Phosphoric Acid and Phosphates

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Monophosphoric Acid

Phosphoric acid was first prepared in 1694 by Boyle from P_4O_{10} soon after the discovery of elemental phosphorus.

1.1. Properties

Physical Properties. Pure, anhydrous phosphoric acid, H_3PO_4, M_r 98, *mp* 42.35 °C [1], ϱ 1.88 g/cm^3, is a colorless, crystalline compound, that is readily soluble in water.

A hemihydrate of phosphoric acid, $H_3PO_4 \cdot {}^1/_2\ H_2O$, *mp* 29.25 °C, is also known.

Figure 1 shows the $H_3PO_4 - H_2O$ phase diagram [2].

Phosphoric acid is infinitely miscible with water. It is commercially available in three standard concentrations:

75 % H_3PO_4 with 54.3 % P_2O_5, *mp* −20 °C
80 % H_3PO_4 with 58.0 % P_2O_5, *mp* 0 °C
85 % H_3PO_4 with 61.6 % P_2O_5, *mp* +21 °C

The 85 % acid (ϱ 1.687 g/cm^3) has syrupy consistency. It tends to supercool, especially when transferred to glass bottles. It is usually stored in heated containers in order to avoid crystallization. The anhydrous acid can be obtained from the 85 % acid by evaporation in vacuum at 80 °C.

Figures 2 and 3 show plots of the density and viscosity of phosphoric acid against concentration and temperature. The density is practically constant in the temperature range 25 – 100 °C. As shown in Figure 4, the same is true of the specific heat.

The boiling point of phosphoric acid as a function of concentration and the composition

DOI: 10.1002/14356007.a19_465.pub3

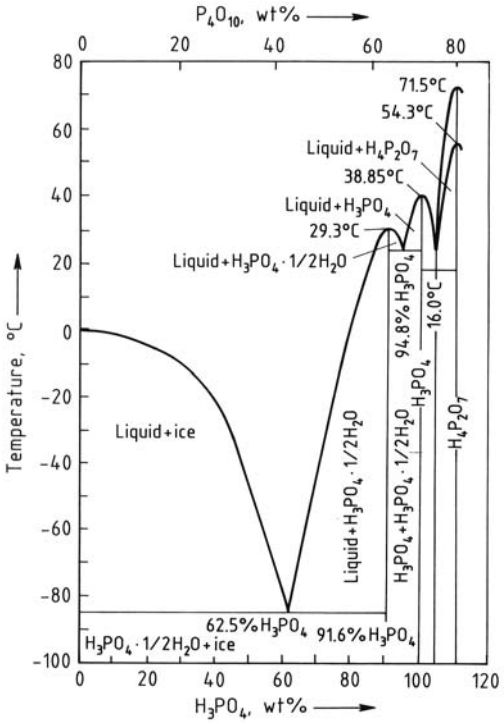


Figure 1. $H_3PO_4-H_2O$ phase diagram

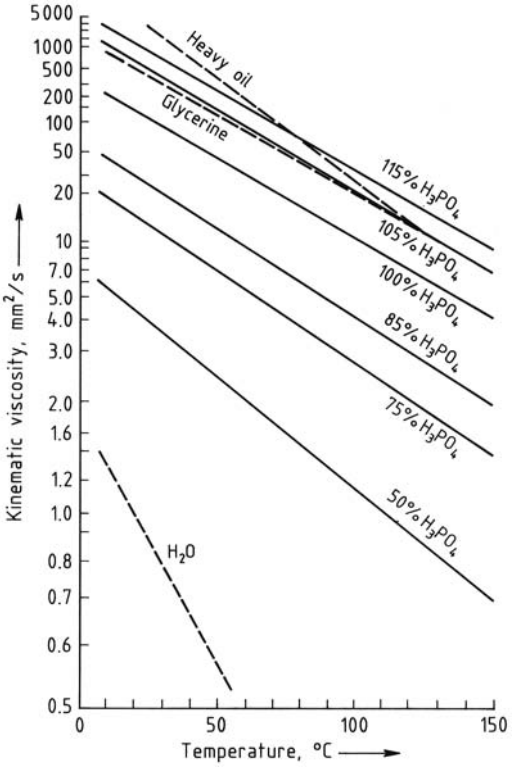


Figure 3. Kinematic viscosity of phosphoric acid as a function of concentration and temperature

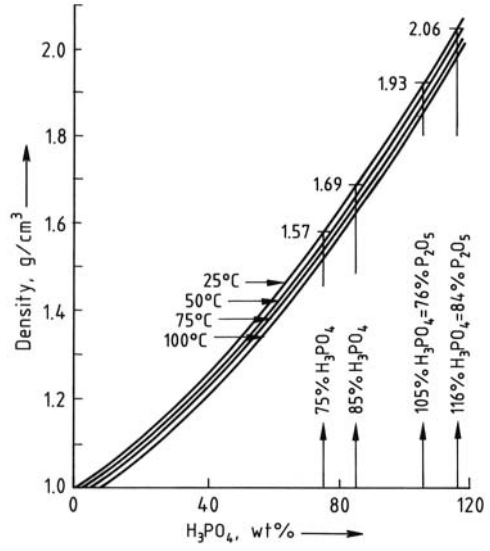


Figure 2. Density of phosphoric acid as a function of concentration and temperature

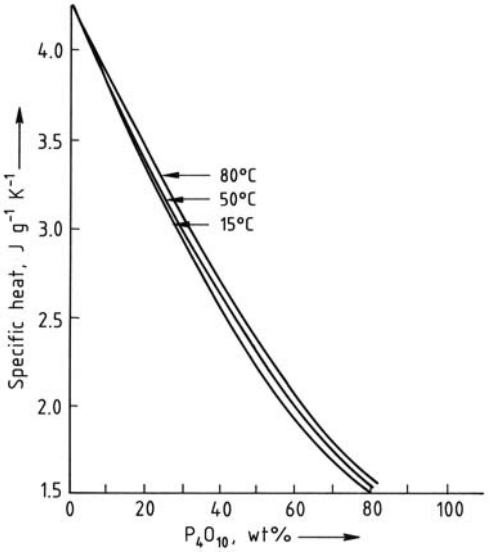


Figure 4. Specific heat of phosphoric acid as a function of concentration and temperature

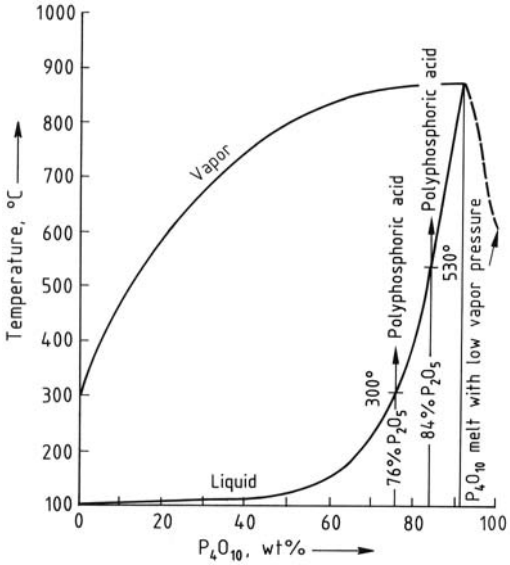


Figure 5. Liquid – vapor equilibrium diagram of the P_4O_{10} – H_2O system

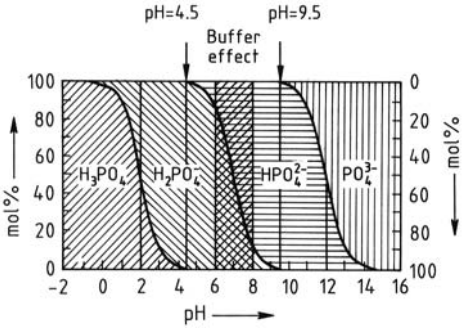


Figure 6. Ion concentration of a phosphoric acid (phosphate) solution as a function of pH

of the corresponding vapor phases are shown in Figure 5 [3]. Only traces of P_4O_{10} are present in the gas phase at temperatures up to 300 °C. P_4O_{10} appears in the vapor phase only above this temperature after condensation of phosphoric acid to form polyphosphoric acids.

Chemical Properties. Monophosphoric acid is tribasic. The dissociation constants are $K_1 = 7.1\times10^{-3}$, $K_2 = 6.3\times10^{-8}$, and $K_3 = 4.7 \times 10^{-13}$.

Accordingly, primary, secondary, and tertiary salts are formed with bases. Aqueous solutions of dihydrogenphosphates are weakly acidic, while those of hydrogenphosphates and tertiary phosphates are weakly or strongly alkaline, respectively. As shown in Figure 6, mixtures of dihydrogenphosphates and hydrogenphosphates act as buffers, e.g., in the range pH 6 to 8.

1.2. Production

Two methods are used for the industrial production of phosphoric acid. The wet digestion of phosphate rock with mineral acids is the most important process in terms of volume. Digestion is usually carried out with sulfuric acid, but nitric acid [4] or hydrochloric acid [5] are also used to a lesser extent. The acid obtained in this process is called wet phosphoric acid.

The second process for the production of phosphoric acid starts with elemental phosphorus, which is obtained from crude phosphate, coke, and silica in an electric resistance furnace (→ Phosphorus), and subsequently oxidized to P_4O_{10}. The acid obtained by hydration of the oxide is generally termed thermal phosphoric acid.

1.2.1. Thermal Processes

The production of phosphoric acid from elemental phosphorus is carried out in two stages: combustion with excess air to give P_4O_{10} and hydration of P_4O_{10} to form H_3PO_4:

$$P_4 + 5\,O_2 \rightarrow P_4O_{10} \quad \Delta H = -3053\ \text{kJ/mol} \qquad (1)$$

$$P_4O_{10} + 6\,H_2O \rightarrow 4\,H_3PO_4 \quad \Delta H = -377\ \text{kJ/mol} \qquad (2)$$

The IG and Tennessee Valley Authority (TVA) processes for the production of phosphoric acid are distinguished by the method of absorption and hydration of P_4O_{10}. The Hoechst process differs from these in that it utilizes the heat of phosphorus combustion for steam generation.

IG Process. [6]. In the IG process (Fig. 7), phosphorus combustion and P_4O_{10} absorption are carried out in a single stage in a common tower. The tower walls are slightly conically inclined so that the recycled acid, overflowing inside from a cup located at the tower head, can completely cover the wall with an acid layer. This

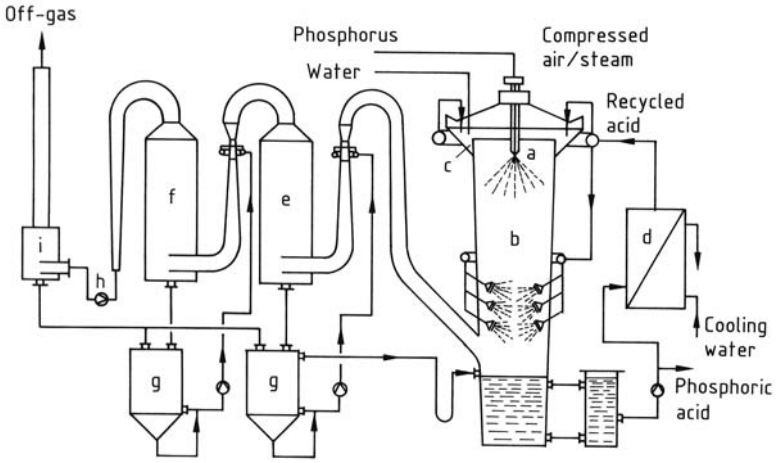


Figure 7. Production of thermal phosphoric acid (IG process)
a) Nozzle; b) Combustion tower; c) Overflow cup; d) Heat exchanger; e) and f) Venturi scrubbers; g) Receiver for wash acid; h) Off-gas fan; i) Separator

protects the wall from the phosphorus flame that descends from the tower head and reaches a temperature > 2000 °C. The recycling phosphoric acid dissolves the phosphorus pentoxide formed and dissipates the heat from the reaction zone. It is collected below the acid tower and recycled to the tower cup after passing through the heat exchanger.

Phosphoric acid overflows from the tower cup at ca. 60 °C and is heated on the way along the tower walls to up to 85 °C. About 80 % of the heat generated is dissipated by the cooling water, 17 % by off-gas and water evaporation, and 3 % by the sensible heat of the acid.

The phosphorus is sprayed into the tower from a binary nozzle by pressurized air or steam at up to 1.5 MPa. It is ejected from the nozzle at such a high speed that the phosphorus flame is kept away from the head and cannot damage it. A slight underpressure is maintained in the tower, generated by a fan which draws the combustion air from an annular aperture around the nozzle at the tower head. The off-gas is discharged in the wash stage. Here, P_4O_{10} that is entrained in the off-gas in the form of aerosol or acid droplets is separated. It accounts for ca. 30 % of the total conversion. The wash acid is added to the tower acid. Venturi systems, wash towers operated with or without packing, or demister elements packed with glass fibers are used as separators [7].

All parts of the equipment which come into contact with P_4O_{10}-containing off-gases are made of rubber-coated steel, stainless steel, or plastic. A stainless steel with very low carbon content, stable against concentrated phosphoric acid at up to 100 °C, has prevailed as construction material for the acid tower.

In addition to the phosphoric acid flowing down on the tower walls, phosphoric acid is sprayed into the tower through nozzles in the lower tower half below the phosphorus flame and perpendicular to the off-gas flow. This decreases the off-gas temperature to ca. 100 °C.

The orthophosphoric acid obtained is virtually free of lower phosphorus oxides and its H_3PO_3 content is 0.1 %.

Thermal phosphoric acid contains only traces of impurities due to the use of pure phosphorus for combustion. Only arsenic, a natural companion of elemental phosphorus which is contained in the acid at a concentration of 5 –30 ppm, need be removed in a further purification step. This is accomplished by precipitation of arsenic sulfide with hydrogen sulfide followed by filtration. The hydrogen sulfide is generated by injecting Na_2S solution into the phosphoric acid. This is done either in a precipitation tower with subsequent filtration after addition of activated charcoal and kieselgel [8], or more directly and simply in a centrifugal pump which immediately conveys the acid to the filter [9].

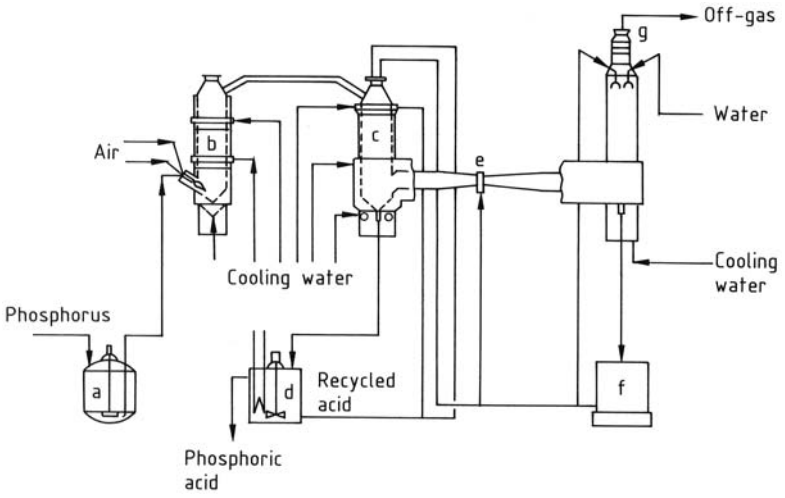


Figure 8. Production of thermal phosphoric acid (TVA process)
a) Storage tank; b) Combustion chamber; c) Absorption tower; d) Cooled receiver; e) Venturi scrubbers; f) Dilute acid tank; g) Separator

TVA Process. [10]. In the Tennessee Valley Authority (TVA) process phosphorus combustion and P_4O_{10} absorption are carried out separately (Fig. 8).

