucleophiles such as aqueous ammonia to yield amidophosphates, which contains a P–N bond. STMP is used for the modification of the physical properties of starch and proteins by reaction with the amino and hydroxyl groups.

Potassium Kurrol's salt, potassium polymetaphosphate [7790-53-6], $(KPO_3)_n$, is easily obtained by thermal dehydration of KH_2PO_4. The degree of polymerization is directly related to the K_2O/P_2O_5 ratio, temperature, and length of heating. Kurrol's salt typically has a high molecular weight, perhaps up to several million. Sodium Kurrol's salt is a fibrous, crystalline material and, unlike the potassium analogue, is difficult to crystallize in preference to other sodium poly- or metaphosphates. Both sodium and potassium Kurrol's salt are slowly soluble in water but readily dissolve to form viscous solutions in the presence of other alkali-metal cations. The potassium salt has limited commercial usage in sausage processing in Europe.

Ammonium polyphosphate [13446-46-3], $(NH_4PO_3)_n$, can be produced directly by thermal dehydration of $NH_4H_2PO_4$ if care is taken to maintain a high ammonia pressure over the system; otherwise the predominant reaction is the loss of ammonia. It is most easily obtained, however, by heating a mixture of $NH_4H_2PO_4$ and urea in an atmosphere of NH_3. Alternative methods include ammoniation of polyphosphoric acid or condensation of ammonium tetrametaphosphate [14693-64-2], $(NH_4PO_3)_4$, a product recovered by stirring P_4O_{10} with concentrated ammonium hydroxide. There are at least five crystalline forms under the generic term ammonium polyphosphate. Form I, NH_4PO_3-I, is used as a water-insoluble fire retardant in intumescent paints and mastics. Form II, having a higher temperature stability than Form I, is used as a fire retardant in thermoplastics. Ammonium polyphosphate liquid fertilizers are made from wet-process acid.

Properties of Condensed Phosphates

Hydrolysis. Condensed phosphates all exhibit hydrolytic instability of the P–O–P linkages and, under the appropriate conditions, can all be cleaved, ultimately affording the monomeric orthophosphate ion (see eq. 10). Aqueous phase diagrams assume metastability for condensed phosphates and ignore hydrolysis to orthophosphates, although limiting the hydrolytic degradation is an important experimental consideration in defining the phase diagram. Like the orthophosphates, condensed phosphates may also exhibit hydrolytic disproportionation, ie, incongruent solubility.

The hydrolysis rates of polyphosphates are mainly affected by temperature, pH, and the location of the phosphate group in a condensed phosphate. P–O–P linkages attached to triply connected phosphate groups (ultraphosphates) undergo extremely rapid hydrolysis in aqueous systems. Pyrophosphate, containing only end (singly connected) phosphate groups, is notably more stable toward hydrolytic degradation than chain phosphates, which also contain middle (doubly connected) phosphate moieties.

Hydrogen ion is a good catalyst for hydrolytic degradation of the P–O–P linkage. Hydrolysis of short-chain phosphates is extremely slow at room temperature and neutral pH. However, raising the temperature and/or lowering the pH can increase the hydrolysis rate. In dilute and moderately concentrated solution, the overall kinetics for hydrolysis is first-order at a given pH. An estimation of hydrolysis rates can be obtained from the nomograph of Figure 10. The rupture of a P–O–P linkage generates acid end groups, causing the pH of phosphate solutions to fall as hydrolysis occurs and is therefore autocatalytic. Activation energies decrease from ca 125–165 kJ/mol (30–40 kcal/mol) at pH 10 to ca 85–125 kJ/mol (20–30 kcal/mol) at pH 4–7 for sodium pyro- and tripolyphosphates, with values dropping in the presence of catalysts.

Many cations have a catalytic effect on hydrolysis, although generally less than that exhibited by hydrogen ions. Hydrolysis rates as a function of pH may exhibit a minimum having higher rates occurring at low pH (H_3O^+ catalysis) and high pH (catalysis by counterion of base, eg, Na^+). For example, for sodium tripolyphosphate, the minimum hydrolysis rate occurs near pH 10, the naturally occurring pH of an STP solution, if NaOH is used to reach pH values higher than 10. The catalytic effect of cations is roughly related to the cation charge/size ratio and the cation concentration. Use of quaternary ammonium hydroxides to increase the pH does not result in increased hydrolysis rates because of poor catalysis by the large, low charged quaternary ammonium cation. Phosphatase enzymes catalyze extremely rapid hydrolysis of polyphosphates, at a rate as much as 10^6 times faster than those without enzyme. The activity of these enzymes is highly influenced by a number of factors, including pH and metal ions.

Long-chain polyphosphate hydrolysis is more complex than that of the shorter chains on account of additional mechanistic pathways and the accompanying formation of cyclic metaphosphates. Three mechanisms for hydrolysis of polyphosphate chains in solution are generally recognized: clipping of a monomeric unit from the end of the chain, concurrent loss of three units from the end of the chain by splitting off a trimetaphosphate ion from the end or interior of the chain, and random cleavage from within the interior of the chain to afford shorter chains. All three may occur simultaneously in longer chain polyphosphates, but the last mechanism occurs relatively less frequently. The end group clipping is generally the most prevalent mechanism, except for low pH where random cleavage predominates and in an alkaline environment where trimetaphosphate formation increases in importance. As well as overall degradation rates, higher temperatures increase the proportion of trimetaphosphate to orthophosphate. The overall hydrolysis rate increases with increasing chain length, approaching a limiting value when the average chain length is above 10. In concentrated solutions or with moist solids, the course of the reaction may be more complex. An apparent variation is the dehydration of solid sodium tripolyphosphate hexahydrate, which appears to follow second-order kinetics and initially generates primarily pyrophosphate but little orthophosphate.

Although reasonably stable at room temperature under neutral conditions, tri- and tetrametaphosphate ions readily hydrolyze in strongly acidic or basic solution via polyphosphate intermediates. The hydrolysis is first-order under constant pH. Small cyclic phosphates, in particular trimetaphosphate, undergo hydrolysis via nucleophilic attack by hydroxide ion to yield tripolyphosphate. The ring strain also makes these structures susceptible to nucleophilic ring opening by other nucleophiles.

Complex Ion Formation. Phosphates form water-soluble complex ions with metallic cations, a phenomenon commonly called sequestration. In contrast to many complexing agents, polyphosphates are nonspecific and form soluble, charged complexes with virtually all metallic cations. Alkali metals are weakly complexed, but alkaline-earth and transition metals form more strongly associated complexes (eg, eq. 16). Quaternary ammonium ions are complexed little if at all because of their low charge density. The amount of metal ion that can be sequestered by polyphosphates generally increases with increasing chain length. For the following reaction, K is $10^{5.2}$.

$$Ca^{2+} + P_3O_{10}^{5-} \rightleftharpoons CaP_3O^{3-}{}_{10} \tag{16}$$

Sequestration forms the basis for detergent and water-treatment applications of polyphosphates. Sequestration of hardness ions by sodium tripolyphosphate used in detergent formulations prevents the precipitation of surfactants by the hardness ions. Sodium polyphosphate glass (SHMP) may be added to water system to prevent the formation of calcium or magnesium scales by reducing the activity of the hardness ions. However, if the ratio of cation to polyphosphate is too high at a given pH, insoluble precipitates such as $Ca_2P_2O_7$ may result instead of the soluble polyphosphate complexes. The application of polyphosphates may be limited in some systems by hydrolytic degradation, depending on the temperatures, pH, and times involved.

Weaker complex ions may also form with orthophosphates, eg, $CaH_2PO^{+}{}_4$ in mildly acidic solutions of calcium phosphates, and $FeHPO^{+}{}_4$ as a colorless species in impure phosphoric acid. Anionic complexes such as $Fe(HPO_4)^{-}{}_2$ are also known.

Colloidal Properties. Polyphosphates are strongly sorbed onto a variety of surfaces where they alter the charge. As a result, the properties of colloidal systems can be dramatically changed by the addition of small amounts of polyphosphate. A striking example is the deflocculation of clays. If a hundredth of a percent of sodium polyphosphate glass is worked into a firm lump of kaolin, the entire mass liquefies to a thin slurry, thereby allowing the clay to be pumped. The same principle of altering the surface charge to repel particles can be used to suspend inorganic materials in aqueous solution.

Calcium carbonate (calcite) scale formation in hard water can be prevented by the addition of a small amount of soluble polyphosphate in a process known as threshold treatment. The polyphosphate sorbs to the face of the calcite nuclei and further growth is blocked. Polyphosphates can also inhibit the corrosion of metals by the sorption of the phosphate onto a thin calcite film that deposits onto the metal surface. When the polyphosphate is present, a protective anodic polarization results.

Analysis. Excellent reviews of phosphate analysis are available (34). Solids characterization methods such as x-ray powder diffraction (xrd) and thermal gravimetric analysis (tga) are used for the identification of individual crystalline phosphates, either alone or in mixtures. These techniques, along with elemental analysis and phosphate species determination, are used to identify unknown phosphates and their mixtures. Particle size analysis, surface area, microscopy, and other standard solids characterizations are useful in relating solids properties to performance. Solid-state nmr is used with increasing frequency.

In most analytical procedures for determining the total phosphorus content (normally expressed in terms of P_2O_5), the phosphates are converted to the orthophosphate form. Typically, condensed phosphates are hydrolyzed to orthophosphate by boiling in dilute mineral acid (0.1 *N*). The orthophosphate is then determined by gravimetric or spectrophotometric methods. For gravimetric determination, insoluble phosphomolybdates (or magnesium ammonium orthophosphate) is formed.

For the determination of condensed phosphate species, hydrolytic conditions must be avoided. Many of the wet analytical methods for species identification, such as selective precipitation, paper, and thin-layer chromatography, have been largely displaced by spectroscopic or automated methods. Advances have made techniques such as ion chromatography, ^{31}P nuclear magnetic resonance, and isotachophoresis practical methods for quantitative analysis. Ion chromatography and ion-exchange chromatography, employing strong-base resins, are widely used for phosphate species analysis. Gradient elution is employed, and excellent resolution of linear phosphates up to 14–18 phosphorus atoms can be obtained. Spectrophotometric analysis following ion-exchange separation and hydrolysis is commonly automated.

3.3. Manufacture of Phosphate Salts. The general manufacturing scheme for phosphate salts is shown in Figure 11. Condensed phosphates are prepared from the appropriate orthophosphate or mixture of orthophosphates, so the preparation of orthophosphates must be considered first for the manufacture of any phosphate salt. Phosphoric acid is neutralized to form a solution or slurry with a carefully adjusted acid/base ratio according to the desired orthophosphate product. The orthophosphate may be recovered either by crystallization from solution, or the entire solution or slurry may be evaporated to dryness. The dewatering (qv) method is determined by the solubility properties of the product and by its desired physical properties such as crystal size and shape, bulk density, and surface area. Acid orthophosphate salts may be converted to condensed phosphates by thermal dehydration (calcination).

Orthophosphates

Alkali Metal Phosphates. A significant proportion of the phosphoric acid consumed in the manufacture of industrial, food, and pharmaceutical phosphates in the United States is used for the production of sodium salts. Alkali metal orthophosphates generally exhibit congruent solubility and are therefore usually manufactured by either crystallization from solution or drying of the entire reaction mass. Alkaline-earth and other phosphate salts of polyvalent cations typically exhibit incongruent solubility and are prepared either by precipitation from solution having a metal oxide/P_2O_5 ratio considerably lower than that of the product, or by drying a solution or slurry with the proper metal oxide/P_2O_5 ratio.

Monosodium phosphate, NaH_2PO_4, is usually marketed as the anhydrous salt made by either crystallization from solution or evaporation of a solution to dryness on steam-heated drum dryers and followed by drying in a rotary dryer. Disodium phosphate, Na_2HPO_4, is produced commercially as the anhydrous salt and as the dihydrate, $Na_2HPO_4{\cdot}2H_2O$. The dihydrate is crystallized from solution between 40–95°C, followed by centrifugation and drying. Anhydrous Na_2HPO_4, precipitated from solution above 95°C, exhibits inverse solubility and may be crystallized by boiling off water (see Fig. 7). The anhydrous salt may also be obtained by dehydration of the dihydrate in a rotary dryer.

Trisodium phosphate (TSP) is manufactured as the anhydrous salt, Na_3PO_4, and as an incompletely dehydrated salt (with a water content equivalent to a monohydrate) by drying a solution or slurry above 80°C. Spray drying, drum drying, and flash drying are used for the evaporation step, but rather high (300–400°C) drying temperatures are needed for complete dehydration. Both salts dissolve incongruently in water, affording the dodecahydrate (crystalline TSP) with an Na_2O/P_2O_5 ratio of about 3.25.

Crystalline TSP is a dodecahydrate with somewhat variable composition between the limits of $(Na_3PO_4{\cdot}12H_2O){\cdot}0.25NaOH$ and $(Na_3PO_4{\cdot}12H_2O){\cdot}1/7NaOH$. It is manufactured by crystallization below 60°C from a solution with an Na_2O/P_2O_5 mole ratio slightly lower than 3.25. Crystals are isolated by centrifugation and air-dried at ca 40°C to minimize dehydration.

Chlorinated TSP (Cl-TSP) is a complex mixture or solid solution approximating the composition $4(Na_3PO_4{\cdot}11H_2O){\cdot}NaOCl$. The composition is variable, having an Na_2O/P_2O_5 mole ratio ranging from ca 3.15–3.35, and 3–5% available chlorine. Sodium chloride and $Na_2HPO_4{\cdot}2H_2O$ are present as impurities in the commercial product. It is manufactured by the addition of sodium hypochlorite solution to a hot, concentrated sodium phosphate solution having an Na_2O/P_2O_5 mole ratio of ca 2.85, followed first by cooling, crystallization, and granulation of the entire reaction mass in a heavy-duty mixer, then by low temperature air-cooling and drying. Chlorinated TSP is unstable above 40°C and up to 20% of the available chlorine in the initial reaction mass may be lost. Chlorine stability is improved by the addition of 0.5% sodium silicate to the reaction mass, cooling the mass rapidly during granulation, applying refrigerated air in the final drying step, and protecting against high ambient temperatures during storage and transportation.

Potassium Phosphates. Potassium phosphate salts are analogous to the sodium salts and share many of the same functional properties. The higher cost of potassium hydroxide has restricted these salts to applications where high solubility or nutrient value is important. Potassium salts are manufactured like their sodium analogues, often on the same equipment. Many of the potassium phosphates are more deliquescent than their sodium analogues and may require special storage and moistureproof containers.

Ammonium Phosphates. In the manufacture of ammonium phosphates, an atmosphere of ammonia may need to be maintained because the partial pressure of ammonia rises rapidly as either the temperature or the NH_3/P_2O_5 mole ratio of the reaction mass increases. Phosphoric acid reacts quickly with ammonia vapor and is used in multistage reactor systems as a scrubber fluid to prevent NH_3 emissions and recover ammonia values. For example, H_3PO_4 scrubbing of coke-oven off-gases produces ammonium phosphates of relatively good purity.

Monoammonium phosphate (MAP), $NH_4H_2PO_4$, is produced by reaction of anhydrous ammonia and phosphoric acid in batch or continuous reactors and crystallized in conventional crystallizers because the partial pressure of ammonia over this acidic solution is relatively low (see CRYSTALLIZATION). Crystals are centrifuged and dried below 100°C in a rotary dryer, and mother liquor is returned to the reactor. Diammonium phosphate (DAP), $(NH_4)_2HPO_4$, solutions, on the other hand, have a high partial pressure of ammonia and the reaction is carried out in a two-stage reactor system in which the feed acid passes countercurrentwise to the flow of ammonia gas. Incoming acid reacts in the scrubber with ammonia from the main reactor and may also serve as a scrubber for dryer off-gases. MAP and DAP fertilizers are made in a granulation process from ammonia and wet-process phosphoric acid. The acid is partially neutralized in a tank reactor, and ammoniation and granulation are completed in a rotary drum. Drying, cooling, and product screening complete the process.

Calcium Phosphates. Because calcium phosphates and calcium bases as raw materials have low solubilities, the manufacture of calcium phosphates must therefore deal with nonequilibrium chemistry in a heterogenous system. Furthermore, several kinetically favored metastable phosphates occur under manufacturing conditions and these salts may hydrolyze to the highly insoluble and stable hydroxyapatite. Calcium phosphates also exhibit incongruent solubility, which means that the mother liquor necessarily has a different CaO/P_2O_5 ratio than the product (Fig. 12). As a result, most commercial calcium phosphates are mixtures of several salts having an average composition approximating that of the pure material. For example, the addition of a slurry of hydrated lime into a well-stirred phosphoric acid solution until a pH of 7 is reached results in the precipitation of dicalcium phosphate, which can be anhydrous or dihydrate, depending on the temperature. If, however, the order of addition is reversed and the phosphoric acid is added into a well-stirred lime slurry until a pH of 7 is reached, tricalcium phosphate (TCP) is obtained. Each product can contain up to about 10% of the other. The TCP product is actually an amorphous basic calcium phosphate similar to hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, rather than $Ca_3(PO_4)_2$, as indicated by the name tricalcium phosphate.

For fertilizer and animal nutrition uses, the primary concern is the CaO and P_2O_5 analysis of the product, which is usually a mixture of salts. Animal feed-grade dicalcium phosphate is made from wet-process acid that has been treated with superheated steam, or with finely divided silica and steam, to reduce the fluorine content to an acceptable level. Various granulation processes produce granules smaller than those used for fertilizer. For industrial, dentifrice, food, and pharmaceutical uses, important functional properties relating to composition or solids characteristics may significantly differ in two products having nearly identical CaO and P_2O_5 content. Manufacture is something of an art and details are often proprietary.

Monocalcium Phosphates. Monocalcium phosphate (MCP) is generally made as a composition equivalent to the monohydrate, $Ca(H_2PO_4)_2{\cdot}H_2O$. The monohydrate is manufactured by several methods. Phosphoric acid and hydrated lime may be mixed in a pan or other heavy-duty mixer that allows the rapid escape of steam. The product is a paste that is dried and sized. The reaction may also be carried out in a more dilute system in conventional mixing equipment to produce a pumpable slurry that is then spray dried to give a lighter and more rapidly soluble product. Both methods, typically running at a CaO/P_2O_5 mole ratio just above 1.0, result in the presence of free acid and dicalcium phosphate as well as unreacted lime particles. Free acid causes caking and MCP is often aged or cured to allow for more complete reaction of the acid. Commercial MCP monohydrate usually contains several percent of dicalcium phosphate, which is acceptable in baking powder as an anticaking agent. MCP may also be manufactured by crystallization from solution. MCP made by this method may contain a small amount of free acid from entrained mother liquor. Thorough washing of an MCP filter or centrifuge cake with water results in partial conversion to dicalcium phosphate.

Anhydrous monocalcium phosphate, $Ca(H_2PO_4)_2$, can be made in a pan mixer from concentrated phosphoric acid and lime. The high heat of reaction furnishes essentially all the necessary thermal input and subsequent drying is minimized. A small amount of aluminum phosphate or a mixture of sodium and potassium phosphates is added in the form of proprietary stabilizers for coating the particles. Heat treatment converts the coating to a protective polyphosphate (22).

Dicalcium Phosphates. Whereas mixtures of calcium phosphates are made by the pan-mixer process and sold as dicalcium phosphate (DCP) for use as animal feed supplements, the dentifrice-abrasive market requires close control of the product. Formation of minor amounts of more basic calcium phosphates results in rendering soluble fluoride in the dentifrice formulation as an inactive and insoluble fluorapatite. A much more dilute slurry reaction is used to obtain good mixing. The more abrasive anhydrous salt, $CaHPO_4$, is precipitated at ca 80°C, whereas the softer dihydrate precipitates below 45°C. Conventional mixing equipment is used for the reaction followed by centrifugation, drying, and milling to the desired particle size. Stability of the DCP dihydrate (DCPD) against reaction with fluoride in toothpaste formulations is of tantamount importance. Fluoride, typically added in 0.1% levels, reacts with phosphates more basic than DCPD to form fluorapatite, thereby inactivating the caries-preventative action of the free fluoride ion. For this reason, the presence of calcium phosphate impurities can be tolerated at only low levels. The dihydrate is often stabilized against disproportionation to more basic calcium phosphates by sodium pyrophosphate and/or trimagnesium phosphate.