The vertical, cylindrical, stainless steel phosphorus combustion chamber is externally cooled. The phosphorus burner is installed laterally and is directed downwards toward the bottom of the combustion chamber at an angle of ca. 40°.

The gas discharge and the connection to the absorption tower are located at the top of the combustion chamber. A layer of polyphosphoric acid is formed from generated P_4O_{10} and atmospheric moisture, which protects the inner walls against corrosion. The polyphosphoric acid contains ca. 92 % P_2O_5, and its vaporization point is 867 °C. Phosphorus and air are introduced in a manner similar to the IG process.

The stainless steel cylindrical absorption tower with a conical head is also externally cooled. The inner tower walls are sprayed with dilute phosphoric acid from the off-gas purification stage and with recycled, concentrated phosphoric acid such that an unbroken acid film is formed. The phosphoric acid so produced contains 54 – 83 % P_2O_5.

A significant part of the P_4O_{10} product is entrained in the gas flow from the absorption tower. Thus, depending on whether the product is orthophosphoric acid (54 % P_4O_{10}) or superphosphoric acid (83 % P_4O_{10}), 40 – 70 % of the acid produced accumulates in the gas purification stage. Venturi scrubbers, wash towers, and demisters with webs made of special steel are used for flue-gas purification.

Hoechst Process. [11]. The heat generated by combustion of phosphorus is unused and is dissipated by cooling in the IG and TVA processes. In the Hoechst process (Fig. 9), operated industrially since 1989, this energy is used for steam generation. Phosphorus combustion and P_2O_5 hydration are performed separately.

Liquid phosphorus and dried air are injected into the bottom of a vertical stainless steel combustion chamber and are combusted to give P_4O_{10}. The walls of the combustion chamber are made of pipe coils through which deionized water is pumped. The steam – condensate mixture formed in the coils by dissipation of the heat of combustion is kept at a pressure of 15 – 18 MPa. The mixture is separated into gas and liquid in a separator. The remaining condensate is returned to the water storage tank, and the evaporated portion is replenished by addition of deionized water. The high-pressure steam is transferred from the separator to the combustion chamber, where the steam temperature is increased to 400 – 500 °C at 15 – 18 MPa in a superheater. The pressure is then released, and the steam is saturated with water and used as a heat-transfer medium. The heat dissipation in the

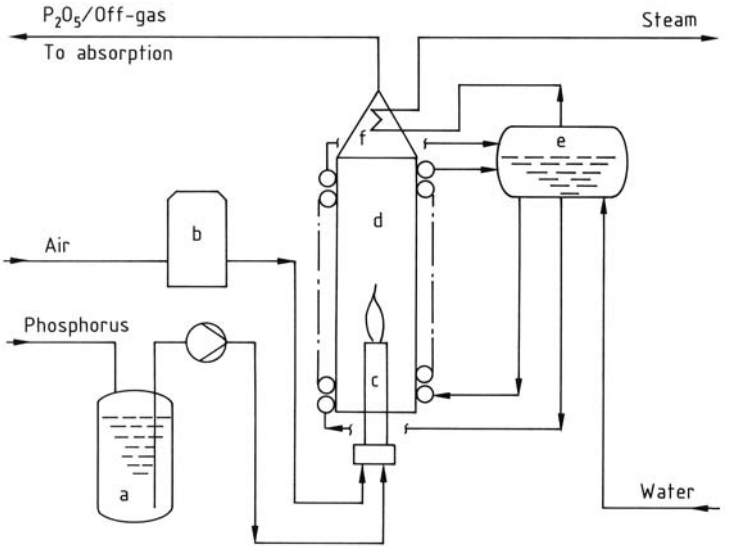


Figure 9. Schematic of the Hoechst process
a) Storage tank; b) Air dryer; c) Burner; d) Combustion chamber; e) Separator; f) Superheater

phosphorus combustion is controlled so that the temperature of the P_4O_{10}-containing off-gas is high enough to avoid separation of P_4O_{10} on the way to the absorption tower, where hydration of P_4O_{10} is carried out. An acid film is formed on the tower walls by concentrated recycled acid, similar to the IG process.

1.2.2. Wet Processes

The digestion of phosphate rock with sulfuric acid has been known since the mid-1880s. However, intensive research and development in this area started only after World War II, due to increased use of mineral fertilizers.

The digestion of fluorapatite with sulfuric acid proceeds according to Equation 3:

$$Ca_5(PO_4)_3F + 5\,H_2SO_4 + 5x\,H_2O \rightarrow 5\,CaSO_4 \cdot x\,H_2O + 3\,H_3PO_4 + HF \quad (3)$$

$x = 0, 1/2, 2$

However, concurrent side reactions occur with other, secondary components of the crude phosphate. Their reaction products are then largely dissolved in the wet phosphoric acid. The typical composition of crude wet phosphoric acid (in wt %) is as follows:

P_2O_5	30.0
SO_3	2.1
F	2.17
Si (mainly as SiF_6^{2-})	0.41
Ca	0.45
Mg	0.13
Fe	0.08
Al	0.04
Cr	0.022
Zn	0.019
V	0.013
Ni	0.0034
Cu	0.0027
Mn	0.0009
As	0.0007
Pb	0.0002

Calcium sulfate can precipitate in three different modifications, depending on the temperature and the phosphoric acid concentration (Fig. 10). The designation of the various wet processes is derived from the modification formed in the digestion stage. Thus, dihydrate (DH) and hemihydrate (HH) processes are distinguished. In other processes, two crystalline forms are formed sequentially and separated by recrystallization (HH/DH or DH/HH processes).

So far, the development of an anhydrite process has failed because the high reaction temperature of 120 – 130 °C required for anhydrite formation causes insurmountable corrosion problems.

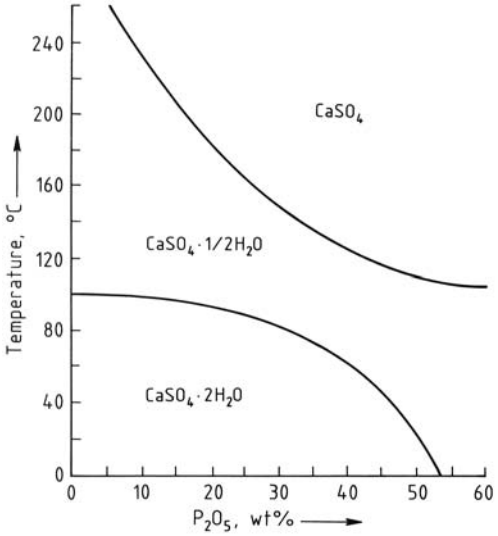


Figure 10. Stability range of calcium sulfate and its hydrates in phosphoric acid

Two basic operations are common to all wet phosphoric acid processes: digestion in a reactor and removal of $CaSO_4$ by filtration.

Reactors. Originally digestion was carried out in several large stirred tanks arranged in series, with recirculation of the digestion slurry by pumps. The introduction of single tanks brought an essential simplification as well as an improvement of the circulation for compensation of temperature and concentration fluctuations, and thus for optimization of the crystallization conditions [12, 13]. Round models (see Fig. 11) as well as rectangular ones were constructed. In the round single tank, the reaction components are slowly moved in a circle in the outer, annular space with vigorous, local agitation. Part of the digestion slurry overflows into the central space and flows to filtration. In medium-sized facilities (200 – 400 t/d P_2O_5), air is blown onto the surface for dissipation of the heat of reaction (2 GJ/t P_2O_5 in a DH process). In larger plants, the heat is dissipated by vacuum evaporation of water from a recycled partial stream of the slurry in a flash cooler [14, 15].

Filters. About 4 – 6 t of $CaSO_4$ per tonne of P_2O_5 produced must be filtered from the wet phosphoric acid. After initially using box band filters [16], producers switched to the use of plane and tilt-cell filters (Prayon, Bird, Eimco, UCEGO

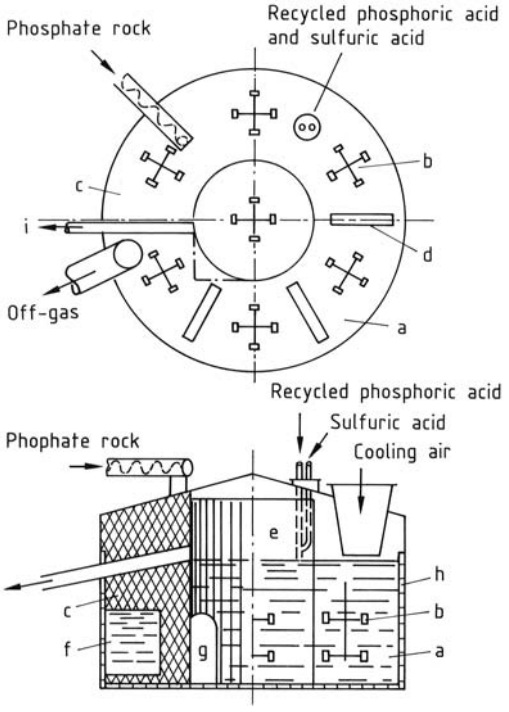


Figure 11. Single tank round model
a) Outer annular section; b) Agitators; c) Partition; d) Cooling air nozzles; e) Center section; f) Outer passage; g) Passage to the center cylinder; h) Carbon bricks; i) Overflow channel

[13, 15, 17, 18]). The effective filter area can approach up to 200 m^2. Later, band filters with larger outputs and filter areas exceeding 100 m^2 became available. In the filtration, the wet phosphoric acid is drawn off from the solids in a partial vacuum. Adhering acid is washed off the solids in two or three stages in countercurrent. The wash acid is discharged separately and recycled to the reactor. The discharge of the filter cake is carried out by tilting the filter pans, by means of a screw conveyor, or by stripping from the band.

Due to technical progress in reactor and filter construction, production units for wet phosphoric acid now have capacities up to 1000 t/d of P_2O_5.

Dihydrate Process. The dihydrate process is the classical method for the production of wet phosphoric acid (Fig. 12). Prior to digestion, the phosphate rock must usually be ground to a fineness of 75 % $<$ 150 μm. Phosphate rock and concentrated sulfuric acid are charged spatially

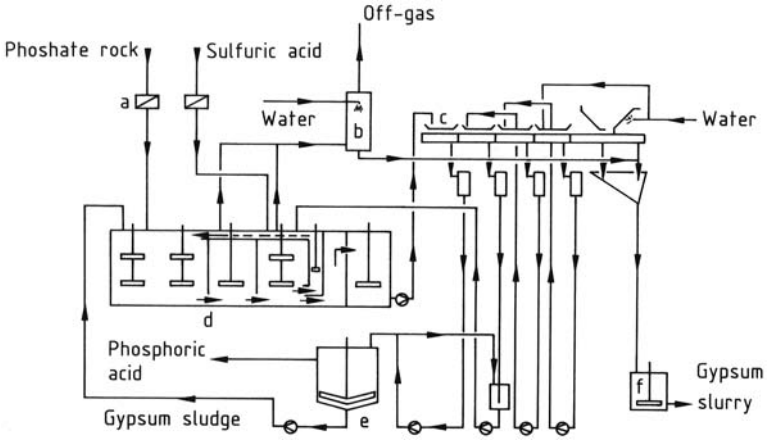


Figure 12. Flow diagram for the DH process
a) Metering device; b) Scrubber; c) Filters; d) Single tank; e) Thickener; f) Discharge tank

separated. In this way, the concentration of sulfuric acid is lowered so that the digestion occurring at the phosphate rock charging point is not hindered by formation of a gypsum layer on the ore particles. In addition, the formation of too many gypsum seed crystals due to supersaturation of Ca^{2+} and SO_4^- ions is avoided. The calcium sulfate is present as the dihydrate at a reaction temperature of 70 – 80 °C and a phosphoric acid concentration of 28 – 31 %. Usually, the filtered acid is further concentrated (see Section 1.2.3).

Advantages of the dihydrate process are the low reaction temperature and, therefore, fewer corrosion problems; its applicability to most grades of phosphate rock; and its suitability for large-volume production. Some disadvantages are the production of a comparatively dilute phosphoric acid which must subsequently be concentrated; the need to grind the phosphate rock; and the relatively high P_2O_5 losses of 4 – 6 % in the gypsum.

Hemihydrate Process. Rising energy costs initiated the development of processes that allow the production of phosphoric acid with 40 – 50 % P_2O_5, without using additional concentration steps, for direct use in fertilizer production. These processes must be carried out at higher temperature in the stability range of calcium sulfate hemihydrate (see Fig. 10). Thus, single-stage (HH) and two-stage (HH/DH, DH/HH) processes were developed in which the hemihydrate is formed as end or intermediate product.

The first commercial HH/DH process was introduced in Japan. The major interest in this process was the production of pure gypsum that could be used for cement production since there are no natural gypsum deposits in this region.

There are currently 60 hemihydrate plants operating worldwide; more than half of them use a HH/DH process. The single-stage HH process has seldom been used because of the unfavorable process yield.

The various processes and some typical features are as follows:

1. *HH Process [19]*
   Features:
   Single filtration stage
   Impure $CaSO_4 \cdot 1/2\ H_2O$
   Yield, 90 – 94 %
   Phosphoric acid, 40 – 48 % P_2O_5

2. *HH/DH Process [20]*
   a. Without intermediate separation of the hemihydrate
      Features:
      Single filtration stage
      Pure $CaSO_4 \cdot 2\ H_2O$
      Phosphoric acid, 30 – 32 % P_2O_5
   b. With intermediate separation
      Features:
      Two filtration stages

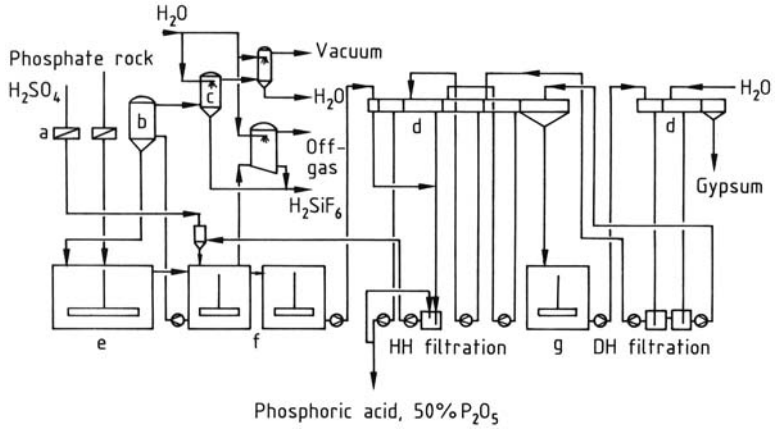


Figure 13. Flow diagram for the HH/DH process
a) Metering device; b) Flash cooler; c) Gas scrubbing; d) Filters; e) Premixer; f) Digester; g) Hydration tank

Very pure gypsum
Yield, 98.5 %
Phosphoric acid, 40 – 52 % P_2O_5

Figure 13 shows the flow sheet for the Fison process as an example of a HH/DH process with intermediate separation of the hemihydrate [14]. In this two-stage processes, the higher digestion temperature of 85 – 110 °C increases the reaction rate and allows the use of unground phosphate rock.Depending on the process, the conversion of the hemihydrate is carried out under different conditions. In the Nissan process, which dispenses with the intermediate separation of hemihydrate, the dihydrate is crystallized after cooling of the digestion slurry from 85 – 90 °C to 55 –65 °C [20]. In the Fison process the hemihydrate is recrystallized after filtration from a washing acid (a mixture of sulfuric and phosphoric acid: 4 – 8 % SO_3, 10 – 20 % P_2O_5) slurry.