Tricalcium Phosphate. Commercial tricalcium phosphate (TCP) is actually an amorphous basic calcium phosphate close to hydroxyapatite in composition. Because of its extremely low solubility in water, TCP is precipitated almost quantitatively from dilute phosphate solutions with a slurry of hydrated lime. TCP is separated by drum-, spray-, or flash-drying the TCP slurry, with or without intermediate sedimentation or filtration steps. It is used as an industrial-grade flow conditioner and parting agent.

Condensed Phosphates. Condensed phosphates are prepared by calcining an orthophosphate composition having the proper metal oxide/P_2O_5 mole ratio. Depending on the metal oxide/P_2O_5 mole ratio of the desired product, this calciner feed composition may include compound(s) of a single metal oxide/P_2O_5 mole ratio or a mixture of compounds having the proper overall ratio. Commercial practice for the manufacture of the condensed sodium or potassium phosphates typically begins with the preparation of an orthophosphate feed liquor (solution) having the proper M_2O/P_2O_5 ratio. The liquor may be processed in two stages by using separate dryer and calciner, or by using specially designed combination dryer–calciner units (35) such as those shown in Figure 13, in which liquor may be sprayed directly onto a hot recycled bed of calcined material. The drying conditions determine in large measure the physical properties of the calcined product, such as bulk density. Rotary calciners, either gas- or oil-fired, are preferred. Following calcination, the product is water-cooled in screw or tube coolers and then sized to granular or powder specifications by screening, air separation, and milling techniques.

Three crystalline polyphosphates can be produced by thermal dehydration of monosodium phosphate at successively higher temperatures (see Fig. 9). Monosodium phosphate (MSP) may be used in any form that has a Na_2O/P_2O_5 mole ratio of 1.0, such as NaH_2PO_4, $NaH_2PO_4{\cdot}2H_2O$, or a slurry or solution of MSP. When heated to about 250°C, MSP converts to sodium acid pyrophosphate (SAPP). For leavening applications, SAPP is manufactured to exacting specifications on the rate of reaction in dough mixtures. Many grades are produced for different leavening applications by various calcination procedures and the addition of trace quantities of other cations and phosphates. Slow and controlled calcination of MSP or SAPP to about 400°C produces insoluble metaphosphate (IMP), a long-chain, crystalline sodium polyphosphate of the Maddrell's salt type. Sodium trimetaphosphate (STMP), $Na_3P_3O_9$, is produced by calcination of MSP, SAPP, STMP, or IMP at 450–500°C. The rates at which the thermal dehydration reactions and crystalline transitions occur depend on temperature profiles, water vapor pressures, impurities, etc. As a consequence, commercial polyphosphates usually contain several percent of one or more of the other members of this group.

Sodium polyphosphate compositions corresponding to average chain lengths from four up to, but excluding, very long chains are amorphous glassy mixtures of various chain lengths, as opposed to crystalline compositions. These sodium phosphate glasses are generally prepared having Na_2O/P_2O_5 mole ratios of approximately 1.1–1.3, and average chain lengths of about 21–27 monomeric phosphate units, respectively. Although the glasses can be made at any molar ratio up to about 1.7, many of the solution properties are similar to that of the crystalline sodium tripolyphosphate. Glass nomenclature is inexact and many trade names are used for glasses of slightly different composition. Glasses are manufactured in refractory-type reverberatory furnaces in which a solution (or less typically a solid feed) is brought to a melt approaching 1000°C and then rapidly quenched on water-cooled stainless steel belts, rolls, or wheels. These processes are energy- and maintenance-intensive.

Sodium tripolyphosphate, $Na_5P_3O_{10}$, is manufactured from a solution having Na_2O/P_2O_5 mole ratios near 1.67, corresponding to a mixture of two moles of disodium phosphate and one mole of monosodium phosphate. Mixtures of phosphate and pyrophosphate salts can also be used, provided that the 1.67 molar ratio is maintained. Because the precursor phosphate salts can convert upon calcination to one or more polyphosphates other than sodium tripolyphosphate, the feed must be an intimate mixture of finely divided crystals to ensure a high assay product. For this reason, most commercial processes start with a carefully adjusted, homogeneous solution that is then dried as rapidly as possible to minimize individual crystal growth. STP with a tripolyphosphate assay as high as 98–99% can be produced from phosphate feeds dried by spray dryer, or in rotary dryers in which the solution is flash-dried on a hot, rolling bed of material. Drum and rotary dryers that evaporate the feed solution more slowly and allow better crystal growth, however, lead to STP having an assay usually no higher than 95%. Some older process dryers allow growth of large crystals that cannot be converted to tripolyphosphate of an assay over ca 85%. However, higher conversion efficiency can be obtained by milling the dried phosphate, calcination in the presence of a high partial pressure of water, and post-treatment of hot calciner product in a steam atmosphere (36). Physical properties of the STP, such as bulk density, dissolution rate, etc, depend in large measure on the drying method. Aside from considerations of assay, the drying method is often selected for control of the STP physical properties. Calcining is typically carried out at 380–500°C, depending on the proportion of STP-I and -II desired.

In most condensed phosphate manufacturing operations using rotary calciners, a mixture of powder and granular product is formed. As a result of newer methods of detergent manufacture (eg, agglomeration and dry mix, as opposed to spray tower methods) and the movement away from phosphate use in home laundry detergents in general, the U.S. STP market has steadily shifted from powder to granular products. Three granular bulk-density-grades are recognized: light at $\sim$0.5 g/cm^3, medium at $\sim$0.75 g/cm^3, and heavy at $\sim$1.0 g/cm^3. In most processes, the granular bulk density is fixed at the phosphate drying stage; thus spray dryers produce light-, drum dryers medium-, and rotary dryers heavy-density granules. Bulk density can be controlled over a wide range in one process by manipulating particle size and moisture content of the feed to an agglomerating calciner (37). Other processes have been developed to convert excess powder or by-product fines from granular operations to a granular product by reagglomeration with water or a phosphate solution and recalcination (38).

Tetrasodium pyrophosphate (TSPP), $Na_4P_2O_7$, is obtained by the calcination of disodium phosphate, or any of its hydrates, at about 400°C. Commercial manufacture is similar to that of sodium tripolyphosphate, often using the same equipment. Relatively little calcining control is required for TSPP because it is the only condensation product of disodium phosphate (DSP). Owing to increased dust generation, however, pyrophosphate processing typically requires some changes in dust-handling procedures.

Ammonium Polyphosphate. The poorly soluble, long-chain crystalline ammonium polyphosphate $(NH_4PO_3)_n$, is used in intumescent fire-retardant coatings and paints where resistance to leaching by water is required. It is manufactured by heating a mixture of (qv) and ammonium phosphate or polyphosphoric acid under a controlled atmosphere of NH_3 and water at $\sim$300°C (39). Urea acts as a condensing agent because the polyphosphate cannot be made by simple thermal dehydration on account of the high partial pressure of ammonia. The higher temperature Form II ammonium polyphosphate is used as a fire retardant in thermoplastics.

Calcium Pyrophosphate. Calcium pyrophosphate, $Ca_2P_2O_7$, is manufactured by high temperature calcination of DCP in a rotary calciner. Temperature is carefully controlled to adjust the proper ratio of β- and γ-forms.

4. Economic Aspects

Phosphoric acid is the leading inorganic acid produced and consumed in terms of production value. It is second to sulfuric acid in terms of volume. Its greatest use is in the manufacture of phosphate chemicals that are then used as fertilizers or animal feed components.

The wet phosphoric acid industry has been depressed since the mid-1980s. The reasons are a buildup of capacity in combination with a slowdown in the use of phosphates as fertilizers. Declines in production and consumption occurred in the former USSR and Eastern and Western Europe in the early 1990s. World production was 22.8×10^6 t in 1993 and showed little or no growth in 2000–2001. It was estimated that recovery occurred in 2002 and that an increase of 2.6%/yr is expected through 2007 (17).

The primary market for wet phosphoric acid is in the production of phosphate fertilizers: ammonium phosphate and triple superphosphate. Fertilizers account for 85% of the global market. The United States is the largest consumer and used about 35% of the total in 2002. Southwest Asia, Africa, and Western Europe accounted for 28%. Use in the former USSR was down. Although no growth was apparent in 2001–2002, world markets for phosphate fertilizers is expected to grow at the rate of 1–2% through 2007. Partial recovery is expected in the former USSR and rapid growth is expected in Asia.

The United States is the major producer of wet phosphoric acid (36% of world production). Production is expected to increase worldwide at a rate of 2.7%/yr through 2007. The largest volume increases are expected in parts of Asia, Africa, the former USSR, Middle East, and the United States. U. S. exports are expected to increase in 2007.

Major commercial nonagricultural phosphate chemicals include sodium phosphates used as detergent builders and for water treatment, calcium phosphates are used in food and industrial markets, ammonium phosphates are used in fire retardants and in foods. However, its biggest use is in fertilizers.

Industrial phosphates are consumed in the United States, Canada, Western Europe, and Japan. Production in this region estimated in 2002 was about 1.20×10^6 t, estimated at $\$1.2 \times 10^9$. There has been a decline in demand as a result of phasing out sodium phosphates as detergent builders because of environmental concerns. These detergent builders are no longer accounted for in the majority of phosphate consumption in the U.S. Canada or Japan. They are still a large market in Western Europe and Mexico. China is expected to become a major user and exporter of phosphates (40).

5. Health and Safety Factors

Phosphoric acid is a human poison by ingestion. It is moderately toxic by skin contact and is a corrosive irritant to eyes, skin, and mucous membranes, and a systemic irritant by inhalation. It is a common air contaminant. Mixtures with nitromethane are explosive. It reacts with chlorides + stainless steel to form explosive hydrogen gas. A violent reaction with sodium tetrahydroborate is possible. It is dangerous when heated to decomposition it emits toxic fumes of PO_x (41).

The OSHA PEL is TWA 1 mg/m^3; STEL 3 mg/m^3;
ACGIH TLV: TWA 1 mg/m^3; STEL 3 mg/m^3.

Inorganic phosphates present little hazard to humans and are mineral nutrients essential to life processes. Attention must be given to the acidity of phosphoric acid, the alkalinity of the bases with which it reacts and the heat released upon neutralization. Appropriate protective gear should be worn when in close contact. Some phosphate salts are reasonably acidic or basic.

6. Environmental Considerations

Larger environmental issues are associated with the manufacture of wet-process acid and elemental phosphorus, than with the manufacture of technical- or food-grade acids and salts from these raw materials. In the manufacture of both wet acid and phosphorus, the P_2O_5 value recovered may represent a minor proportion of the phosphate rock as mined. With the exception of the removal of traces of arsenic, phosphorus can be cleanly converted to thermal acid and then to salts. Purified wet acid is also converted into salts with little waste generation. The raffinate and by-product streams from wet-acid purification are generally returned to the fertilizer complex from where the wet-acid feed originated.

Because of the nutritive value, phosphates have been implicated in promoting the growth of algae in lakes. Problems apparently caused by sewage-borne phosphates are mostly localized to areas that have traditionally employed lakes as receiving waters for sewage effluents. It is believed that much of the phosphate is precipitated in an insoluble form and trapped in sediments where it is ultimately converted to an apatite. Considerable controversy has centered on the contribution of phosphate-built detergents to excessive algae growth and subsequent eutrophication of natural receiving water. Legislation against the use of phosphates in detergents has resulted in a patchwork of restrictions worldwide. Home laundry detergents have been the most regulated. Societal pressure has resulted in the voluntary reduction or elimination of phosphates in many cleaning products by the manufacturers. It is open to question, however, as to whether a banning of phosphate detergents and cleaners can indeed sufficiently reduce phosphorus input to the low levels needed to control algal growth, when, in fact, natural wastes and fertilizers provide most of the phosphorus input to receiving waters. A more logical but also more costly approach is phosphorus removal during sewage treatment. Excellent reviews of this area are available(42,43).

BIBLIOGRAPHY

"Phosphoric Acids and Phosphates" in *ECT* 1st ed., Vol. 10, pp. 403–411, J. R. Van Wazer, Monsanto Chemical Co.; in *ECT* 2nd ed., Vol. 15, pp. 234–276, by J. R. Van Wazer, Monsanto Co.; in *ECT* 3rd ed., Vol. 17, pp. 426–472, by R. B. Hudson and M. J. Dolan, Monsanto Co.; in *ECT* 4th ed., Vol. 18, pp. 699–718, by David R. Gard, Monsanto Co.;

"Phosphoric Acids and Phosphates" in *ECT* (online), posting date: December 4, 2000, by David R. Gard, Monsanto Co.

CITED PUBLICATIONS

1. J. E. Such, in A. A. Eldridge, G. M. Dyson, A. J. E. Welch, and D. A. Pantony, eds., *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longman, London, U.K., Vol. VIII, Suppl. III, 1971, p. 726.
2. U.S. Pat. Appl. 2005 000 284 (Jan. 16, 2005), A. E. Holanson, D. Williams, and C. S. Williams.
3. U.S. Pat. 2,708,619 (May 17, 1955), H. S. Winnicki and C. P. Roberts (to FMC Corp.).
4. H. Y. Allgood and co-workers, *Ind. Eng. Chem.* **59**(6), 18 (1967).
5. J. A. Brink, Jr., *Can. J. Chem. Eng.* **41**, 134 (1963).
6. U.S. Pat. 3,129,057 (Apr. 14, 1964), L. Germain and P. Desire (to Progil S.A.).
7. Eur. Pat. 0 037 735 B1 (July 31, 1985), R. B. Hudson, G. W. Cadwallader, and D. C. Taylor (to Monsanto Co.).
8. Jpn. Kokai 79-84890 (July 6, 1979), Y. Takahashi and T. Kobayashi (to Kawasaki Heavy Ind. Ltd.).
9. E. J. Lowe, *Proceedings of the Second International Congress on Phosphorus Compounds*, 1980, p. 493.
10. H. M. Stevens, in J. R. Van Wazer, ed., *Phosphorus and Its Compounds*, Vol. 2, Interscience Publishers, New York, 1961.
11. U.S. Pat. 3,914,382 (Oct. 21, 1975), T. A. Williams (to Albright and Wilson, Ltd.).
12. R. Fitoussi and J. Helgorsky, *Ind. Miner., [Ser.] Tech.* (3) 225 (1982).
13. A. Davister and M. Peeterbroeck, *Chem. Eng. Prog.* **78**(3), 35 (1982).
14. Ger. Offen. 2,334,019 (Jan. 30, 1975), B. Wojtech, K. P. Ehlers, and W. Scheibitz (to Farbwerke Hoechst A.G.).
15. R. F. Jameson, *J. Chem. Soc.*, 752 (1959).
16. E. H. Brown and C. D. Whitt, *Ind. Eng. Chem.* **44**, 615 (1952).
17. M. Malveda, "Wet-Process Phosphoric Acid," *Chemical Economics Handbook*, SRI Consulting, Menlo Park, Calif., June 2003.
18. U.S. Pat. Appl. 20040137736 (May 15, 2004), J. Daviot, C. Reid, and D. Holmes.
19. J. R. Van Wazer, ed., *Phosphorus and Its Compounds*, Vol. 1, Interscience Publishers, New York, 1958, p. 493.
20. B. Wendrow and K. A. Kobe, *Chem. Rev.* **54**, 891 (1954).
21. D. R. Gard, in J. J. McKetta and W. A. Cunningham, eds., *Encyclopedia of Chemical Processing and Design*, Marcel Dekker, Inc., New York, 1990, Vol. 35, 429–495.
22. U.S. Pat. 2,462,104 (Feb. 22, 1949), W. H. Knox and co-workers (to Victor Chemical Co.); U.S. Pat. 2,631,102 (Mar. 10, 1953), F. E. Hubbard and J. S. Metcalf (to Monsanto Co.).
23. U.S. Pat. Appl. 20040112256 (June, 17, 2004), A. C. Tas.
24. U.S. Pat. Appl. 20040173122 (Sept. 1, 2004), M. Zimmerman.
25. T. Kanazawa, ed., *Inorganic Phosphate Materials*, Kodansha, Tokyo, Japan, 1989.
26. U.S. Pat. 4,515,772 (May 7, 1985), (to Procter and Gamble Co.); U.S. Pat. 4,627,977 (Dec. 9, 1986), A. Gaffar and T. G. Polefka (to Colgate-Palmolive Co.).
27. "Tetrapotassium Pyrophospahtes, Chemical Profiles," *Chem. Market Rept.* (May 9, 2005).
28. J. G. Rabatin, R. H. Gale, and A. E. Newkirk, *J. Phys. Chem.* **64**, 491 (1960).

29. T. D. Farr, *Phosphorus, Properties of the Element and Some of Its Compounds*, in *Chemical Engineering Report*, No. 8, Tennessee Valley Authority, Wilson Dam, Ala., 1950, pp. 39 and 58.
30. J. D. McGilvery, *ASTM Bull.* (19), 45 (1933).
31. C. Y. Shen and R. A. Herrmann, *Ind. Eng. Chem. Prod. Res. Dev.* **5**(4), 357 (1966); A. C. Zettlemoyer and C. H. Schneider, *J. Am. Chem. Soc.* **78**, 3870 (1956).
32. C. Y. Shen and C. F. Callis, *Soap Chem. Specialities*, **41**(2), 64 (1965); C. Y. Shen, *Ind. Eng. Chem., Prod. Res. Develop.* **5**(3), 272 (1966).
33. E. J. Griffith, *Ind. Eng. Chem.* **51**, 240 (1959).
34. M. Halmann, ed., *Analytical Chemistry of Phosphorus Compounds*, Wiley-Interscience, New York, 1972.
35. U.S. Pat. 3,661,514 (May 9, 1972), J. Herink (to FMC Corp.); U.S. Pat. 2,419,148 (Apr. 15, 1947), C. S. King (to Blockson Chemical Co.).
36. U.S. Pat. 3,309,174 (Mar. 14, 1967), R. Pals (to FMC Corp.).
37. U.S. Pat. 3,233,967 (Feb. 8, 1966), C. Y. Shen (to Monsanto Co.).
38. U.S. Pat. 3,932,590 (Jan. 13, 1976), R. Pals, R. J. Fuchs, and J. C. Schwartz (to FMC Corp.); U.S. Pat. 4,251,498 (Feb. 17, 1981), P. Hensler, D. F. Church, and R. W. Beger (to FMC Corp.); U.S. Pat. 4,255,274 (Mar. 10, 1981), P. Hensler, D. F. Church, and R. W. Beger (to FMC Corp.).
39. U.S. Pat. 3,495,937 (Feb. 17, 1970), C. Y. Shen (to Monsanto Co.).
40. B. Suresh and M. Yoneyama, "Industrial Phosphates," *Chemical Economics Handbook*, SRI Consulting, Menlo Park, Calif., March 2002.
41. R. J. Lewis, Sr., ed., *Dangerous Properties of Industrial Materials*, 11th ed., John Wiley & Sons, Inc., Hoboken, N. J., 2004.
42. E. J. Griffith and co-workers, eds., *Environmental Phosphorus Handbook*, Wiley-Interscience, New York, (1973).
43. *Phosphorus in the Environment: Its Chemistry and Biochemistry*, Ciba Foundation Symposium 57, Excerpta Medica, Amsterdam, 1979.

GENERAL REFERENCES

J. R. Van Wazer, ed., *Phosphorus and Its Compounds*, Vol. 1 (1958) and Vol. 2 (1961), Interscience Publishers, Inc., New York.

D. E. C. Corbridge, *Phosphorus: An Outline of Its Chemistry, Biochemistry, and Technology*, 4th ed., Elsevier, Amsterdam, the Netherlands, 1990.

K. Schrödter and co-workers, in B. Elvers, S. Hawkins, and G. Schulz, eds., *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, Germany, 1991, Vol. A19, 465–503.