3. *DH/HH Process [14, 21]*

Features:
Repeated filtration with intermediate conversion
Very pure $CaSO_4 \cdot 1/2\ H_2O$
Yield, 96 – 98 %
Phosphoric acid, 32 – 36 % P_2O_5

This process is only of interest where very high purity hemihydrate is required, for example, in plaster.

1.2.3. Concentration of Wet Phosphoric Acid

Most of the wet phosphoric acid produced worldwide is made by the dihydrate process. For further processing to fertilizers, the major application (→ Phosphate Fertilizers, Chap. 11), the concentration of the phosphoric acid must be increased from 28 – 30 % P_2O_5 to 40 – 55 % or even 70 % P_2O_5 (superphosphoric acid). Submerged combustion burners and vacuum circulation evaporators are customary concentration devices. In the older submerged burner process, hot combustion gases from an oil burner are blown through a dip tube or directly into phosphoric acid [22]. At an acid temperature of 350 °C, the off-gases entrain high proportions of phosphoric acid as aerosols as well as volatile fluorine compounds. Purification of these off-gas streams is expensive.

Today, submerged combustion burners are still in use only in older plants. Currently, vacuum evaporation with forced circulation is the concentration method generally used (Fig. 14). Depending on the amount of water to be evaporated, one or more evaporators are used in parallel or in series. Multistage evaporators arranged in tiers of usually three stages have the advantage of lower energy costs. The energy savings result from effective heat utilization. The vapors of an evaporator stage operated at a higher temperature are used for heating another operated at a lower temperature [23]. In the concentration of

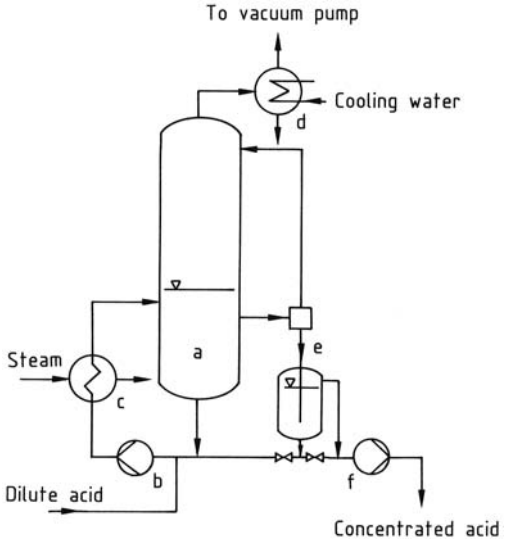


Figure 14. Recycling evaporator for concentration of wet phosphoric acid
a) Recycle evaporator; b) Circulation pump; c) Heat exchanger; d) Condenser; e) Product takeoff; f) Pump

phosphoric acid from 30 to 50 % P_2O_5, the steam requirements can be reduced from 1.25 t to 0.7 t per tonne of evaporated water. Rubber-proofed steel is the predominant material of construction for containers, piping, and pumps at operating temperatures below 120 °C. At higher temperatures, e.g., in the production of superphosphoric acid at up to 200 °C, alloys such as Hastelloy G 3 or Sanicro 28 are used. The heat exchanger tubes are usually made of graphite or nickel alloys.

Apart from water vapor, a mixture of SiF_4 and HF is generated during the concentration of wet phosphoric acid. About 50 – 60 % of the fluorine content of wet phosphoric acid is volatilized on concentration from 30 to 55 % P_2O_5. In order to comply with the fluorine emission limits of the plant or to obtain a salable coproduct, concentration units are equipped with facilities for the production of H_2SiF_6. Thus, 90 – 95 % of the generated fluorine can be converted to a 15 – 25 % H_2SiF_6 solution [24].

1.2.4. Purification of Wet Phosphoric Acid

Wet phosphoric acid produced by wet digestion contains variable amounts of inorganic impurities, depending on the origin of the phosphate rock.

Depending on the further application, these impurities must be partially or completely removed from crude phosphoric acid. Precipitation and extraction processes are used.

Precipitation Processes. The separation of arsenic and, to an increasing extent, of cadmium is required for the use of wet phosphoric acid in fertilizer production. For separation of arsenic, a Na_2S solution is added to the crude acid, and the precipitated arsenic sulfide is removed by filtration.

The separation of cadmium by means of a complexing agent such as alkyldithiophosphoric acid alkyl ester [25] can also be classified as a precipitation reaction because the precipitated cadmium complex is separated in solid form either directly or after addition of a filter aid or absorbent. Such a process is operated on a commercial scale by Tessenderlo Chemie in Belgium.

Further purification of wet phosphoric acid by precipitation of cationic impurities, especially Fe, Al, Mg, and Ca, is possible by neutralizing the acid with caustic soda. The precipitated metal phosphates are filtered under pressure from the resulting sodium phosphate solution, which contains 18 – 20 % P_2O_5. In order to decrease P_2O_5 losses in the filter cake from > 10 % to < 5 %, [26] the filter cake is worked up with more caustic soda to give a trisodium phosphate solution and precipitatable metal hydroxides. Since the phosphoric acid in this neutralization process is converted to a phosphate salt solution, its uses are limited. For instance, wet phosphoric acid is used for the production of detergent phosphates (pentasodium triphosphate, see Section 3.3.4) via this route in Western Europe.

Extraction Processes are the predominant methods for the purification of wet phosphoric acid. Processes are operated for the separation of single components as well as of practically all impurities in wet phosphoric acid. However, this complete purification includes measures (e.g., acid discoloration and removal of traces of arsenic and fluorine) which supplement the extraction process. The quality of such purified phosphoric acid equals that of thermally produced acid.

In 1990, production capacities for extractively purified P_2O_5 amounted to 740 000 t/a worldwide, including 300 000 t/a in Western Europe.

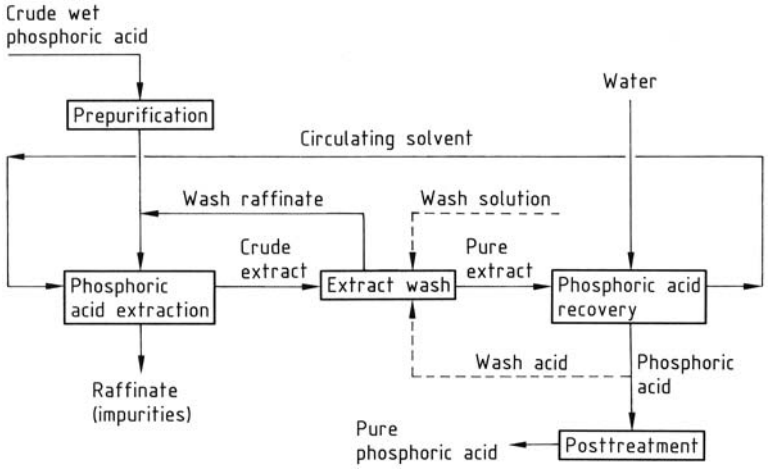


Figure 15. Schematic of extractive purification of wet phosphoric acid

The basic concept for extractive purification of wet phosphoric acid is the same in all processes. Figure 15 shows a schematic of the purification steps. Crude wet phosphoric acid containing 40 – 50 % P_2O_5 is prepurified in order to largely separate, if necessary, arsenic, sulfate, and organic components by precipitation or adsorption. In the subsequent extraction process, prepurified acid is contacted with solvent countercurrently in several stages. Together with small amounts of impurities, the phosphoric acid is transferred to the organic phase, while most of the impurities remain in the aqueous phase. If a high yield of P_2O_5 (95 – 98 %) is desired, sulfuric acid is added during the extraction so that the cationic impurities remain in the aqueous phase as sulfates. In addition, so-called splitting processes are customary. In these, only 50 – 70 % of the phosphoric acid are extracted in simple plant. Phosphoric acid contained in the aqueous phase, together with the impurities, is treated further in fertilizer production.

The crude extract containing the phosphoric acid is washed countercurrently with small amounts of water, phosphoric acid, or phosphate salt solutions. Depending on the wash liquid, anionic components such as SO_4^{2-} or F^- are also removed with the metal cations. The wash extract – phosphoric acid enriched in impurities – is recycled to the extraction stage. The phosphoric acid product is obtained from the purified extract by addition of water or by distillation of solvent. If further processing of the acid to commercial phosphates is intended, a phosphate salt solution can be obtained directly by addition of alkalies to the extract. The recovered solvent is recycled to the extraction stage. Usually, a partial stream is purified, for example, by distillation.

Generally, stripping for complete solvent separation and concentration of the phosphoric acid to 50 – 70 % P_2O_5 are among the posttreatment steps. In these operations, the fluoride content of the acid is also further decreased. Pressure stripping of the acid with steam to decrease the fluoride content to <10 ppm and oxidative degradation of organic trace impurities are used for the production of food-grade phosphoric acid.

The choice of solvent is an important feature of the extraction processes. With solvents that are infinitely miscible with water, such as isopropanol [27], extraction may be complete in one or two stages. Alkali-metal or ammonium ions are added for better development of the organic and aqueous phases. Phosphoric acid is recovered from the extract by solvent distillation.

Frequently, alcohols that are partially miscible with water, such as butanol [7] or amyl alcohol [28, 29], are used. Six- to ten-stage mixer –settler units are used to attain essentially quantitative phosphoric acid extraction.

The IMI process, developed for the extraction of phosphoric acid from phosphate rock digested with hydrochloric acid, is a special case [28]: $CaCl_2$ is added as extraction aid to increase the equilibrium concentration of phosphoric acid in the alcoholic phase.

Methyl isobutyl ketone (MIBK) [30], tributyl phosphate [31], diisopropyl ether [7], or mixtures of the latter two [32] are immiscible with water. Usually, the processes based on these solvents are splitting processes without quantitative P_2O_5 extraction. The use of diisopropyl ether for extraction and reextraction is based on the temperature dependent solubility of phosphoric acid in this solvent. Extraction is carried out at 0 – 5 °C, and the acid is reseparated after addition of a small amount of water at 30 °C.

Extraction of Single Components. The first commercial processes for the separation of single components involved the production of uranium, which can be present in wet phosphoric acid at concentrations of up to 200 ppm. Large industrial plants were first operated in the 1950s with alkyl diphosphate esters [33], and in the 1970s improved processes with octyl phenyl phosphate esters, octyl diphosphate esters [34], or mixtures of di-2-ethylhexyl phosphate and tri-*n*-octyl phosphine oxide [35, 36] were introduced. However, these extraction plants were closed after several years of operation, mainly because of declining uranium prices. Only in Belgium is uranium still produced extractively from wet phosphoric acid by Prayon [37].

A process developed for the removal of cadmium involves prepurification of the acid to separate solids and subsequent extraction of cadmium into an organic phase [38]. Alkylamines are used as extractive agents in the presence of halide ions (Cl^-, I^-, Br^-). In the reextraction stage, cadmium is transferred back to the aqueous phase. Cadmium is precipitated and separated from this solution as the sulfide.

1.3. Uses and Economic Aspects

After sulfuric acid, phosphoric acid is the most important mineral acid in terms of volume and value. This is mainly due to the enormous demand for wet phosphoric acid for further processing to fertilizers. As shown in Figure 16 for the United States, the world's largest producer and consumer of wet phosphoric acid, its share of the total phosphoric acid production amounts to more than 90 %. Besides the fertilizers area, industrial phosphates (see Chap. 3) and feedstuff

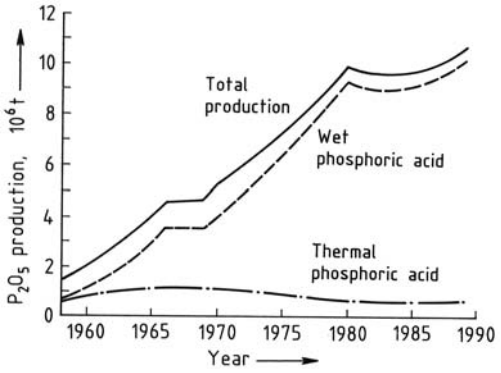


Figure 16. Phosphoric acid production in the United States

are other areas of application of wet phosphoric acid.

About 80 – 90 % of the thermal phosphoric acid produced is used for the production of industrial phosphates, especially the sodium, potassium, calcium, and ammonium salts. Pentasodium triphosphate is always the largest single product, although purified wet phosphoric acid is being used increasingly for its production. Thermal acid is used in metal surface treatment (→ Metals, Surface Treatment, Chap. 3.) and, in food-grade quality, for the acidulation of beverages.

After decades of strong growth, a decrease of worldwide phosphoric acid production occurred in the 1980s (see Fig. 16). Ecological problems related to rising phosphate consumption are an essential cause of this development. Among these are the impairment of subsoil water by phosphate fertilizers and the eutrophication of surface waters by phosphates from fertilizers and detergents. These ecological pressures have already resulted in extensive replacement of phosphate-containing detergents and a decrease in the use of mineral fertilizers in agriculture.

1.4. Environmental Aspects

Phosphoric acid is now mainly produced (ca. 95 %) by the wet process. Because of the high energy consumption, only ca. 5 % is produced by the thermal process. An overview of the worldwide capacity in 1989 (40.6×10^6 t P_2O_5) is given in [39]. Gypsum and fluoride are the main byproducts of the wet process; phosphorus slag is a

Table 1. Typical phosphogypsum analyses (%)

	Production process		
	Dihydrate	Hemihydrate	Hemidihydrate
CaO	32.50	36.9	32.20
SO_3	44.00	50.3	46.50
P_2O_5	0.65	1.5	0.25
F	1.20	0.8	0.50
SiO_2	0.50	0.7	0.40
Fe_2O_3	0.10	0.1	0.05
Al_2O_3	0.10	0.3	0.30
MgO	0.10		
H_2O	19.00	9.0	20.00
Process yield, t/t P_2O_5	4.9	4.3	4.9

byproduct of phosphorus production by the electric furnace process.

Phosphogypsum. A quantity of 4.5 – 5.5 t impure calcium sulfate is obtained as byproduct during the production of 1 t P_2O_5 by the wet process. In 1988, 27.7×10^6 t P_2O_5 were produced and hence ca. 140×10^6 t gypsum. Disposal of these large amounts of gypsum is causing considerable problems, especially from an environmental and ecological viewpoint [40]. The gypsum contains production- and source-specific constituents (Table 1) [41]. Three possibilities for the disposal of phosphogypsum exist:

1. Dumping at sea (currently 10 %)
2. Dumping on land (ca. 88 %)
3. Use as a raw material

The disposal of gypsum from production facilities near the sea is usually by outflow into the sea. Three aspects for the evaluation of the ecological consequences must be considered: (1) the large amounts of gypsum involved, (2) traces of heavy metals in the gypsum, and (3) changes in the pH of the water due to residual phosphoric and hydrofluoric acids.