A. D. F. Toy, *Phosphorus Chemistry in Everyday Living*, American Chemical Society, Washington, D.C., 1987.

P. Becker, *Phosphates and Phosphoric Acid*, 2nd ed., Marcel Dekker, Inc., New York, 1989.

DAVID R. GARD
Monsanto Company

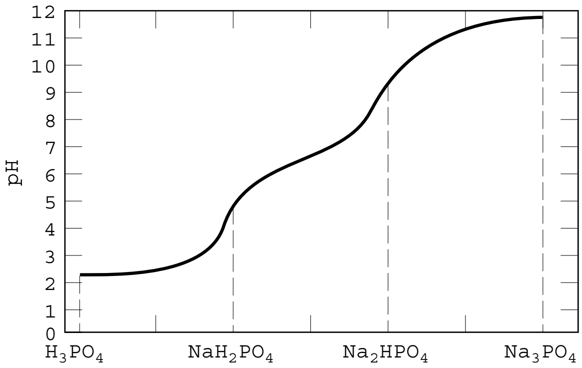


Fig. 1. Titration curve of orthophosphoric acid in the presence of sodium hydroxide.

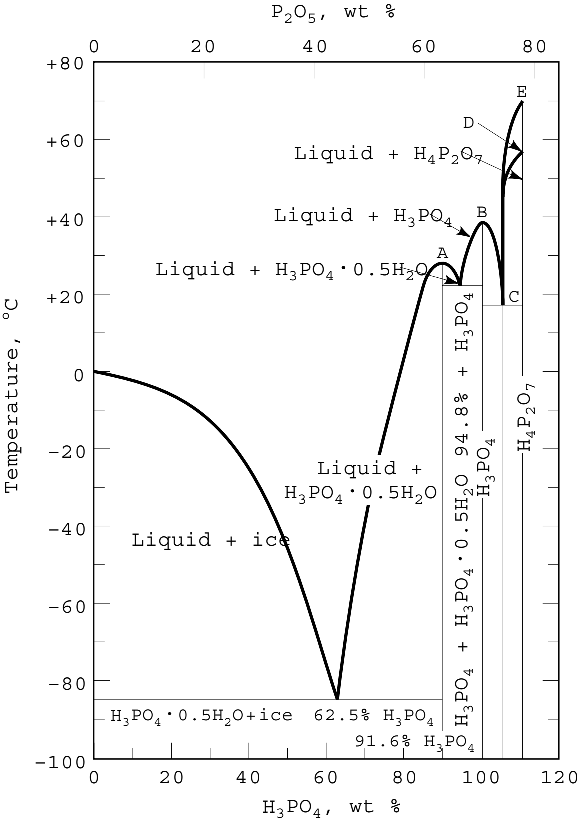


Fig. 2. Solid–liquid phase diagram of the H_2O–P_2O_5 system. The peaks A–E correspond to temperatures of 29.3, 38.85, 16.0, 54.3, and 71.5°C, respectively.

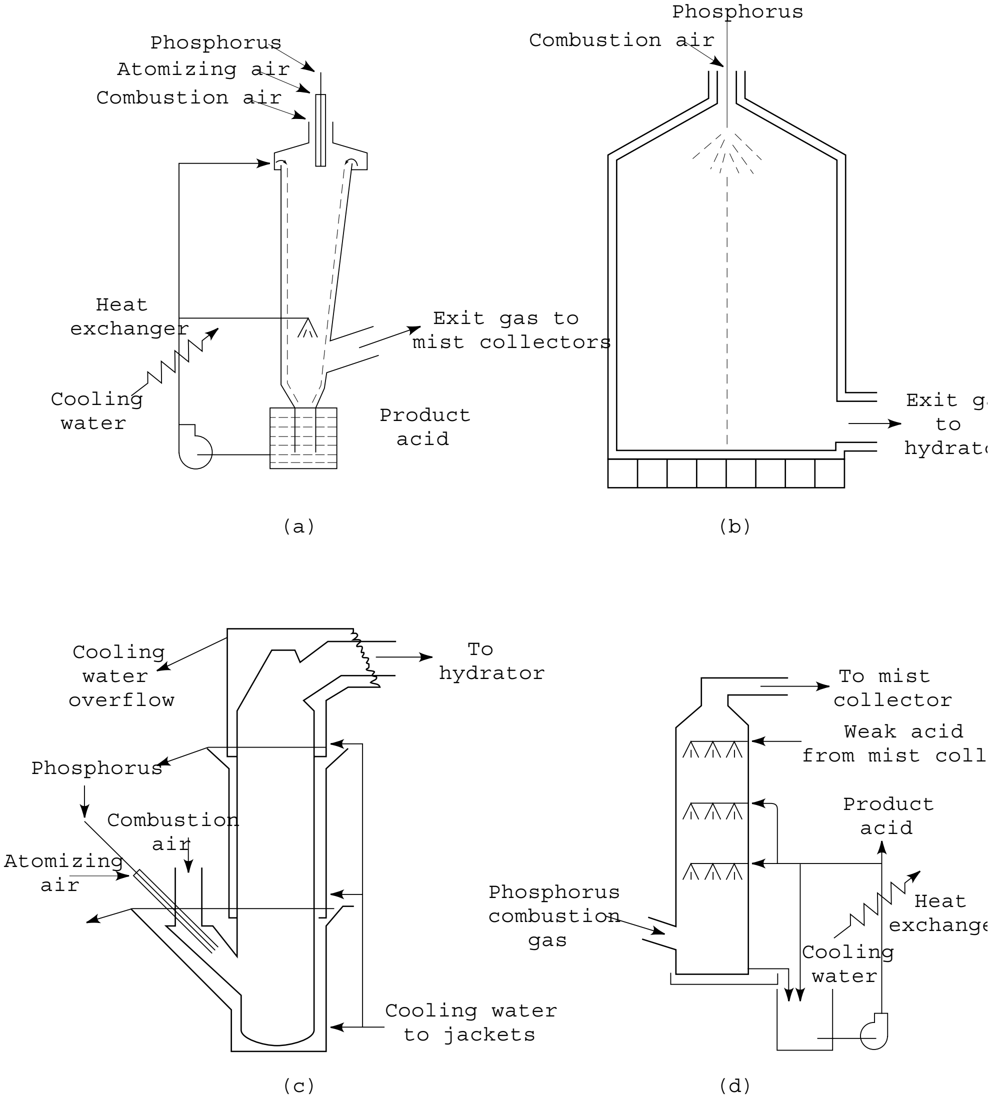


Fig. 3. Thermal phosphoric acid processes: (**a**) wetted-wall combustion chamber; (**b**) air-cooled combustion chamber; (**c**) water-cooled combustion chamber; and (**d**) hydrator–absorber.

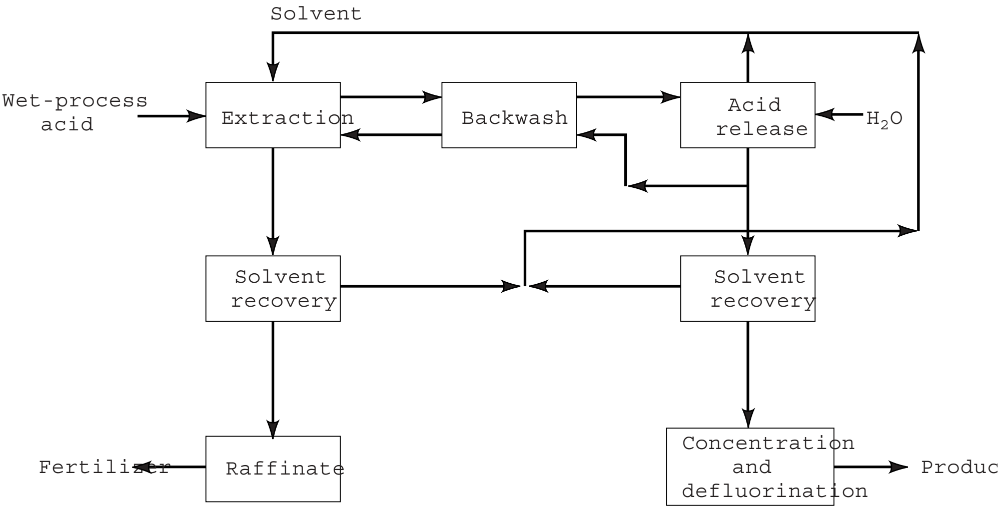


Fig. 4. Schematic diagram of the solvent extraction purification of wet-process phosphoric acid.

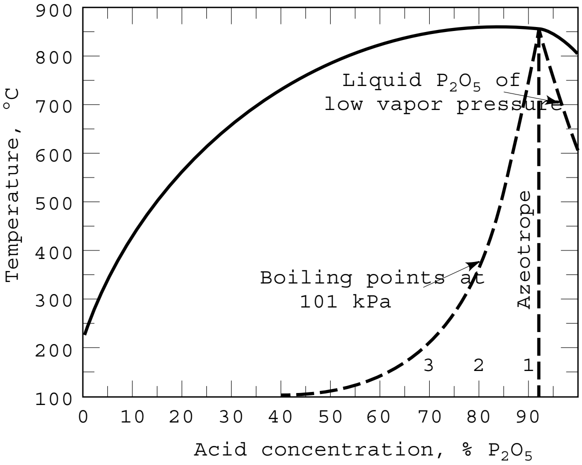


Fig. 5. Vapor−liquid phase diagram of the H_2O–P_2O_5 system at 101 kPa (1 atm), where 3 is ortho, 2 pyro, and 1 meta phosphoric acid. The solid line represents the approximate vapor composition.

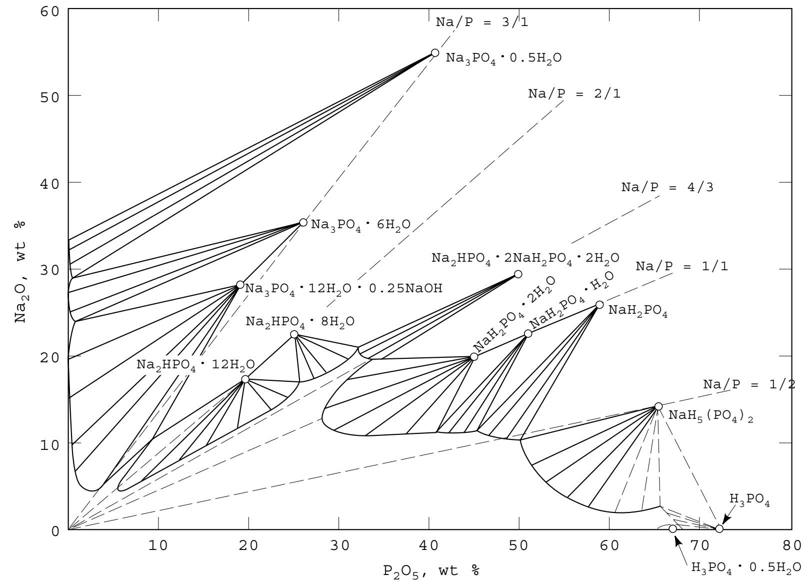


Fig. 6. Phase diagram of the $Na_2O-H_2O-P_2O_5$ (sodium orthophosphate) system at 25°C.