The solubility of calcium sulfate in water is 2.4 g/L; in seawater it is ca. 3.5 g/L [42]. Seawater naturally contains 1.6 g/L calcium sulfate, so that, given sufficient tidal and natural movement of the water, a rapid dissolution of the gypsum is observed. SiO_2, Al_2O_3, and organic constituents remain undissolved.

Table 2. Trace elements in phosphate rock from Morocco and Florida and percentages thereof in phosphogypsum

Element	Morocco, ppm	Florida, ppm	Percentage in phosphogypsum
Cadmium	17	10	15 – 25
Chromium	150	$\leq$ 90	5 – 10
Copper	28	5 – 20	4 – 8
Manganese	10	min. 100	10 – 15
Nickel	16	25 – 75	25 – 50
Uranium	120	200	15 – 20
Zinc	200	10	4 – 8

The amount of heavy metals added to seawater due to phosphogypsum is relatively small in comparison to the existing levels; see Tables 2 and 3 [43, 44]. Hence, there is no enrichment of heavy metals in seawater due to this disposal method. The enrichment of the highly toxic heavy metal cadmium in the environment as a result of industrial emission is, however, viewed critically. As the result of a study [45], cadmium will be subject to increasing strict emission limits, for example, in the Netherlands [46]. The amount of cadmium in phosphogypsum discharged into seawater in the EC in 1979 was 62 t [47].

The pH of a 10 % phosphogypsum suspension in water is 3.3. Seawater is buffered by hydrogencarbonate ions and has a pH of 7.9. Therefore, the introduction of even large amounts of slurry cannot cause the pH to drop below the critical level of 5.5 [48]. However, particular attention must be paid to the effects of dumping gypsum in the sea. Permanent surveillance of the effects of the dumping (especially with regard to accumulation) on marine flora and fauna must be carried out.

The dumping of phosphogypsum proceeds in two ways:

Table 3. Trace elements in seawater

Element	Concentration, kg/km^3
Chromium	48
Cadmium	120
Copper	3 360
Manganese	2 160
Nickel	2 160
Uranium	3 360
Zinc	11 280

1. The gypsum is slurried with water and then pumped to settling vessels. The used water is generally recycled [49]. This disposal method is used especially in the United States. Problems can arise due to the difficulty of evaluating the emission of fluoride and of seepage water containing phosphate and other constituents [50]. Here, too, supervision of the ecological effects should be considered [51]. In Sweden an artificial island has been developed for the dumping of gypsum [52].
2. The dried gypsum (residual water content 20 % min.) is stored in a dump. Another possibility is the filling of empty brown coal mines with protection of the groundwater by confining the dried gypsum with polyethylene sheets [53].

For the disposal of dried phosphate sludge, special isolated disposal sections and treatment of seepage water should be undertaken to avoid environmental risks.

Due to the large amounts of phosphogypsum, the sensitivity with regard to environmental problems, and the scarcity of dumping areas, the following attempts have been made to use it as a raw material [54]:

1. Use as building material (e.g., plasterboard)
2. Cement additive
3. Use in agriculture
4. Use as a filler in the paper industry
5. Recycling to sulfuric acid and cement

The use of large amounts of phosphogypsum as raw material is generally only of economic interest in countries that do not have any natural source of gypsum. Examples are Japan and South Korea, where ca. 3×10^6 t of phosphogypsum is used, mainly in the cement industry. Otherwise only small amounts are utilized. Reasons include the impurities, the water content, the transport costs, the low price of high-purity natural gypsum, and the increased accumulation of gypsum from flue gas desulfurization [55].

Fluoride. Phosphate ore contains ca. 3.6 – 4.1 % fluoride that – depending on the process – is distributed in various amounts among the acid, in the phosphogypsum, the reactor off-gas, and the off-gases from cooling or concentration of the acid (Table 4) [56].

Table 4. Distribution of fluoride in the production of wet phosphoric acid

	Dihydrate process, %	Hemihydrate process, %
Acid	15	12
Phosphogypsum	45	50
Reactor off-gas	5	8
Flash cooler vapor		30
Concentration vapor	35	

Because of its damaging effects on the environment [57] fluoride from off-gases is either precipitated in a basic wash as CaF_2 or in an acid wash as fluorosilicate [58]. Depending on the demand the CaF_2 or fluorosilicate is either utilized or dumped. In Germany the maximum emission values for the off-gas [59] are 50 mg/m^3 for solid particles and 5 mg/m^3 for gaseous fluorine compounds.

Phosphorus Furnace Slag. Eight tonnes of slag are obtained during the production of 1 t of phosphorus by the furnace process. The slag, which consists mainly of calcium silicate, is obtained as lumps or granules.

Typical percentage slag composition is as follows:

P_2O_5	1.0
CaO	48.4
SiO_2	42.5
F	3.3
Al_2O_3	2.5
Fe_2O_3	0.2
MgO	0.6
Na_2O	0.9
K_2O	0.5

Uses of the phosphorus furnace slag are in waste-disposal technology, in road building, and as a filler and insulating material [60].

2. Condensed Phosphoric Acids

During concentration of aqueous orthophosphoric acid, formation of pyrophosphoric acid can already be detected chromatographically at an orthophosphoric acid concentration of 95 %, corresponding to 68.8 % P_4O_{10}. In liquid, anhydrous orthophosphoric acid, 12.7 % is present as

Table 5. Percentage contents of individual polyphosphoric acids in a concentrated polyphosphoric acid mixture as a function of P_4O_{10} content [63]

Total	Number of P atoms in the low-molecular polyacids														Highly		
P_4O_{10}, %	1	2	3	4	5	6	7	8	9	10	11	12	13	14	condensed	Trimeta	Tetrameta
67.4	100.0																
68.7	99.7	0.33															
70.4	96.2	3.85															
71.7	91.0	8.86	trace														
73.5	77.1	22.1	0.79														
73.9	73.6	25.1	1.34														
75.7	53.9	40.7	4.86	0.46													
77.5	33.5	50.6	11.5	2.86	0.74	trace											
79.1	22.1	46.3	20.3	7.82	2.26	1.02	0.34										
80.5	13.8	38.2	23.0	13.0	6.86	3.38	1.67	1.03	0.22								
81.0	12.2	34.0	22.7	14.6	8.42	4.36	2.27	1.41	0.56	trace							
81.2	10.9	32.9	22.3	15.0	9.36	5.41	2.85	1.75	0.97	0.36	0.05						
82.4	7.32	23.0	19.3	15.9	12.3	8.21	5.73	3.89	2.52	1.36	0.91	0.14			trace		
84.0	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	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	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	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	trace	
87.1	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	trace	
87.9	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	1.88	1.52	0.7	0.61	0.62	0.68	0.54	0.71	0.36	1.03	0.98	1.16	1.23	1.37	86.8	1.17	0.41

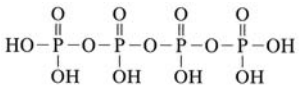
pyrophosphoric acid, which however, reverts to orthophosphoric acid upon crystallization [61]. Upon further concentration, a mixture of straight-chain polyphosphoric acids, $H_{n+2}P_nO_{3n+1}$, is formed initially; eventually, it is converted to a mixture of polymetaphosphoric acids, $H_nP_nO_{3n}$ [62]. The acidity increases during this endothermic condensation process.

The contents of the individual polyphosphoric acids present in a concentrated phosphoric acid mixture for various P_4O_{10} concentrations are compiled in Table 5.

Diphosphoric acid. [*2466-09-3*], pyrophosphoric acid, $H_4P_2O_7$, M_r 177.98, exists in two crystalline modifications with *mp* 54.3 and 71.5 °C. It is readily soluble in water and is converted to orthophosphoric acid, especially upon boiling or in the presence of strong acids. Pure pyrophosphoric acid cannot be obtained by concentration of orthophosphoric acid or by addition of dry P_4O_{10} to the latter (cf. Table 5). It can be prepared from sodium pyrophosphate by ion exchange, or by reaction of insoluble lead pyrophosphate with hydrogen sulfide.

Unlike monophosphoric acid, aqueous solutions of pyrophosphates do not give a yellow precipitate with silver nitrate but a white one. Compared with metaphosphoric acids, which also form a white precipitate, pyrophosphate differs in that it does not coagulate albumin.

Polyphosphoric and Metaphosphoric Acids. In low-molecular, linear polyphosphoric acids ($n = 2 - 15$) such as tetraphosphoric acid, $H_6P_4O_{13}$,



each phosphorus atom bears a strongly acidic OH group. In addition, the two terminal P atoms are each bonded to a weakly acidic OH group. Cyclic metaphosphoric acids, $H_nP_nO_{3n}$, which are formed from low-molecular polyphosphoric acids by ring closure, have a comparatively small number of ring atoms ($n = 3 - 8$). Each P atom in the ring is bound to one strongly acidic OH group, i.e., all H atoms are equally acidic.

In high-molecular polyphosphoric acids, $H_{n+2}P_nO_{3n+1}$ ($n = 16 - 90$), the two terminal H atoms exhibit only low acidity and cannot be replaced by metal atoms. The composition of these acids are close to that of cyclic metaphosphoric acids $H_nP_nO_{3n}$. Upon continual

concentration they are initially converted to cross-linked chain structures. These are further transformed from a two-dimensional network to three-dimensionally cross-linked, glassy metaphosphoric acid [62, 64].

Production. Polyphosphoric acid can either be produced from wet phosphoric acid by evaporative concentration, or thermally by combustion of elemental phosphorus.

Wet phosphoric acid is concentrated by direct heating with hot gases in reactors lined with carbon bricks [65] or by indirect heating under vacuum [66]. In the former process, the heating gas is usually injected below the acid surface.

Concentration of wet phosphoric acid also improves its transportability. Commercial wet phosphoric acid with ca. 50 % P_2O_5 contains relatively high concentrations of impurities, which deposit on pipes and containers unless during shipment and storage the acid is constantly agitated. Because polyphosphoric acid has a higher lime binding strength, the impurities are held in solution and cannot deposit.

Phosphoric acid plants in which combustion of phosphorus and absorption of P_2O_5 vapors are performed separately are best suited to the thermal production of polyphosphoric acid (see TVA process). An externally water-cooled tower made of stainless steel is used for combustion. A hydration tower, also made of stainless steel, cooled externally with water and internally with recycled acid, is used for the absorption of P_2O_5 mist. The phosphoric acid recycled in the hydration tower can be kept at the concentration of the desired polyphosphoric acid if an appropriately intensive cooling facility is available [67]. A polyphosphoric acid plant differs from an orthophosphoric acid plant by more expensive cooling and circulation equipment because, in contrast to orthophosphoric acid production, water evaporation cannot be used as a contribution to cooling capacity during production of polyphosphoric acid, and the viscosity of polyphosphoric acid is much higher than that of orthophosphoric acid.

In another process, polyphosphoric acid is produced in a tower in which phosphorus is combusted and P_2O_5 mist is absorbed (cf. IG process). The tower consists of two sections of different diameters so that a step is formed at the joint, which serves as an acid collection cup. A second collection cup is located below the tower.

The tower walls are protected by two phosphoric acids of different concentrations. In the upper section, polyphosphoric acid containing 76 % P_2O_5 flows from an overflow cup down the tower walls. In the lower section, polyphosphoric acid with 84 % P_2O_5 is sprayed onto the tower walls. Both acid recycle streams are cooled by cooling facilities. It is advantageous to operate this plant in combination with other production units for phosphoric acid. Such a plant can for instance use the flue gases from production of dry P_2O_5 and pass its own flue gases on to the absorption section of the orthophosphoric acid plant [68].

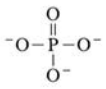
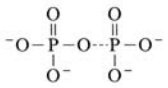
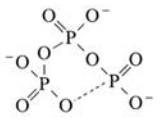
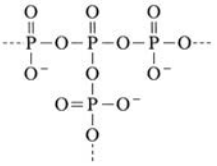
Commercial Products and Uses. The fertilizer industry was the largest area of application of polyphosphoric acids until about 1973. Especially in the United States, large amounts of ammonium phosphate, triple superphosphate, and liquid fertilizers were made from polyphosphoric acids. This application has declined strongly. Polyphosphoric acid is used in organic chemistry as an acidic catalyst and dehydrating agent as well as for cyclization reactions [69].

3. Phosphates

The salts of phosphoric acid are technically and commercially the most important group of phosphorus compounds besides the acid itself. According to their applications, fertilizer phosphates (→ Metals, Surface Treatment, Chap. 3) are distinguished from other commercial phosphates discussed here. While the use of phosphates as fertilizers started in the mid-1800s with the introduction of mineral fertilization, other phosphates were used industrially at the turn of the century only sporadically. They attained greater commercial importance since ca. 1930 with the production of condensed phosphates, especially for the detergent industry.

Structure and Nomenclature. All phosphate salts contain PO_4 units as characteristic structural element. The central phosphorus atom is surrounded by a tetrahedral arrangement of oxygen atoms. The tetrahedral symmetry is based on formation of sp^3 hybrid orbitals on the phosphorus atom, which is linked to the four oxygen atoms by sigma bonds. The P – O bond

Table 6. Structure and nomenclature of phosphates

Oxide ratio	Group name	General formula	Anion structure	Examples
3	monophosphate (isolated PO_4 tetrahedra)	$M^I_3PO_4$		Na_3PO_4 trisodium phosphate $Ca(H_2PO_4)_2$ calcium dihydrogen phosphate
> 1–2	polyphosphates (chain form)	$M^I_{n+2}P_nO_{3n+1}$		$Na_2H_2P_2O_7$ disodium dihydrogen phosphate $Na_5P_3O_{10}$ pentasodium triphosphate
1	metaphosphates (cyclic)	$M^I_3P_nO_{3n}$		$Na_3(PO_3)_3$ sodium trimetaphosphate $Na_6(PO_3)_6$ sodium hexametaphosphate
<1[a]	cross-linked or ultraphosphates (branched chains or rings)			CaP_4O_{10} $Ca_2P_6O_{17}$

[a] Special cases: isopolyphosphate, oxide ratio >1 to 2; isometaphosphate, oxide ratio 1.

strength is enhanced by π bonding with participation of phosphorus *d* orbitals. Ideal tetrahedral structure with a theoretical O – P – O bond angle of 109°28′ can only be expected for a free PO_4^{3-} ion. In most crystalline phosphates, especially in condensed phosphates, deformation of the PO_4 tetrahedra occurs due to unsymmetrical lattice forces, so that bond angles of 95 – 125° are found. The bond lengths are shorter than expected for a single bond due to the double bond character. Average P – O distances of 154 pm are found.

Polymers with chain, ring, or cross-linked structure are obtained by linkage of several PO_4 tetrahedrons via common oxygen atoms. The tetrahedra are joined exclusively by vertex sharing.

Since polyphosphates are prepared from acidic monophosphates by condensation, they are usually referred to as condensed phosphates. Three types of condensed phosphates are distinguished according to the structure of their anions [62]: polyphosphates with chain structure, cyclic metaphosphates, and cross-linked or ultraphosphates with branched chains and/or rings.

All phosphate salts can be described as combinations of oxides, e.g., $Na_2H_2P_2O_7$ as $Na_2O \cdot H_2O \cdot P_2O_5$. The ratio of cationic oxides (Na_2O, CaO, H_2O) to P_2O_5 is characteristic for the individual structural types. Table 6 shows the structural relations and classifications.

The polyphosphates ($M^I_{n+2}P_nO_{3n+1}$) are named according to the IUPAC rules as di-, tri-, tetraphosphates, etc. Frequently, the older designations pyro-, tripoly-, tetrapolyphosphate, etc., are also still used. Moreover, it is customary to distinguish between chromatographically separable, oligomeric phosphates with $n < 12$ and high-molecular polyphosphates with $n = 13$ to $> 10\,000$. Both glassy and crystalline forms are known in both groups. While mixtures of various chain lengths are always present in glassy phosphates, crystalline oligomeric phosphates are uniform with regard to anion size. It is debatable whether crystalline, high-molecular polyphosphates are also uniform [62].

The oxide ratio in metaphosphates, $M^I_nP_nO_{3n}$, is exactly 1. Polyphosphates with very high molecular masses have practically the same oxide ratio, and are therefore often incorrectly called "metaphosphates" (e.g., sodium hexametaphosphate for Graham's salt). According to the newer nomenclature, the term "metaphosphate" is reserved for condensed phosphates

with cyclic anions. So far, metaphosphates are known for $n = 3 - 8$. There is no evidence for the existence of a dimeric anion with $n = 2$. Although there are indications for the occurrence of ring structures with $n > 8$ in some phosphate glasses, they have so far not been isolated. Cross-linked or ultraphosphates contain P atoms which are linked with each other via three O atoms. Additional designations are commonly used in special cases: isometaphosphate when a ring is linked with one or more chains, and isopolyphosphate if only branched chains are present. Compounds with rings linked directly or via chains are more specifically called ultraphosphates. Commercially, cross-linked phosphates are not very important. So far, only a few well-defined examples of this structural type are known.

3.2. Sodium Monophosphates

As a tribasic acid, monophosphoric acid (orthophosphoric acid) forms three series of sodium salts, i.e., mono-, di-, and trisodium monophosphate. Besides the anhydrous compounds, defined hydrates and some double salts are known. Table 7 lists the monophosphates characterized in the $Na_2O - P_2O_5 - H_2O$ system.

Table 7. Sodium monophosphates

Compound	Density, g/cm^3	*mp*	Crystal system
NaH_2PO_4	2.36	200*	
$NaH_2PO_4 \cdot H_2O$	2.04	100	orthorhombic
$NaH_2PO_4 \cdot 2\ H_2O$	1.91	60	orthorhombic
$2\ NaH_2PO_4 \cdot Na_2HPO_4 \cdot 2\ H_2O$			
$2\ NaH_2PO_4 \cdot Na_2HPO_4$			
$NaH_2PO_4 \cdot H_3PO_4$		127 – 131	
Na_2HPO_4	1.10		monoclinic
$Na_2HPO_4 \cdot 2\ H_2O$	2.07	95	orthorhombic
$Na_2HPO_4 \cdot 7\ H_2O$	1.68	48	monoclinic
$Na_2HPO_4 \cdot 8\ H_2O$			
$Na_2HPO_4 \cdot 12\ H_2O$	1.52	48	monoclinic
Na_3PO_4, low temp.	2.63	700**	hexagonal
Na_3PO_4, high temp.	2.54	1583	cubic
$Na_3PO_4 \cdot 12\ H_2O$		180	monoclinic
$Na_3PO_4 \cdot 6\ H_2O$		110	
$Na_3PO_4 \cdot 8\ H_2O$		86	triclinic
$Na_3PO_4 \cdot 12\ H_2O$	1.64	73 – 76 (decomp.)	hexagonal

* Decomposition.
** Transformation.

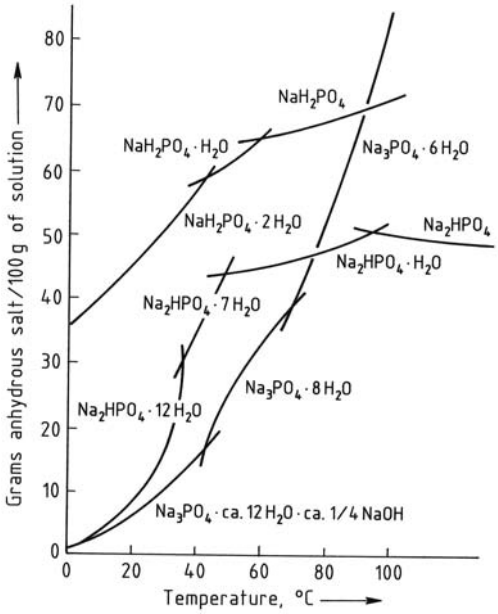


Figure 17. Solubility of sodium monophosphates [70]

Figure 17 shows the solubility of sodium monophosphates as a function of temperature. As salts of a tribasic acid whose dissociation decreases greatly from the first to the third stage ($pK_1 = 2.15$, $pK_2 = 7.1$, $pK_3 = 12.4$), alkali-metal monophosphates exhibit buffer properties.

Sodium monophosphates are usually produced by neutralization of phosphoric acid with soda ash or caustic soda. The latter is predominantly used in Germany, while in the United States, the less expensive soda ash prevails. The basicity of sodium carbonate is insufficient for the formation of trisodium phosphate, so that caustic soda must be used in this step. The phosphates crystallize from the solutions as hydrates and are separated by centrifugation. Anhydrous salts are obtained by dehydration in rotary dryers or directly from the solutions by spray drying or in rotary kilns.

Both thermal phosphoric acid and the cheaper wet phosphoric acid are used as starting materials. The very pure thermal phosphoric acid is generally used in the production of food-grade phosphates.

Monosodium dihydrogenmonophosphate. [*7558-80-7*], monosodium phosphate, NaH_2PO_4, M_r 119.98, crystallizes in anhydrous form and as

the mono- and dihydrates. The pH of a 1 % aqueous solution is 4.5. The anhydrous salt decomposes upon heating from 169 °C to 240 °C, with elimination of water and formation of $Na_2H_2P_2O_7$.

Thermal phosphoric acid is used preferentially for production of monosodium phosphate. Wet phosphoric acid is less suitable because the impurities are only partially precipitated in the neutralization with soda ash or caustic soda up to the first stage, so that additional recrystallization would be required to purify the phosphate. The dihydrate and the anhydrous salt are the usual commercial forms. Due to its acidity, monosodium phosphate is used as phosphating agent for metal surface treatment and as component of acidic detergents. Mixtures of mono- and disodium phosphate are used as buffers in the pH range 5 – 8, especially in textile finishing processes. In water conditioning, monosodium phosphate is frequently added for correction of the alkalinity of water purified by ion exchange. Monosodium phosphate serves as a mineral supplement for feeds and as a pH stabilizer for soups and juices in the food area. Monosodium phosphate is used as raw material for the production of disodium diphosphate and higher condensed phosphates.

Disodium Hydrogenmonophosphate [*7558-79-4*], disodium phosphate, Na_2HPO_4, M_r 141.97, crystallizes in the anhydrous form as well as with 2, 7, 8, and 12 H_2O. The crystal structure is composed of HPO_4^{2-} anions in a hexagonal close-packed arrangement, in which Na^+ cations occupy octahedral and tetrahedral interstices.

Both thermal and purified wet phosphoric acid are used in production. In a process developed in the 1980s, acidic phosphate solution ($CaHPO_4$ in the presence of H_3PO_4) is reacted with $NaHSO_4$, whereby purification occurs through precipitation of gypsum [71]. Neutralization with NaOH is carried out in a second stage. Salts are obtained from the neutralized solutions by evaporation, crystallization, and centrifugation. The desired hydrate is obtained by appropriate temperature control. The anhydrous product is also produced by dehydration of the solution in a spray drying tower. Careful temperature control is required to avoid formation of tetrasodium diphosphate.

Anhydrous Na_2HPO_4, $Na_2HPO_4 \cdot 2\ H_2O$, and $Na_2HPO_4 \cdot 12\ H_2O$ are the commercial forms. Disodium phosphate is blended with monosodium phosphate to prepare buffer mixtures. Other applications are treatment of boiler feedwater (see Trisodium Monophosphate), addition to detergents and cleansers, and preparation of mineral feedstuff supplements. In the food industry, disodium phosphate is used in the production of evaporated milk and other concentrated dairy products such as milk powder and cream to prevent coagulation on heating. It is also used as a component of instant desserts and puddings. Another application of Na_2HPO_4 is for silk weighting in the textile industry. Disodium phosphate is used as starting material for the production of tetrasodium diphosphate and, together with monosodium phosphate, for the production of higher condensed phosphates.

Trisodium Monophosphate [*7601-54-9*], trisodium phosphate, Na_3PO_4, M_r 163.95, crystallizes in the anhydrous form and with 1/2, 6, 8, or 12 H_2O. The pH of a 1 % aqueous solution is ca. 11.9. The dodecahydrate always crystallizes from aqueous solutions with an excess of NaOH. Products with compositions ranging from $Na_3PO_4 \cdot 12\ H_2O \cdot {}^1/_4$ NaOH to $Na_3PO_4 \cdot 12\ H_2O \cdot {}^1/_7$ NaOH are obtained, depending on the composition of the starting solution and the temperature. The stoichiometric compound $Na_3PO_4 \cdot 12\ H_2O$ is unstable in aqueous solution and can therefore only be obtained by isothermal hydration of the other hydrates, which are free of NaOH. Depending on composition, the dodecahydrate dissolves at 70 – 74 °C in its water of hydration.

In addition to NaOH, several other sodium compounds such as NaOCl, NaCl, $NaNO_3$ form double salts with trisodium phosphate [72]. Of these, the addition compound with sodium hypochlorite (chlorinated trisodium phosphate) is commercially important.

Production Trisodium phosphate is mainly produced as the dodecahydrate by complete neutralization of phosphoric acid with caustic soda or soda ash and subsequent crystallization. Since neutralization with soda ash does not proceed beyond the stage of the disodium salt, caustic soda must be added to complete the reaction. Frequently, mother liquors of mono- or disodium phosphate production or crystalline disodium phosphates are used as starting materials. In another process, trisodium phosphate is obtained

by digestion of the phosphate-rich neutralization sludges, which accumulate in the purification of wet phosphoric acid by precipitation, with caustic soda and with addition of water glass [73]. In this process, aluminum and iron phosphates are converted to $Fe(OH)_3$ and $Na_2Al_2SiO_6$ and separated from the Na_3PO_4 solution by filtration. On a commercial scale, it is also possible to react $CaHPO_4$ with H_2SO_4 to form $CaSO_4$ and H_3PO_4. Caustic soda can be added to the latter to give $Na_3PO_4 \cdot 12\ H_2O$ [74].

For production of the dodecahydrate, the most widely used form, the solutions are concentrated. The solid salt is obtained in the form of flakes on cooled rollers or as powder in spray towers. Cooling the solution gives the salt as needles, which are centrifuged and dried with hot air. The anhydrous salt is mostly produced from the molten dodecahydrate by spray drying.

The dodecahydrate tends to cake during storage. In order to obtain a free-flowing and storage-stable product it is mixed with hydrophilic materials such as magnesium salts or silicates [75].

Uses The most widely used commercial product is the dodecahydrate, in the form of flakes, needles, or spray dried powder. The anhydrous salt is marketed as a powder. Due to hydrolysis, trisodium phosphate reacts strongly alkaline in aqueous media, and thus causes saponification of fats.

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$$

Due to its fat- and dirt-solving properties it is used as an industrial cleansing agent for machine parts, occupational clothing, milk cans, dishes, and bottles. Trisodium phosphate is also used for surface treatment of aluminum to obtain a gloss effect.

Trisodium phosphate is the standard agent for water softening, especially of feedwater for steam boilers. Ions such as Ca^{2+} or Mg^{2+} react with trisodium phosphate to form water insoluble phosphates as voluminous, sludgy precipitates, which are removed by sedimentation or filtration before the purified water enters the boiler:

$$3\ Ca(HCO_3)_2 + 2\ Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\ NaHCO_3$$

$$3\ MgSO_4 + 2\ Na_3PO_4 \rightarrow Mg_3(PO_4)_2 + 3\ Na_2SO_4$$

Trisodium phosphate is also used to remove residual hardness from water treated by ion exchange or precipitation processes. An advantage is that the phosphate precipitates do not form deposits and are easily removed. Moreover, a small excess of phosphate in the boiler water decreases corrosion by formation of a strongly adhering protective layer of iron phosphate. For complete softening, 14 g $Na_3PO_4 \cdot 12\ H_2O$ is needed for 1° d carbonate hardness (German hardness scale), and 42 g for 1° d non-carbonate hardness per cubic meter of water.

Chlorinated Trisodium Phosphate, $Na_3PO_4 \cdot {}^1/_4\ NaOCl \cdot 11\ H_2O$; the pH of a 1 % aqueous solution is ca. 11.8. The addition compound of trisodium phosphate with sodium hypochlorite is usually produced by the same process as trisodium phosphate itself but with replacement of a part of the required caustic soda by NaOCl. Special processes for production of a storage-stable product are described in the patent literature [76]. Due to its active chlorine content, chlorinated trisodium phosphate has bleaching and bactericidal properties in addition to the fat- and dirt-solving effect resulting from its high alkalinity. Therefore, it is used as a disinfecting cleanser. The product has gained considerable importance especially in the United States where it is used in detergents for automatic dishwashers and in the sanitary area. However, in Europe it is only of minor importance.

Sodium Monofluorophosphate. [*10163-15-2*], Na_2PO_3F, M_r 144, is a white odorless powder. Its solubility in water is 25 g per 100 g H_2O at 25 °C. The $NaPO_3$ – NaF phase diagram (Fig. 18) shows polymorphic transformations of Na_2PO_3F at 370 °C and 410 °C. The salt melts congruently at 635 °C; prolonged heating of Na_2PO_3F gives pyrophosphate. Hydrolysis occurs in the presence of moist air or in solution:

$$Na_2PO_3F + H_2O \rightleftharpoons HF + Na_2HPO_4$$

Structure The NMR spectrum of sodium monofluorophosphate shows that the monofluorophosphate anion has the structure of the tetrahedral orthophosphate group in which an oxygen atom is substituted by a fluorine atom [78].

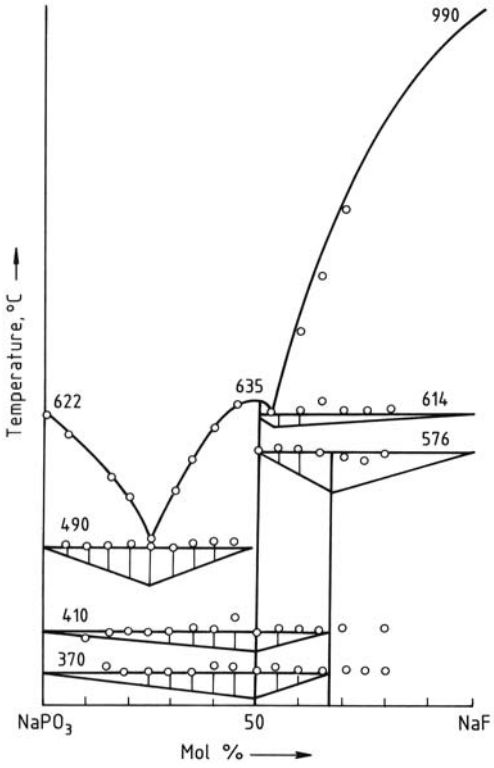
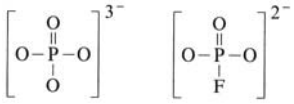


Figure 18. Phase diagram of the $NaPO_3$ – NaF system [77]



The PO_3F^{2-} ion is isoelectronic with SO_4^{2-} and hence possesses similar chemical properties to the sulfate group.