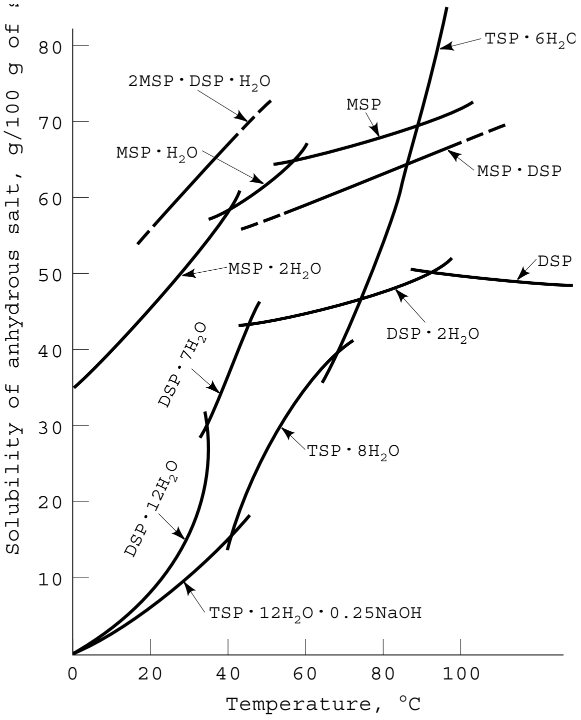


Fig. 7. Solubility of sodium orthophosphates as a function of temperature (20,21). MSP, DSP, and TSP are mono-, di-, and trisodium phosphates, respectively. (Courtesy of Marcel Dekker, Inc.)

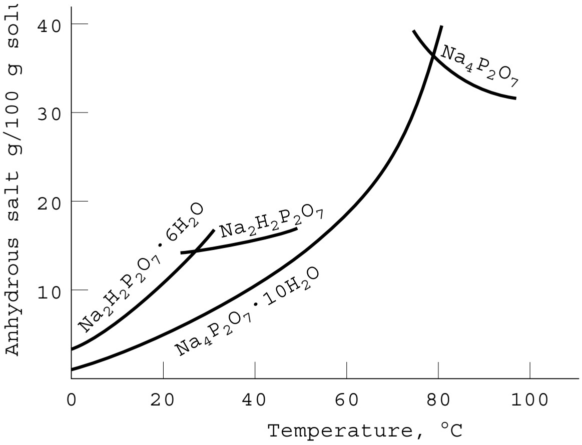


Fig. 8. Solubilities of sodium acid pyrophosphate and tetrasodium pyrophosphate.

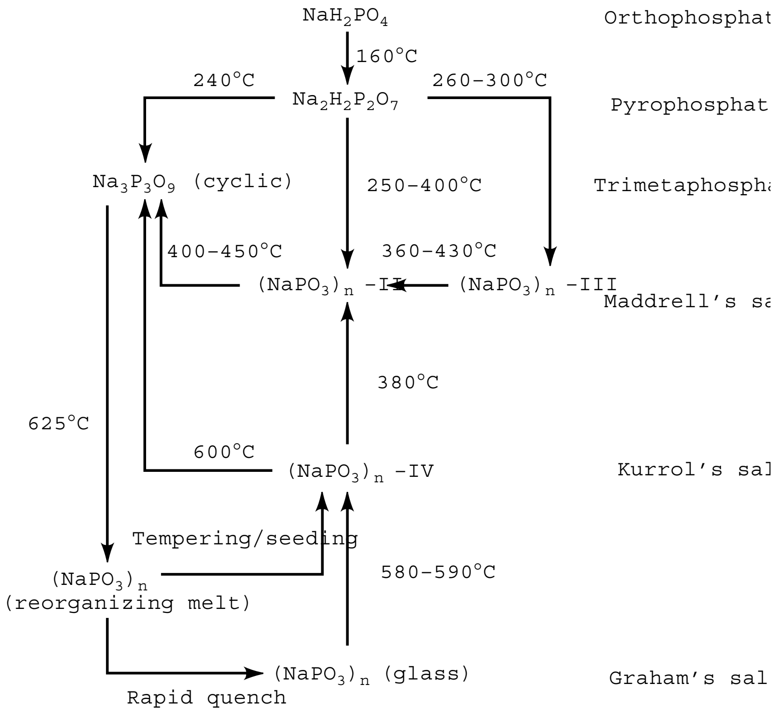


Fig. 9. Sodium polyphosphate conversions.

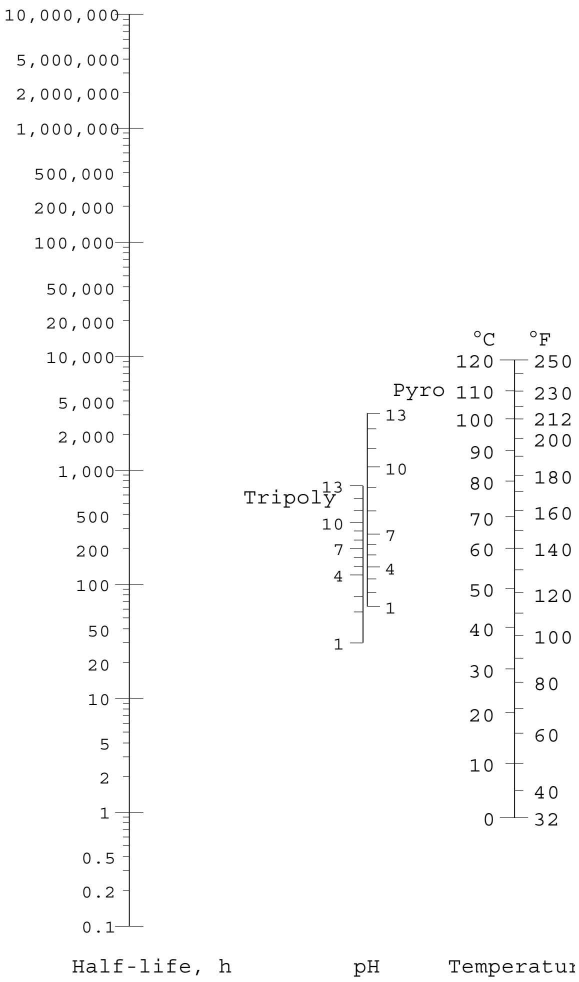


Fig. 10. Nomograph for estimating the rate of hydrolytic degradation of pyrophosphate and tripolyphosphate (tetramethylammonium salts) (33). For sodium salts at pH <11, multiply half-life by 0.7. (Courtesy of the American Chemical Society.)

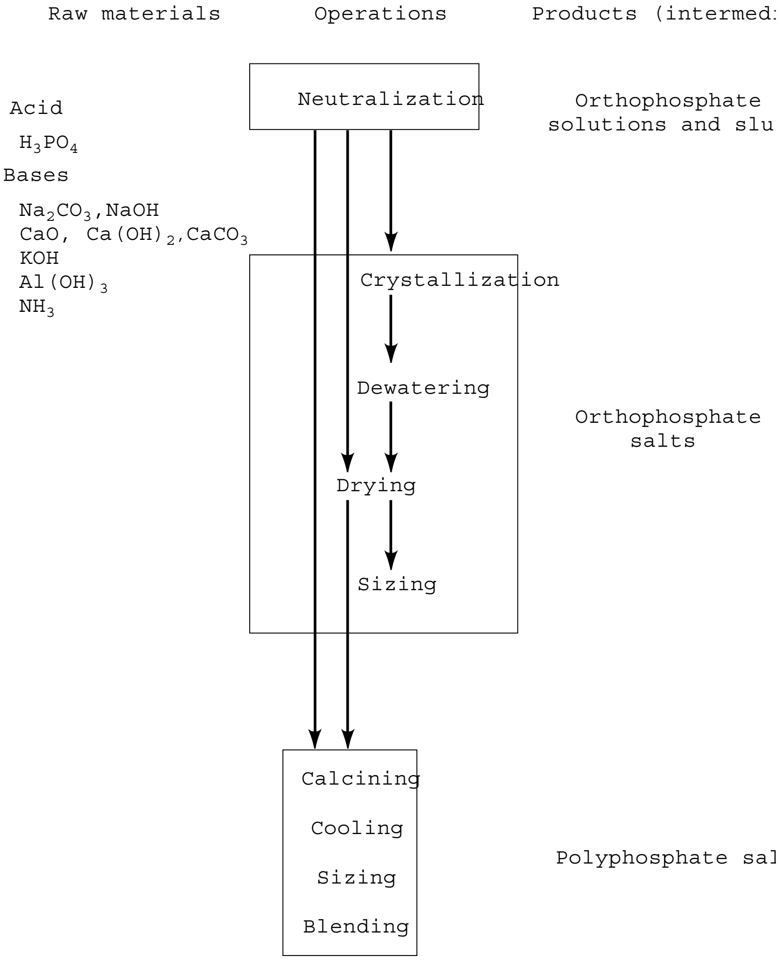


Fig. 11. General manufacturing scheme for phosphate salts.