Production. There are two main processes used in the commercial production of Na_2PO_3F. The most common process involves the reaction of sodium fluoride with sodium (meta)phosphates by melting at the eutectic point [79]; the reaction is exothermic:

$$NaF + NaPO_3 \rightleftharpoons Na_2PO_3F$$

Since the molten mixture of Na_2PO_3F, NaF, and $NaPO_3$ can react with many metals and metal oxides, the choice of reactor material is important. Platinum, platinum alloys, and glass – carbon composites are usually used for the reactor walls [80–82]. Other reactor materials used are graphite [81], silver, and iron.

With oligophosphates the rate of reaction increases with increasing chain length. Cyclic tri- and tetrametaphosphates react even faster. Maddrell's salt can also be used to prepare Na_2PO_3F, as can a mixture of tetrasodium pyrophosphate and phosphorus pentoxide [80, 83]:

$$Na_4P_2O_7 + 4\,NaF + P_2O_5 \rightleftharpoons 4\,Na_2PO_3F$$

The second process for the production of Na_2PO_3F involves the reaction of tetrasodium pyrophosphate or disodium phosphate with preheated hydrogen fluoride at 200 – 460 °C in a nickel or aluminum reactor [84, 85]:

$$Na_4P_2O_7 + 2\,HF \rightleftharpoons 2\,Na_2PO_3F + H_2O$$

$$Na_2HPO_4 + HF \rightleftharpoons Na_2PO_3F + H_2O$$

Uses Sodium monofluorophosphate is used in applications where fluoride ions are needed for human physiological processes. It has lower toxicity than sodium fluoride [199]. Sodium monofluorophosphate is mostly used in toothpastes, where it serves as a carrier for the fluoride ion, which is a caries prophylactic [86]. It performs a similar function in pharmaceuticals for the treatment of osteoporosis. In special concrete materials, sodium monofluorophosphate is used as a setting retarder [200, 201] and to improve the adhesion strength of cement-based mortars on concrete surfaces [202].

Analysis Detection of PO_3F^{2-} is based on the fact that Ag_2PO_3F, unlike AgF, is insoluble in water. Hence determination of PO_3F^{2-} can be carried out gravimetrically or complexometrically. Detection of PO_3F^{2-} by ion chromatography is also possible [86].

3.3. Condensed Sodium Phosphates

Condensed sodium phosphates are formed by condensation of two or more hydrogenphosphate units to form chain or cyclic phosphates, with elimination of water, usually thermally. For example, tetrasodium diphosphate (commercial name, sodium pyrophosphate) is formed from two moles of Na_2HPO_4 upon heating:

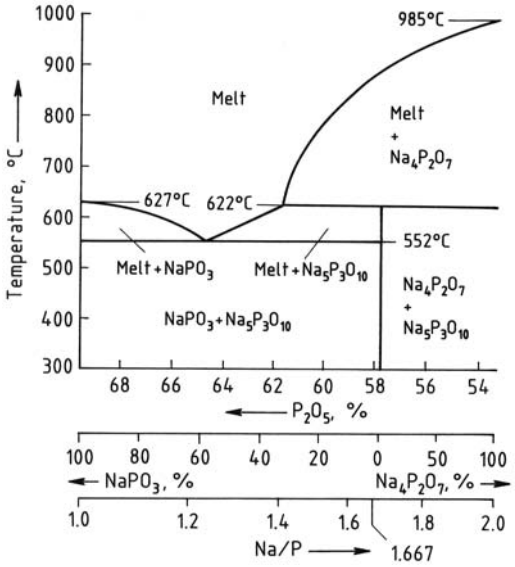
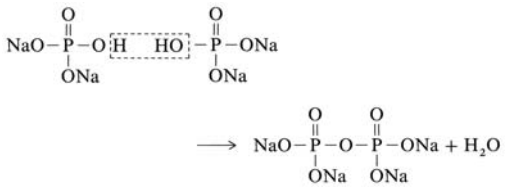


Figure 19. Phase diagram of the $Na_2O - P_2O_5$ system [87]



The composition and structure of the products formed depend on temperature and the Na_2O : P_2O_5 ratio. Figure 19 shows the possible products by means of the phase diagram.

3.3.1. Properties

Condensed sodium phosphates are all water soluble except for high-molecular, crystalline salts such as Maddrell's and Kurrol's salts. The acids from which polyphosphates are derived contain two types of OH groups that differ greatly in their degree of dissociation. Each P atom bears a strongly acidic OH group, while the terminal P atoms additionally have a weakly acidic OH group. Since with increasing chain length the number of strongly acidic groups becomes very large compared with the two weak terminal groups, higher condensed polyphosphates react like salts of a strong, monobasic acid. The buffer capacity, strongly pronounced in monophosphates, decreases with increasing chain length and is absent in higher condensed products such as Graham's salt. Accordingly, the pH of 1 % aqueous solutions of "neutral salts" decreases from trisodium phosphate (11.5) through tetrasodium phosphate (10.2) and pentasodium phosphate (9.7) to Graham's salt (6.0). Due to their cyclic structure, metaphosphates contain no terminal acid groups. Consequently, they react in aqueous solution like salts of strong, monobasic acids.

Hydrolytic Decomposition. In aqueous solution, polyphosphates decompose hydrolytically in reversal of the condensation reaction, eventually forming monophosphates [88]. The decomposition rate is strongly dependent on the temperature and pH of the solution. It usually increases with increasing temperature and decreasing pH. At pH 7 and 25 °C the half-life for the degradation into shorter chains has been calculated to be in the range of 3.5 years [203].

The decomposition is influenced by metal ions. Alkali metal, alkaline earth metal, Al^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} cations retard the hydrolysis of phosphates in acid media. The efficiency increases from univalent to trivalent ions and within the first group of the periodic table from bottom to top. In alkaline solution, however, metal cations accelerate the hydrolysis of phosphates and the catalytic effectiveness decreases with increasing ionic radius [204]. The degree of acceleration increases in the following order:

$$Al^{3+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

Sodium triphosphate in aqueous solution has a half-life of more than a year at pH 8 and room temperature. However, its half-life is in the range of minutes at pH 3 and 100 °C. Under neutral to alkaline conditions, decomposition mainly involves successive cleavage of monosphosphate units from the chain ends, whereas in strongly acidic medium, internal chain cleavage, with formation of low molecular mass fragments, also occurs. In addition to cleavage of phosphate units from the chain ends, a second decomposition reaction occurs for polyphosphates of higher molecular mass, which is accelerated in acidic solution and in which metaphosphates are formed initially [62].

In neutral aqueous solutions at room temperature metaphosphates are also very stable. At elevated temperature and low pH they decom-

pose rapidly, giving initially the corresponding polyphosphates, which, however, themselves undergo rapid hydrolysis to give monophosphates. The metaphosphate rings are also cleaved practically quantitatively in alkaline solution, albeit at a relatively slow rate.

In acidic solution, linear oligomers are hydrolyzed faster than cyclic oligomers, except for cyclotriphosphate. For the linear phosphates, the rate gradually increases with increasing degree of polymerization. In alkaline solution, large differences are observed between the rates for cyclic (fast hydrolysis) and linear oligomers (slow). However, with increasing degree of polymerization the differences become smaller. The first-order hydrolysis rate constants for cyclic and linear penta- and heptaphosphate at 50 °C in 0.1 mol/L HCl are 0.128 h^{-1} (*cyclo*-P_5), 0.764 h^{-1} (P_5), 0.136 h^{-1} (*cyclo*-P_7), 1.54 h^{-1} (P_7), and at the same temperature in 0.5 mol/L NaOH: 0.0166 h^{-1} (*cyclo*-P_5), 6.7×10^{-3} h^{-1} (P_5), 7.4×10^{-3} h^{-1} (*cyclo*-P_7), 0.0234 h^{-1} (P_7) [205].

Tri- and tetrametaphosphate can be converted completely to the corresponding polyphosphates with caustic soda because the latter are comparatively stable under these conditions. However, a similar preparation of higher polyphosphates is not possible because the stability of metaphosphates increases greatly with ring size, so that the polyphosphates are largely decomposed before all the metaphosphate is cleaved [62, 89].

The hydrolytic degradation is easily monitored by ^{31}P NMR spectroscopy or ion chromatography. The ^{31}P NMR spectra of polyphosphates show two major peaks, with chemical shifts in the range of 5 – 10 and 15 – 20 ppm. The high-field signal can be attributed to the end-group phosphate units, and the other signal to the middle groups [206]. The middle to end group integral ratio is related to the average degree of polymerization, which decreases during hydrolysis.

Ion chromatography of polyphosphate solutions can be performed with an anion-exchange column (Dionex AS7) and gradient elution. The eluent is a NaOH/NaCl solution whose content of NaCl is increased during elution. Detection by hydrolysis to orthophosphoric acid and post-column derivatization (as molybdatovanadatophosphate complex) has proved best [207]. Each polyphosphate species (e.g., pentaphosphate, hexaphosphate, etc., up to P_{50}) gives a peak whose integral corresponds to the concentration. Hence this method allows a detailed look at the alteration of the concentration of distinct molecules. Figure 20 gives an example for a highly condensed polyphosphate.

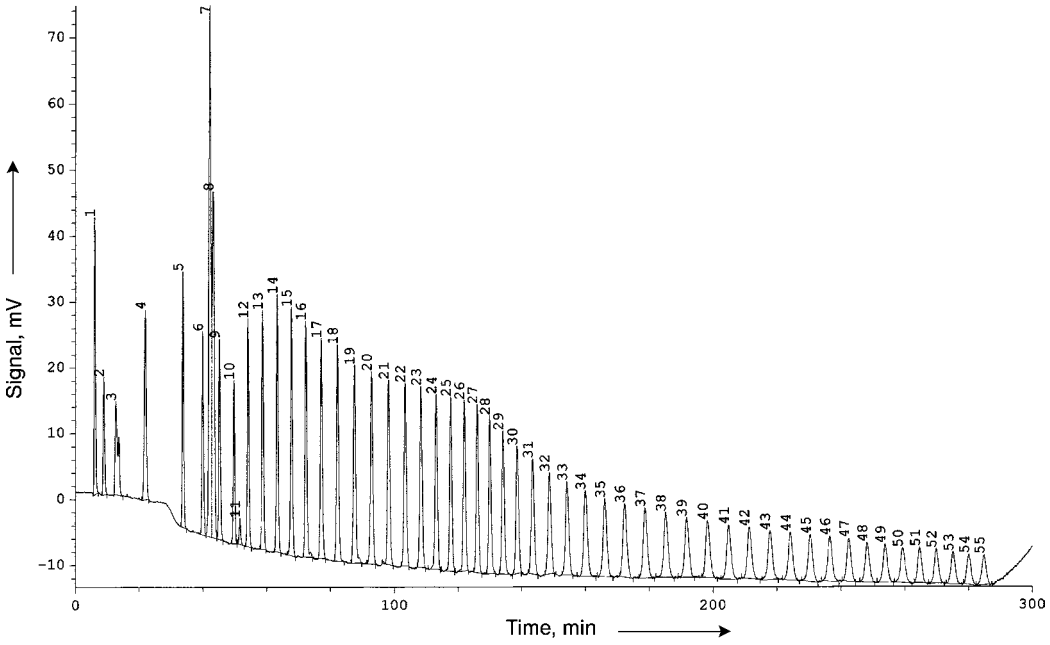


Figure 20. Ion chromatograph of a highly condensed polyphosphate $Na(PO_3)_n$ with a P_2O_5 content of 68 % [208]

Cation-Binding Capacity. The cation-binding capacity of polyphosphates is of considerable commercial importance. This term denotes the capability to bind cations of multivalent metals, especially of Ca, Mg, and Fe, and to hold them in solution such that they can no longer be detected with the usual precipitation reagents. For example, calcium ions are not precipitated by oxalate in an aqueous solution containing sodium triphosphate. Numerous investigations have shown that the effect of polyphosphates is not due to the formation of well-defined, soluble complexes but that they behave like soluble ion exchangers [90, 91]. In aqueous solution, polyphosphates are at most 30 % dissociated [92], although all OH groups of the corresponding polyacids, apart from the two terminal groups, can be titrated as strong acids.

3.3.2. Metal Complexing by Phosphates

3.3.2.1. Introduction

One of the major effects of phosphates is their ability to mask metal ions such as for example calcium or iron ions. Many applications of phosphates are due to their complexing behavior. Even orthophosphoric acid, which is commonly used as an acidulant in soft drinks and jams, not only contributes a tart flavor but also complexes traces of iron, thereby preventing dulling of the colors of the naturally occurring vegetable dyes [93]. The stability of a complex is described by the stability constant K, which is defined the general case of a metal ion M^{n+} and a ligand L^{x-} as:

$$M^{n+} + L^{x-} \rightleftarrows ML^{(x-n)-} \quad K_C = [M^{n+}][L^{x-}]/[ML^{(x-n)-}]$$

The phosphate ligand may also be present in one of the acidic forms. In the case of diphosphate, for example, there is $P_2O_7^{4-}$, $HP_2O_7^{3-}$, $H_2P_2O_7^{2-}$, $H_3P_2O_7^{-}$, and the nondissociated form $H_4P_2O_7$. If a metal ion is present with phosphates in solution, there is a "competition" between the metal ions and the protons for the ligand ions:

$$n\,H + L^{x-} \rightleftarrows H_nL^{(x-n)-} \quad K_A = [H]^n\,[L^{x-}]/[HL^{(x-n)-}]$$

Metal ions release protons from the ligand and thus decrease the pH of the solution compared to that of the metal-free state. In the case of pyrophosphate (diphosphate), the following two equilibria have to be satisfied simultaneously:

$$H_2O + P_2O_7^{4-} \rightleftarrows HP_2O_7^{3-} + OH^-$$

$$Ca^{2+} + P_2O_7^{4-} \rightleftarrows CaP_2O_7^{2-}$$

The complex constant K_C can be found from the decrease of the pH on addition of the metal chloride. In this way, equilibrium constants for a number of metal phosphate complexes were determined at 25 °C and 40 °C [94].

$[M^{n+}]$, $[L^{x-}]$, $[ML^{(x-n)-}]$, and $[HL^{(x-n)-}]$ are activities, not concentrations. Because many of the ions in phosphate solutions carry high charges, the activity corrections are quite high. In order to obtain thermodynamic stability or dissociation constants from concentration data, the Debye–Hückel activity corrections (proportional to the square root of the ionic strength μ) may be applied.

3.3.2.2. Analytical Methods

Analytical methods to determine the thermodynamic stability constant include: acid-base titrations (titration of a phosphate in presence of various metals); photometric measurements (many phosphate salts are colorless, therefore not widely used); ion exchange studies (the linear relation between phosphate concentration and the reciprocal of the distribution coefficient of the metal between resin and solution is cited as evidence of a 1:1 complex); conductivity (a minimum of conductivity or a maximum of cell resistance represents a complex formed); polarography (the metallic ions bound in the complex are deposited at a more negative potential than the free cations). See [93] for more details.

3.3.2.3. Complexing by Individual Phosphates

In general, the chain phosphates (including di- and triphosphates) are relatively strong complexing agents, the ring phosphates are much less effective, and the orthophosphate is a poor complexing agent. The latter may act, especially in an alkaline medium, as a precipitating agent for alkaline-earth metal ions.