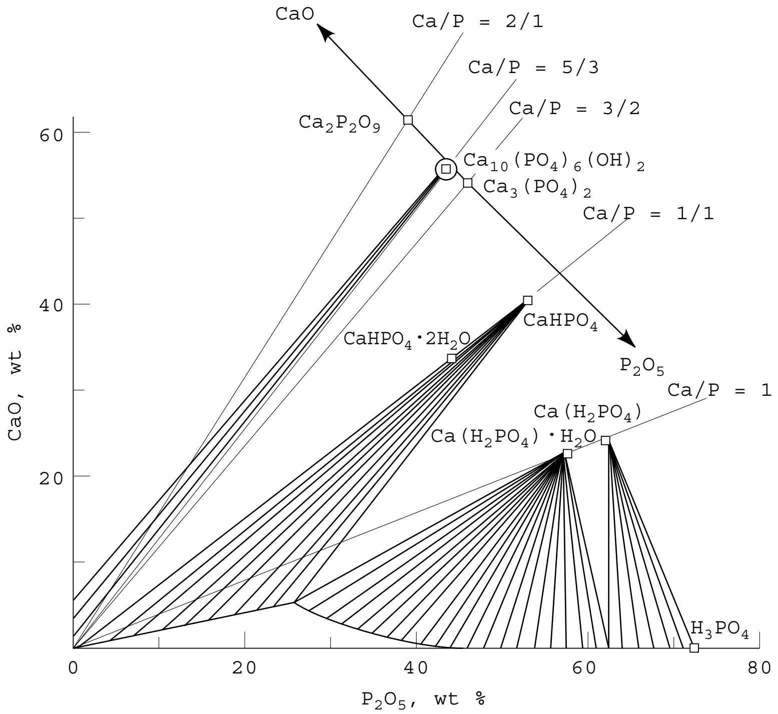


Fig. 12. Phase diagram of the $CaO-H_2O-P_2O_5$ (calcium orthophosphate) system where the circle represents the variable hydroxylapatite composition and (⊓⊔) the molecular species indicated.

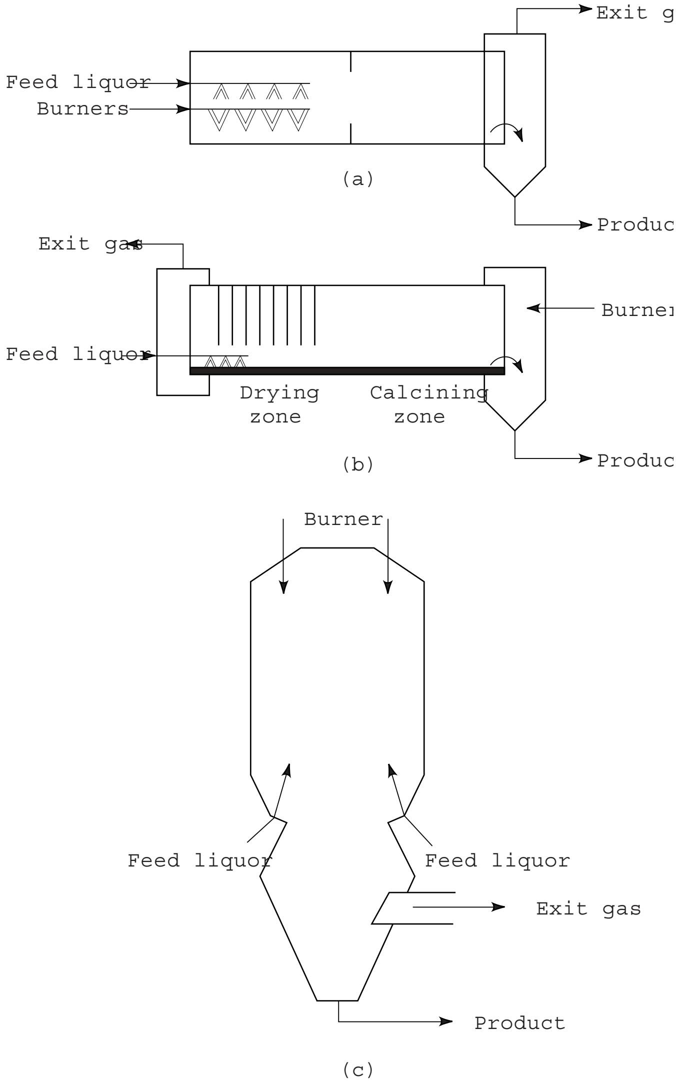


Fig. 13. Combined dryer–calciner processes for sodium tripolyphosphate: (**a**) cocurrent rotary dryer–calciner; (**b**) countercurrent rotary dryer–calciner; and (**c**) spray dryer–calciner.

Table 1. **Classification of Phosphate Anions**

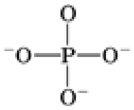
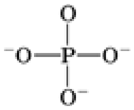
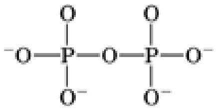
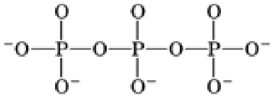
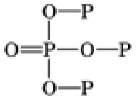
Designation	Oxide ratio, R	General formula	Structure/comment
phosphate + metal oxide	>3		mixtures; includes double salts and solid solutions
orthophosphate	3	PO_4^{3-}	
polyphosphates, $n = 2,3,4\ldots$	1–2	$P_nO_{3n+1}^{(n+2)-}$	
pyrophosphate	2	$P_2O_7^{4-}$	
tripolyphosphate	1.67	$P_3O_{10}^{5-}$	
metaphosphates			
$n = 3,4,5\ldots$	1	ca $(PO_3)_n$	cyclic
very large n	~1		very long chain
ultraphosphates, $0<x<1$	0–1	$P_2O_5(O^{2-})$	cross-linked chains and/or rings; some 
phosphorus pentoxide	0	$(P_2O_5)_n$	P_4O_{10} or continuous structures

Table 2. **Physical Properties of Aqueous Solutions of Phosphoric Acid**

Concentration, wt %		Density at 25°C, g/cm^3	Boiling point, °C	Freezing point, °C	Viscosity, mPa(=cP)		
H_3PO_4	P_2O_5				20°C	60°C	100°C
0	0	0.997	100.0	0	1.0	0.48	0.30
5	3.62	1.025	100.1	−0.8	1.1	0.54	0.33
10	7.24	1.053	100.2	−2.1	1.2	0.61	0.38
20	14.49	1.113	100.8	−6.0	1.6	0.78	0.48
30	21.73	1.182	101.8	−11.8	2.2	1.0	0.62
50	36.22	1.333	108	−44.0	4.3	1.8	1.1
75	54.32	1.573	135	−17.5	15	4.8	2.4
85	61.57	1.685	158	21.1	28	8.1	3.8
100	72.43	1.864	261	42.35	140	25	9.2
105	76.10	1.925	>300	16.0	600	70	1.9
115	83.29	2.044	>500			1500	250

Table 3. **Vapor Pressure of Phosphoric Acid Solutions, kPa**[a]

Concentration, wt %, H_3PO_4	Temperature, °C							
	20°C	30°C	40°C	60°C	80°C	100°C	110°C	140°C
0	2.35	4.24	7.37	20.0	47.3	101.3	143.3	
5	2.33	4.20	7.27	19.6	46.9	100.7	142.4	
10	2.31	4.13	7.23	19.5	46.7	100.4	142.1	
20	2.27	4.00	7.07	18.8	45.5	98.0	138.7	
30	2.17	3.85	6.73	18.1	43.6	94.0	120.8	
50	1.73	3.08	5.37	14.4	34.3	76.7	108.5	
75	0.75	1.33	2.33	6.27	14.8	32.0	45.3	119.3
85	0.29	0.53	0.93	2.63	6.51	14.8	21.3	59.3
100	0.004	0.008	0.016	0.057	0.177	0.487	0.773	2.71

[a] To convert kPa to mm Hg, multiply by 7.50.

Table 4. **Typical Analysis of Phosphoric Acids, wt %**

	Wet-process acid		Thermal acid
Assay	Merchant-grade[a]	Technical-grade[b,c]	Technical-grade[d]
P_2O_5	53.1	57	54.32
CaO	0.06		0.001
F	0.8	0.02	<0.0001
Al_2O_3	1.7		0.0003
Fe_2O_3	1.23	0.004	0.0004
MgO	0.58		0.0002
K_2O	0.01		0.0007
Na_2O	0.12		0.0025
SiO_2	0.07		0.0015
SO_4	2.2	0.04	<0.002

[a] Tennessee Valley Authority.

[b] Merchant-grade acid is purified to yield technical-grade.

[c] Société Chimique Prayon-Rupel.

[d] Monsanto Co.

Table 5. **Equilibrium Composition of the Strong Phosphoric Acids**[a]

P_2O_5, wt %	P_2O_5/H_2O	Percentage composition in terms of the constituent polyphosphoric acids[b], $n = 15$														High poly		
		1	2	3	4	5	6	7	8	9	10	11	12	13	14		$H_3P_3O_9$	$H_4P_4O_{12}$
67.4	0.263	100.0																
68.7	0.279	99.7	0.33															
70.4	0.302	96.2	3.85															
71.7	0.321	91.0	8.86	[f]														
73.5	0.352	77.1	22.1	0.79														
73.9	0.360	73.6	25.1	1.34														
75.7	0.394	53.9	40.7	4.86	0.46													
77.5	0.438	33.5	50.6	11.5	2.68	0.74	[f]											
79.1	0.481	22.1	46.3	20.3	7.82	2.26	1.02	0.34										
80.5	0.523	13.8	38.2	21.0	13.0	6.86	3.38	1.67	1.03	0.22								
81.0	0.542	12.2	34.0	22.7	14.6	8.42	4.36	2.27	1.41	0.56	[f]							
81.2	0.549	10.9	32.9	22.3	15.0	9.36	5.41	2.85	1.75	0.97	0.36	0.05						
82.4	0.594	7.32	23.0	19.3	15.9	12.3	8.21	5.73	3.89	2.52	1.36	0.91	0.14					
84.0	0.667	3.92	11.8	12.7	12.0	10.5	8.97	7.99	6.62	5.63	4.54	3.72	3.03	2.46	1.68	6.63		
85.0	0.717	2.28	6.36	7.32	8.01	8.17	7.67	7.22	6.93	6.42	5.89	5.27	4.69	3.99	3.83	16.9		
85.3	0.736	1.87	4.73	6.33	6.58	6.66	6.71	6.36	6.11	5.88	5.46	5.07	4.90	4.64	4.38	25.6		
86.1	0.787	1.46	2.81	3.74	4.43	4.52	4.77	4.79	4.93	4.67	4.54	4.67	4.63	4.38	4.17	43.5	0.17	
87.1	0.860	0.83	1.81	2.17	2.53	3.09	3.39	3.46	3.33	3.55	3.47	3.45	3.52	3.26	3.24	61.1		
87.0	0.920	0.50	0.82	1.56	1.76	1.72	2.03	2.13	2.26	2.07	2.26	2.06	2.20	1.99	2.30	76.4	0.42	0.11
89.4	1.066	1.88	1.52	0.77	0.61	0.62	0.68	0.54	0.71	0.86	1.03	0.98	1.16	1.23	1.37	86.8	1.17	0.41

[a] Ref. 15.