Orthophosphate. By acid-base titrations the negative (decadic) logarithm of the stability constant pK_s was found to be 1.88 (Mg); 1.70 (Ca); 1.52 (Sr) and 2.58 (Mn) at 25°C and an ionic strength of 0.2 [93].

Table 8. Negative decadic logarithm of dissociation constants of pyrophosphate complexes, solutions containing tetramethylammonium bromide, 25°C, pH 10–12 [96]

Ionic strength	$-\log K_C$ ($CaP_2O_7^{2-}$)	$-\log K_C$ ($MgP_2O_7^{2-}$)
0	5.60	7.2
0.1	5.39	
1	4.89	5.41

Diphosphate (Pyrophosphate). Diphosphoric acid has two strongly and two weakly dissociated protons. In alkaline applications, the tetravalent pyrophosphate anion is most important. Quantitative studies show that the stability constant for the pyrophosphate–calcium complex is ten times smaller than that for the corresponding complex of the tripolyphosphate ion [95] (Table 8)

Triphosphate (Tripolyphosphate). The corresponding triphosphoric acid has three strongly and two weakly dissociated protons. Aqueous solutions of alkali metal triphosphates have an alkaline reaction. As in the case of diphosphate, increase of ionic strength of the solution diminishes the stability of the complex strongly (Table 9).

Metaphosphates. The cyclic metaphosphates are of minor importance concerning complexation. This is due to the reduced solubility of the earth alkali salts and the possible ring cleavage under alkaline conditions. Measurements of electrical conductivity on trimetaphosphate (the chief representative of the metaphosphates) solutions containing also other cations as sodium have led to dissociation constants of ion pairs containing the trimetaphosphate anion, which are for Ca^{2+} 3.5×10^{-4} and for Mg^{2+} 4.8×10^{-4} [95].

Chain Polyphosphates. The concept of stoichiometric complexes between a ligand and one metal ion is not applicable to chain polyphosphates. The complexation of calcium and magnesium by long-chain alkali-metal polyphosphates can be described more easily by the concepts of "calcium binding" or ion exchange between alkali metal and calcium ions. Even in dilute solutions of polyphosphates, alkali metal ions are only partially dissociated - up to a maximum of 30–40 % [97, 98]. The degree of dissociation becomes smaller with increasing chain length and increasing concentration. The same rule applies also for earth-alkali metal ions except that they are much more strongly bound than the alkali metal ions (Table 10).

Table 9. Negative decadic logarithm of dissociation constants of tripolyphosphate complexes [96], conditions as in Table 8

Ionic strength	$-\log K_C$ ($CaP_3O_{10}^{3-}$)	$-\log K_C$ ($MgP_3O_{10}^{3-}$)
0	6.90	8.6
0.1	6.41	5.8
1	5.36	5.83

Table 10. Negative decadic logarithm of dissociation constants of calcium polyphosphate complexes with different chain length* [96], conditions as in Table 8

	$-\log K_C$ of calcium polyphosphate		
Ionic strength	$n = 6$	$n = 14$	$n = 60$
0	7.28	7.23	7.54
0.1	6.8	6.77	6.99
1	5.78	5.80	5.80

* n = average condensed PO_3 units in the polyphosphate chain

In addition to the ability of polyphosphates to bind cations, they also possess the ability of hindering the growth of large crystals of $CaCO_3$ even at very small concentrations. This inhibition effect is due to the adsorption of polyphosphate chains on the surface of the crystal nucleus. This scale inhibition effect is widely used in water treatment or detergent application. It also may be responsible for calcium "sequestering" or "binding" values exceeding the 1:1 stoichiometry.

3.3.2.4. Other Concepts Besides the Stability Constant

Early quantitative studies of calcium phosphate complexes dealt with the sequestering ability or "calcium value" which expressed the amount of calcium needed to form a barely discernible precipitate upon addition of a soluble calcium salt to a solution of the phosphate. The experimental technique commonly used is nephelometric titration with visual, photometric, or electrical detection. The term sequestration was introduced by Hall to describe the process whereby ions such as Ca^{2+} could remain in solution and act as if they were not there. Later extensions of the concept have broadened the term sequestration so that it now includes the combined complexing and dispersing action of the chain phosphates in water-softening applications.

In order to obtain comparable values, the following variables have to be considered:

1. Concentration of the precipitating anions (others than phosphates, e.g., carbonates)
2. Concentration of the precipitable metal ions
3. The (chain) phosphate used and its concentration
4. The concentration of neutral salts (e.g., sodium chloride)
5. The pH and the temperature of the solution

The amount of calcium needed to form a precipitate in a calcium titration is dependent upon two competing equilibria:

$$Ca^{2+} + \text{(chain)phosphate} \rightleftarrows \text{calcium complex of phosphate}$$

$$Ca^{2+} + \text{pecipitating anion (may be identical with the phosphate anion)} \rightleftarrows \text{calcium precipitate}$$

The latter equilibrium, which defines the solubility product, may be affected by the inhibition effect of the phosphate. In the case of phosphate solutions (0.01 – 0.05 mol/L) and titration with a $CaCl_2$ solution of 0.1 mol/L at pH 8, the following values are obtained (P is the complexing agent) [93]:

Pyrophosphate:	
Ca/P:	2.2 mol/100 mol (theory 50 mol/100 mol)
$CaCO_3$/P:	17 mg/g (theory 376 mg/g)
Tripolyphosphate:	
Ca/P:	23 mol/100 mol (33 mol/100 mol)
$CaCO_3$/P:	190 mg/g (272 mg/g)
Sodium polyphosphate (average chain length 14)	
Ca/P:	34 mol/100 mol (50 mol/100 mol)
$CaCO_3$/P:	334 mg/g (490 mg/g)

In the case of 0.10 – 0.15 mol/L orthophosphate present, the calcium values are much lower, with the exception of those with pyrophosphate:

Pyrophosphate:	
Ca/P:	2.8 mol/100 mol
$CaCO_3$/P:	21 mg/g
Tripolyphosphate:	
Ca/P:	12 mol/100 mol
$CaCO_3$/P:	99 mg/g
Sodium polyphosphate (average chain length 14)	
Ca/P:	13 mol/100 mol
$CaCO_3$/P:	225 mg/g

In the case of other precipitating anions such as carbonate, the values may differ.

For use by customers, in strict adherence of instructions parameter, the nephelometric-titration-specific calcium value can be consulted to appraisement of the different builder.

Experimental conditions for the nephelometric titration to give calcium values of various phosphates (Table 11) are given in the following (internal method of research and development from BK Giulini GmbH):

Precipitating anion:	oxalate
Concentration of precipitating anion:	potassium oxalate, 0.5 mmol/100 mL
Precipitable metal ion:	Ca^{2+} as 0.1 M $CaCl_2$
Flow of precipitable metal ion:	2.5 mL/min
Detection:	photometrical detection of the turbidity with white-light fiber optics
Concentration of complexing agents:	100 mg/100 mL
pH control:	combined pH electrode, the pH is held constant automatically with 0.1 M NaOH
Temperature control:	thermostated double-shell titration vessel with inline stirrer

Table 11. Calcium values (amount of Ca per amount of complexing agent) of different phosphates obtained by nephelometric titration

	Calcium value, mg/g			
	pH 7		pH 10	
Phosphate	20 °C	60 °C	20 °C	60 °C
Tetrasodium diphosphate	66	31	133	91
Sodium tri(poly)phosphate	151	137	203	173
Sodium tetra(poly)phosphate (short chain)	171	151	229	200
Sodium polyphosphate (medium chain)	195	191	219	282
Sodium hexametaphosphate (long chain)	228	226	247	307
Sodium polyphosphate (branched chain)	215	214	236	313
Sodium acid polyphosphate	250	238	276	409

Reading of the measured data:	light transmission (y axis) and volume of the added $CaCl_2$ solution (x axis)
Evaluation:	calcium value, in milligram Ca per gram complexing agent $= \frac{V \times C \times M \times f}{E}$ V = volume of 0.1 M $CaCl_2$ in mL C = concentration of $CaCl_2$ in mol/L M = molar mass of Ca (40.08 g/mol) f = factor of 0.1 M $CaCl_2$ E = weighted sample (g)

Bonding of the cation is primarily attributed to electrostatic attraction by the negatively charged polyanions. In addition, formation of relatively stable chelates, in which the cations are bonded to several PO_3 groups in the flexible polyphosphate chain, also must be assumed [62]. Since multivalent cations are bound much more strongly than the monovalent ions of alkali metals, the latter can readily be exchanged for alkaline earth or heavy metal ions. This exchange and binding capacity is used for numerous purposes to mask and inactivate interfering cations.

Various methods are used to determine the exchange capacity. The lime-binding capacity or lime-binding value denotes the amount of CaO kept in solution by a specific amount of alkali-metal polyphosphate in the presence of reagents which precipitate Ca^{2+}. For the determination, a predetermined amount of polyphosphate is titrated with $CaCl_2$ in the presence of sulfate ions to the onset of turbidity. Alternatively, the end point is determined by formation of sparingly soluble calcium polyphosphate without addition of calcium-precipitating anions [99].

The lime-binding capacity of polyphosphates increases with increasing chain length up to $n = 8$. For higher degrees of condensation it remains essentially unchanged. Figure 21 shows the amount of phosphate which is necessary to prevent precipitation of an insoluble calcium compound (e.g., calcium oxalate) as a function of chain length. The lime-binding capacity is also dependent on concentration, pH, temperature, and the presence of electrolytes [100]. In contrast to polyphosphates, cyclic metaphosphates exhibit only minor exchange capability toward multivalent cations.

Colloidal Behavior. Many applications of polyphosphates are based on colloidal effects. These are secondary effects because polyphosphates themselves exhibit no colloidal properties in pure, aqueous solution. Essentially, the effect is due to adsorption of multiply charged polyphosphate anions on suspended or emulsified particles, electrical charging of the latter, and consequent change of the physicochemical characteristics [101].

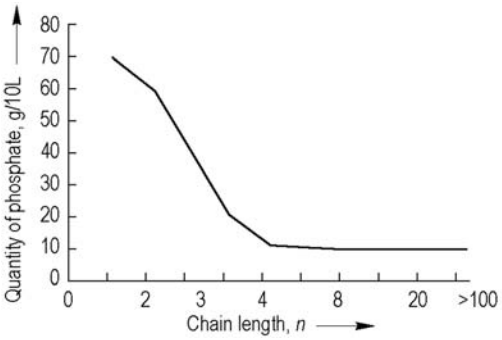


Figure 21. Lime-binding capacity of polyphosphates as a function of chain length
The figure shows the amount of polyphosphate which is necessary to complex all calcium ions in 10 L of water with a hardness of 10° dH

The dispersive action of polyphosphates is one of the most prominent effects. Viscosity reduction, which always occurs concurrently, is directly related to this effect. For instance, stiff, tenacious pastes such as blanc-fixe ($BaSO_4$) can be converted to stable, free-flowing suspensions by addition of small amounts of Graham's salt. Kaolin suspensions of high solids content and low viscosity can be prepared with small amounts of polyphosphate.

The improvement of the soil antiredeposition capacity in the laundry process by polyphosphates can also be regarded as suspension stabilization. Although polyphosphates themselves are not surface-active and thus are not really emulsifiers, they increase the surface activity of wetting agents. Presumably, the effect is due to a dispersion of the surface-active substances.

The peptization of proteins is another colloid chemical effect. It plays an important role in the production of processed cheese and in meat processing. Protein is partially digested by polyphosphate and converted to a sol.

In many cases the dispersing effect of polyphosphates is due to adsorption and is supplemented by stabilization due to elimination of interfering factors (calcium binding).

3.3.3. Sodium Diphosphates

The following sodium diphosphates (pyrophosphates) are known as crystalline compounds [102]:

$NaH_3P_2O_7$	$Na_3HP_2O_7 \cdot H_2O$
$Na_2H_2P_2O_7$	$Na_3HP_2O_7 \cdot 9\ H_2O$
$Na_2H_2P_2O_7 \cdot 6\ H_2O$	$Na_4P_2O_7$
$Na_3HP_2O_7$	$Na_4P_2O_7 \cdot 10\ H_2O$

Of these, only disodium diphosphate and tetrasodium diphosphate are produced on a large scale.

Disodium dihydrogendiphosphate. [*7758-16-9*], disodium diphosphate, acidic sodium pyrophosphate, $Na_2H_2P_2O_7$, M_r 221.97, *d* 2.31. Its solubility in water is 13 g $Na_2H_2P_2O_7$/100 g H_2O at 20 °C, and 20 g at 80 °C. The pH of a 1 % aqueous solution is 4.1. The usual commercial product is the anhydrous, nonhygroscopic salt in powder form. The hexahydrate, $Na_2H_2P_2O_7 \cdot 6\ H_2O$, *d* 1.85, crystallizes from aqueous solution below 27 °C. Above this temperature, it is converted to the anhydrous form.

Disodium dihydrogendiphosphate is produced from sodium dihydrogenmonophosphate by heating at 200 – 250 °C:

$$2\ NaH_2PO_4 \rightarrow Na_2H_2P_2O_7 + H_2O$$

Careful control of reaction temperature and time is required to achieve complete conversion of the monophosphate and to avoid formation of higher condensed phosphates. Reaction times of 1 – 6 h at 215 – 245 °C are used [103]. The degree of condensation can be influenced by regulating the partial pressure of water vapor [104].

Usually, monophosphate is converted to diphosphate continuously in rotary kilns. Smaller plants also use batch processes with plate dryers or electrically heated pans.

A monophosphate solution made from phosphoric acid and caustic soda in situ is used in the so-called "return" process. The crystal slurry obtained by evaporation is combined with recycled material in a twin screw and charged to a rotary dryer [105].

In another process, NaH_2PO_4 solution is spray dried at 140 – 195 °C, giving 10 – 40 % $Na_2H_2P_2O_7$. Subsequent calcination at 200 – 220 °C gives pure $Na_2H_2P_2O_7$ [106].

Disodium diphosphate is used as a (tropically stable) acid carrier in baking powder, for improvement of flow properties in flour, for pH regulation, and in dental care products for prevention of tartar formation.

Tetrasodium Diphosphate. [*7722-88-5*], tetrasodium pyrophosphate, neutral sodium pyrophosphate, $Na_4P_2O_7$, M_r 265.91, *d* 2.50, *mp* 985 °C. Its solubility in water is 5 g $Na_4P_2O_7$/100 g H_2O at 20 °C and 35 g at 80 °C. The pH of a 1 % aqueous solution is 10.4. The usual commercial product is the anhydrous salt in the form of a white, nonhygroscopic powder. However, in contact with moist substances it acts as a drying agent with formation of $Na_4P_2O_7 \cdot 10\ H_2O$.

The decahydrate, $Na_4P_2O_7 \cdot 10\ H_2O$, *d* 1.83, *mp* 79.5 °C (with loss of H_2O), is also marketed but on a much smaller scale. It crystallizes from aqueous solution below the melting point. Anhydrous $Na_4P_2O_7$ is known in five different modifications with transition temperatures between 400 and 545 °C. Only the low-temperature form is stable below 400 °C.

Tetrasodium diphosphate is produced by calcination of disodium hydrogenphosphate at 300 – 900 °C:

$$2\ Na_2HPO_4 \rightarrow Na_4P_2O_7 + H_2O$$

In the two-stage process, a concentrated monophosphate solution is dehydrated to give anhydrous disodium hydrogenphosphate in a spray drying tower and subsequently condensed to diphosphate in a rotary kiln. For improvement of the heat economics, the hot off-gases from the second stage can be used for spray drying. In another process, phosphoric acid and caustic soda are metered separately into a spray drying tower in order to utilize the heat of neutralization [107].