[b] $n = 1$, H_3PO_4; 2, $H_4P_2O_7$; 3, triphosphoric acid [10380-08-2], $H_5P_3O_{10}$; 4, tetraphosphate; etc.

[c] High poly material is retained by resin and includes the phosphoric acid of $n = 15$.

[d] Trimetaphosphoric acid [13566-25-1].

[e] Tetrametaphosphoric acid [13598-74-8].

[f] Trace.

Table 6. **Sodium Orthophosphates**

Compound	CAS Registry Number	Formula
sodium hemiphosphate	[14887-48-0]	$NaH_2PO_4{\cdot}H_3PO_4$
sodium dihydrogen phosphate monohydrate	[10049-21-5]	$NaH_2PO_4{\cdot}H_2O$
sodium dihydrogen phosphate dihydrate	[13472-35-0]	$NaH_2PO_4{\cdot}2H_2O$
sodium dihydrogen phosphate compound with disodium hydrogen phosphate (MSIDSP)	[39413-44-0]	$NaH_2PO_4{\cdot}Na_2HPO_4$
disodium hydrogen phosphate dihydrate	[10028-24-7]	$Na_2HPO_4{\cdot}2H_2O$
disodium hydrogen phosphate heptahydrate	[7782-85-6]	$Na_2HPO_4{\cdot}7H_2O$
disodium hydrogen phosphate octahydrate	[67417-37-2]	$Na_2HPO_4{\cdot}8H_2O$
disodium hydrogen phosphate dodecahydrate	[10039-32-4]	$Na_2HPO_4{\cdot}12H_2O$
trisodium phosphate hemihydrate	[60593-58-0]	$Na_3PO_4{\cdot}0.5H_2O$
trisodium phosphate hexahydrate	[15819-50-8]	$Na_3PO_4{\cdot}6H_2O$
trisodium phosphate octahydrate	[6053-59-1]	$Na_3PO_4{\cdot}8H_2O$
trisodium phosphate dodecahydrate (TSP crystalline)	[10101-89-0]	$4(Na_3PO_4{\cdot}12H_2O){\cdot}NaOH$

Table 7. **Potassium Orthophosphates**

Compound	CAS Registry Number	Formula
phosphoric acid, potassium salt (2:1)	[14887-42-4]	$KH_2PO_4 \cdot H_3PO_4$
potassium dihydrogen phosphate compound with dipotassium hydrogen phosphate monohydrate		$KH_2PO_4 \cdot 2K_2HPO_4 \cdot H_2O$ or $KH_2PO_4 \cdot 3K_2HPO_4 \cdot H_2O$
monopotassium phosphate (MKP)	[7778-77-0]	KH_2PO_4
dipotassium phosphate (DKP)	[7758-11-4]	K_2HPO_4
dipotassium hydrogen phosphate trihydrate	[16788-57-1]	$K_2HPO_4 \cdot 3H_2O$
dipotassium hydrogen phosphate hexahydrate	[78436-04-1]	$K_2HPO_4 \cdot 6H_2O$
tripotassium phosphate	[7778-53-2]	K_3PO_4
tripotassium phosphate trihydrate	[22763-03-7]	$K_3PO_4 \cdot 3H_2O$
tripotassium phosphate heptahydrate	[22763-02-6]	$K_3PO_4 \cdot 7H_2O$
tripotassium phosphate nonahydrate	[78436-05-2]	$K_3PO_4 \cdot 9H_2O$

Table 8. **Calcium Phosphates in the CaO–P_2O_5–H_2O System**

Compound	CAS Registry Number	Formula	*Chemical Abstracts* or common name
calcium hydrogen phosphate	[7757-93-9]	$CaHPO_4$	dicalcium phosphate; monetite [21063-37-6]
calcium hydrogen phosphate hemihydrate	[78436-06-3]	$CaHPO_4 \cdot 0.5H_2O$	metabrushite [78436-06-3]
calcium hydrogen phosphate dihydrate	[7789-77-7]	$CaHPO_4 \cdot 2H_2O$	brushite [14567-92-1]
α-tricalcium phosphate	[7758-87-4]	$\alpha\text{-}Ca_3(PO_4)_2$	
β-tricalcium phosphate	[7758-87-4]	$\beta\text{-}Ca_3(PO_4)_2$	
octacalcium phosphate	[14096-86-7]	$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	
hydroxyapatite	[1306-06-5]	$Ca_{10}(PO_4)_6(OH)_2$	
fluorapatite	[1306-05-4]	$Ca_{10}(PO_4)_6F_2$	
phosphoric acid, calcium salt (2:1)	[7758-23-8]	$Ca(H_2PO_4)_2$	monocalcium phosphate (MCP)
phosphoric acid, calcium salt hydrate (2:1:1)	[10031-30-8]	$Ca(H_2PO_4)_2 \cdot H_2O$	monocalcium phosphate monohydrate
phosphoric acid, calcium salt hydrate (2:1:2)	[5221-07-5]	$Ca(H_2PO_4)_2 \cdot 2H_2O$	monocalcium phosphate dihydrate

Table 9. **Other Phosphates of Commercial Interest**

Compound	CAS Registry Number	Formula
aluminum dihydrogen tripolyphosphate	[13939-25-8]	$AlH_2P_3O_{10}$
aluminum phosphate dihydrate (variscite)	[13477-75-3]	$AlPO_4\cdot 2H_2O$
monoaluminum phosphate sesquihydrate	[78436-09-6]	$Al(H_2PO_4)_3\cdot 1.5H_2O$
dialuminum phosphate trihydrate	[78436-10-9]	$Al_2(HPO_4)_3\cdot 3H_2O$
poly(aluminum metaphosphate)	[13776-88-0]	$(Al(PO_3)_3)_n$
monoiron(III) phosphate	[18718-09-7]	$Fe(H_2PO_4)_3$
trimagnesium phosphate octahydrate	[13446-23-6]	$Mg_3(PO_4)_2\cdot 8H_2O$
aluminum hemiphosphate	[66906-44-3]	$AlH_3(PO_4)_2\cdot H_2O$
phosphoric acid, aluminum salt hydrate (2:1:3)	[39611-87-5]	$AlH_3(PO_4)_2\cdot 3H_2O$
phosphoric acid, aluminum salt (1:1) hydrate (2:7)	[78436-11-0]	$AlPO_4\cdot 3.5H_2O$
phosphoric acid, aluminum sodium salt (8:2:3)	[110279-59-1]	$Na_3Al_2H_{15}(PO_4)_8$
phosphoric acid, aluminum sodium salt (3:3:1) tetrahydrate	[10305-76-7]	$NaAl_3H_{14}(PO_4)_8\cdot 4H_2O$
phosphoric acid, iron(III) salt hydrate (2:1:2.5)	[31359-25-8]	$FeH_3(PO_4)_2\cdot 2.5H_2O$
triphosphoric acid, monosodium salt	[15575-11-8]	$NaH_4P_3O_{10}$
triphosphoric acid, disodium salt	[33689-84-8]	$Na_2H_3P_3O_{10}$
triphosphoric acid, trisodium salt	[13772-25-3]	$Na_3H_2P_3O_{10}$
triphosphoric acid, tetrasodium salt	[25616-37-3]	$Na_4HP_3O_{10}$
pentasodium salt	[7758-29-4]	$Na_5P_3O_{10}$
sodium potassium tripolyphosphate	[24315-83-1]	$Na_5P_3O_{10}\cdot K_5P_3O_{10}$
sodium trimetaphosphate	[7785-84-4]	$Na_3P_3O_9$
sodium tetrametaphosphate	[13396-41-3]	$Na_4P_4O_{12}$
sodium hexametaphosphate	[10124-56-8]	$(NaPO_3)_n$[a]
poly(sodium metaphosphate) (insoluble metaphosphate (IMP))	[10361-03-2]	$(NaPO_3)_n$
zirconium phosphate monohydrate	[13933-56-7]	$Zr(HPO_4)_2\cdot H_2O$
zirconium phosphate dihydrate	[13772-31-1]	$Zr(HPO_4)_2\cdot 2H_2O$

[a] $n = \sim 6–20$.

Table 10. **Pyrophosphates**

Compound	CAS Registry Number	Formula
aluminum pyrophosphate	[14696-66-3]	$Al_4(P_2O_7)_3$
calcium dihydrogen pyrophosphate (calcium acid pyrophosphate)	[14866-19-4]	$CaH_2P_2O_7$
calcium pyrophosphate	[7790-76-3]	$Ca_2P_2O_7$
potassium trihydrogen pyrophosphate	[16270-75-0]	$KH_3P_2O_7$
dipotassium dihydrogen pyrophosphate (potassium acid pyrophosphate)	[14691-84-0]	$K_2H_2P_2O_7$
tripotassium hydrogen pyrophosphate	[16270-76-1]	$K_3HP_2O_7$
tetrapotassium pyrophosphate	[7320-34-5]	$K_4P_2O_7$
sodium trihydrogen pyrophosphate (monosodium pyrophosphate)	[13847-74-0]	$NaH_3P_2O_7$
disodium dihydrogen pyrophosphate (sodium acid pyrophosphate)	[7758-16-9]	$Na_2H_2P_2O_7$
disodium dihydrogen pyrophosphate hexahydrate	[13510-98-0]	$Na_2H_2P_2O_7 \cdot 6H_2O$
trisodium hydrogen pyrophosphate (trisodium pyrophosphate)	[14691-80-6]	$Na_3HP_2O_7$
trisodium hydrogen pyrophosphate monohydrate	[26573-04-6]	$Na_3HP_2O_7 \cdot H_2O$
trisodium hydrogen pyrophosphate nonahydrate	[16457-94-6]	$Na_3HP_2O_7 \cdot 9H_2O$
tetrasodium pyrophosphate (TSPP)	[7722-88-5]	$Na_4P_2O_7$
tetrasodium pyrophosphate decahydrate	[13472-36-1]	$Na_4P_2O_7 \cdot 10H_2O$
silicon pyrophosphate	[13827-38-8]	SiP_2O_7
titanium pyrophosphate	[13470-09-2]	TiP_2O_7