Both rotary kilns and spray drying towers are used in the single-stage production of $Na_4P_2O_7$. In the rotary kiln process, the phosphate solution is sprayed onto a bed of already formed, solid monophosphate (return process). A single-stage spray tower process is described below (see Pentasodium Triphosphate; Properties). Generally, the processes for production of sodium triphosphate can also be used for sodium diphosphate.

Tetrasodium diphosphate is used in detergents and cleansers, in metal surface treatment, and in oil well drilling fluids for viscosity adjustment. In

the food area, $Na_4P_2O_7$ is used as a component of cold puddings and ice cream for regulating the consistency. The stabilization of toothpastes based on calcium hydrogenphosphate is another important application.

3.3.4. Pentasodium Triphosphate

Pentasodium triphosphate [*7758-29-4*], sodium triphosphate, sodium tripolyphosphate, is one of the commercially most significant phosphorus compounds.

Properties. Pentasodium triphosphate, $Na_5P_3O_{10}$, M_r 367.93; solubility of the hexahydrate in water, 14.6 g $Na_5P_3O_{10}$/100 g H_2O at 20 °C, 23.7 g at 80 °C; pH of a 1 % aqueous solution, 9.7.

Pentasodium triphosphate exists in two anhydrous modifications, i.e., the low-temperature (LT) form (*d* 2.57, monoclinic) and the high-temperature (HT) form [*d* 2.62, monoclinic, *mp* 622 °C (decomp.)], and as the hexahydrate, $Na_5P_3O_{10} \cdot 6\ H_2O$ (*d* 2.12, triclinic). In the technical literature, the HT form is often referred to as form II, and the LT form as form I. The LT form is converted completely to the HT form on heating to 500 °C. However, the HT form is transformed to the LT form only very slowly on tempering below 400 °C (transition temperature, 417 ± 8 °C [108]). At 622 °C the anhydrous salt decomposes to a melt and crystalline $Na_4P_2O_7$ (see also Fig. 19). Above 865 °C a homogeneous melt is obtained, which on rapid cooling yields a glassy product. This can be converted to the crystalline modifications by heating under specific conditions [109, 110].

The two modifications differ in their reaction with water. Both forms are metastable in water and undergo complete conversion to the hexahydrate in an exothermic reaction. However, the hexahydrate is formed much faster from the HT modification than from the LT form. The anhydrous modifications are more soluble than the hexahydrate. Therefore, on dissolution a concentration of ca. 32 % $Na_5P_3O_{10}$ is attained initially which is considerably higher than that of a solution in equilibrium with the hexahydrate (ca. 13 % $Na_5P_3O_{10}$). This occurs especially on dissolution of the LT form, from which the hexahydrate is formed at a slower rate.

On heating to 100 – 120 °C, the hexahydrate hydrolyzes to give mono- and diphosphate:

$$Na_5P_3O_{10} \cdot 6\ H_2O \rightarrow Na_3HP_2O_7 + Na_2HPO_4 + 5\ H_2O$$

$$Na_3HP_2O_7 + Na_2HPO_4 \rightarrow Na_4P_2O_7 + NaH_2PO_4$$

On further heating to 140 – 220 °C the hydrolyzed products recondense to form anhydrous $Na_5P_3O_{10}$ in the LT modification. Commercial products contain a mixture of the HT and LT forms, depending on application and processing requirements. Formerly products with a high content of the LT form were preferred for the manufacture of detergent powders, the major application of sodium triphosphate. The reason was that the rapidly hydrated HT form tends to cake during the production of detergent slurries and is thus more difficult to process. Later it was recognized how much the hydration properties of the triphosphate are also affected by the content of hexahydrate crystal nuclei. Now, the detergent industry tends not to specify certain contents of the two modifications but rather overall hydration characteristics measurable by the heat of hydration as a function of time [111].

Production. Pentasodium triphosphate is usually produced from a mixture of two moles of disodium phosphate and one mole of monosodium phosphate:

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

The reaction is carried out in the temperature range 300 – 550 °C, whereby the reaction temperature determines the LT/HT form ratio. For the production of triphosphate with a minimum content of $Na_4P_2O_7$ and higher condensed polyphosphates, the monophosphates must be present in precise stoichiometric ratio in a homogeneous, finely crystalline mixture. In most cases, a stoichiometrically adjusted monophosphate solution, obtained by neutralization of phosphoric acid with caustic soda or soda ash, is used as starting material. Both single-stage and two-stage processes are used for dehydration of the solution and subsequent condensation to triphosphate.

In the two-stage processes (Fig. 22), the solution is dehydrated in the first stage to give an anhydrous monophosphate mixture. Frequently, partial condensation with formation of diphosphate already occurs in this stage. The actual

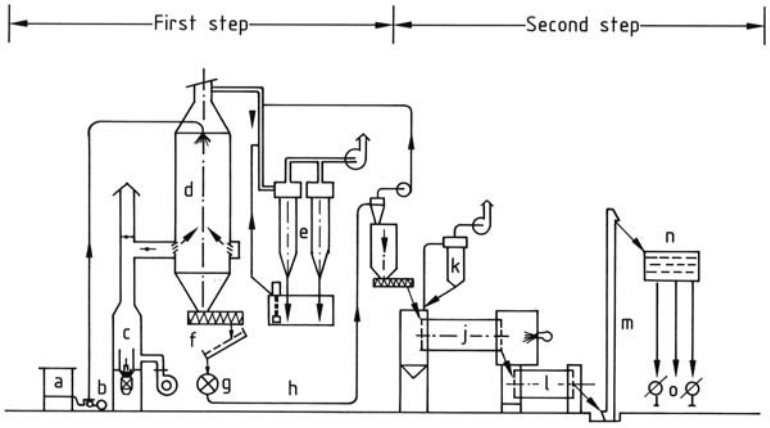


Figure 22. Two-stage process for production of pentasodium triphosphate [112]
a) Receiver; b) Heavy-duty pump; c) Combustion chamber; d) Spray tower; e) Wet dust removal from flue gas; f) Sieve; g) Mill; h) Pneumatic conveyor; i) Silo; j) Rotary kiln; k) Flue gas purification; l) Condenser; m) Bucket chain; n) Sieve; o) Bagging scale

condensation to triphosphate then follows in the second stage.

Generally, spray dryers are used for dehydration of the monophosphates, and rotary kilns for the conversion to triphosphate. The required energy is supplied by hot gases from a combustion chamber or by an oil or gas flame in the rotary kiln.

A fluidized-bed reactor has also been recommended for the conversion of dried monophosphates to triphosphate [113]. In another process rotary kilns are used in both stages, and a granular end product is obtained by grinding the intermediate product and adding water before calcination [114].

In the single-stage process, rotary kilns or spray drying towers are used. In the Hoechst-Knapsack process (Fig. 23), the monophosphate solution is sprayed at 1 – 2 MPa [115] into a stainless-steel spray tower [116]. Burners, arranged concentrically around the nozzle, generate a flame zone directed conically towards the center of the tower. The sprayed solution moves downward cocurrent with the burner gases and is

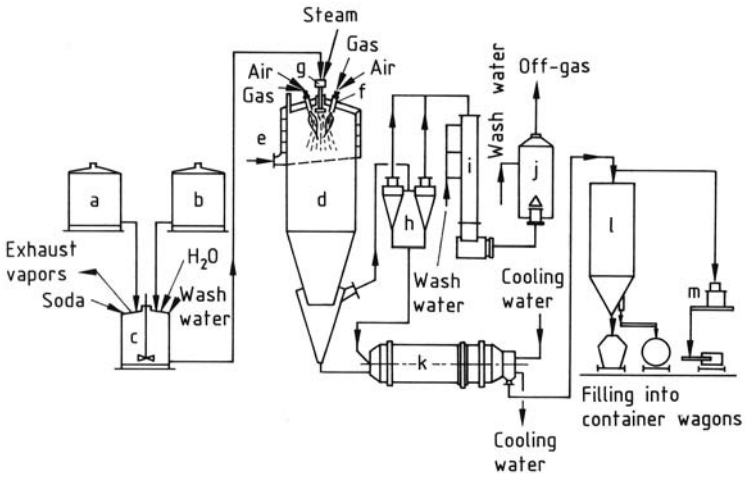


Figure 23. Production of pentasodium triphosphate by the Hoechst-Knapsack process [112]
a) Caustic soda; b) Phosphoric acid; c) Neutralization; d) Spray tower; e) Cooling jacket; f) Burner; g) Spray nozzle; h) Cyclone; i) Cooling pipe; j) Wash tower; k) Rotary cooling drum; l) Product silo; m) Bag filling and weighing machine

rapidly dehydrated and converted to triphosphate. Most of the $Na_5P_3O_{10}$ is collected in the tower cone and discharged. Finer particles are separated from the off-gas by cyclones. The off-gas is then further purified by a liquid washing.

Free-flowing, powdery products are obtained, with triphosphate contents of up to 98 %. The ratio of LT/HT form can be varied over a wide range by controlling the temperature and the water content in the gas phase. Moreover, a particular crystalline form can be obtained by simultaneously spraying seed crystals of the desired modification [117]. Coarse $Na_5P_3O_{10}$ particles (> 0.15 mm) can also be prepared by this seed crystal method. The required crystallites are taken from the residues of the dust filter bag because these flue dusts have favorable spray and suspension characteristics.

In the FMC process, the monophosphate solution is sprayed upwards from nozzles at the bottom of the tower [118]. The particles move upward to the flame zone at the top of the tower and are then carried downward with the hot gas stream.

Single-stage rotary kiln processes are carried out both according to the cocurrent and countercurrent principle. The monophosphate solution is sprayed through a flame directed into the rotary kiln and onto a hot bed of previously calcined material [119]. The product then moves cocurrently with the hot combustion gases to the discharge port and thus is posttempered at a reduced temperature. Advantages of this mode of operation are the avoidance of caking and the possibility to produce a product with a high content of the LT form. The high energy consumption is, however, a disadvantage.

A countercurrent rotary kiln process is described by FMC [120]. The material is conveyed countercurrently to the heating gases, which are generated in a combustion chamber outside of the rotary kiln. This process permits a substantially better heat utilization than the cocurrent process. However, the frequent occurrence of caking at the charging point is a disadvantage.

Numerous suggestions for modification of the commercial processes are found in the patent literature. They are aimed at the preparation of pentasodium phosphate with special application properties and concern especially production of the low-temperature modification [121, 122], attainment of low bulk densities [123], and increase of abrasion resistance [124]. Partially hydrated products are prepared for improvement of the solubility characteristics [125, 126].

Sodium triphosphate Hexahydrate is produced by hydration of anhydrous $Na_5P_3O_{10}$. It is important that too high a temperature rise is avoided in the exothermic hydration reaction because the triphosphate anion is cleaved hydrolytically by the water of hydration at elevated temperatures. In the Hoechst-Knapsack process an excess of water is sprayed onto $Na_5P_3O_{10}$ in a rotary kiln. The excess water is evaporated by simultaneously blowing air over the product, dissipating part of the heat of hydration and maintaining the product temperature at 60 – 70 °C [127]. In the Monsanto process crushed ice is used for the hydration of $Na_5P_3O_{10}$ to the hexahydrate [128].

3.3.5. Higher Condensed Sodium Polyphosphates

If mixtures of NaH_2PO_4 and Na_2HPO_4 in a ratio $> 1:2$ are heated until the water of constitution is released, a mixture of polyphosphates of different chain lengths is formed. The degree of condensation n (average number of P atoms per molecule) is used for characterization. Glassy, amorphous products are obtained by fast cooling of the melts of such mixtures. They are commercially important as glassy phosphates or fused phosphates. Products with $n = 4$ (tetraphosphate) to $n = 25$ (Graham's salt) are produced, depending on the application.

Frequently, the incorrect designation "hexametaphosphate" is used for Graham's salt in the literature, especially in the United States. However, it consists essentially of high-molecular, straight-chain polyphosphates with ca. 6 % trimetaphosphate.

Upon tempering, the glassy Graham's salt is converted to crystalline, high-molecular forms (Kurrol's and Maddrell's salt) or to cyclic sodium trimetaphosphate, $Na_3P_3O_9$. Figure 24 shows the various condensed phosphates which can be obtained from NaH_2PO_4 and their conditions of preparation [62].

Fused Phosphates. (glassy polyphosphates), $Na_{n+2}P_nO_{3n+1}$, are all hygroscopic and

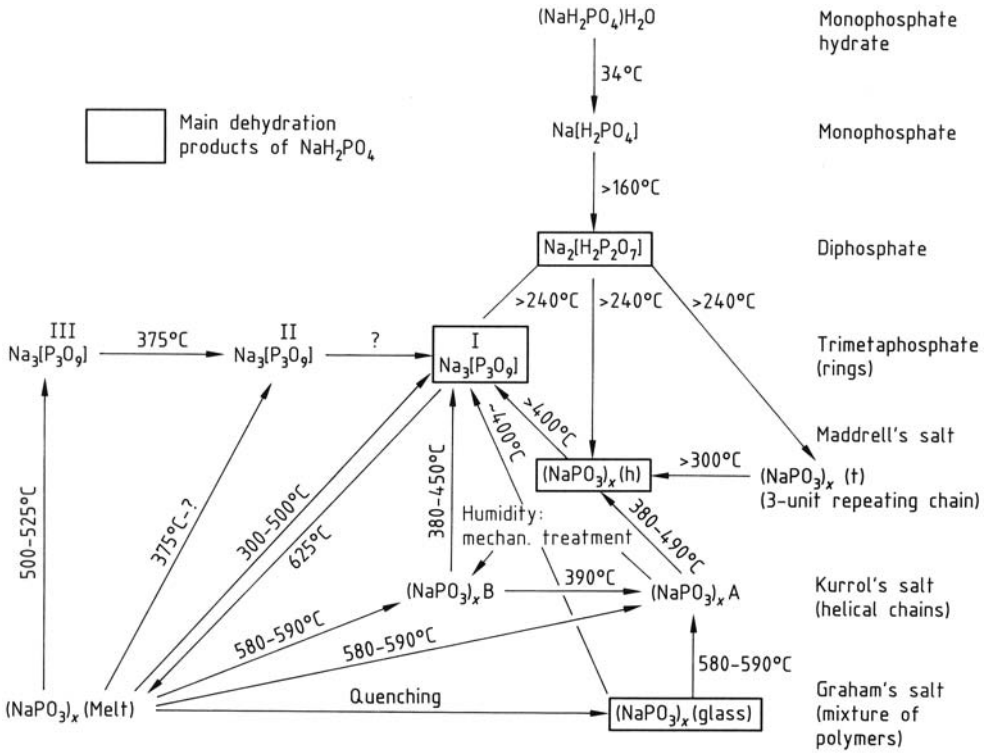


Figure 24. Condensed phosphates which can be prepared from NaH_2PO_4 by heating and their interrelationship [62]

water soluble. The pH depends on the degree of condensation. In 1 % aqueous solutions it ranges from 8.4 for hexasodium tetraphosphate to 4.0 for long-chain polyphosphates ($n > 20$).

High-molecular fused phosphates are produced from acidic monophosphates in tank furnaces lined with zircon mineral bricks (Fig. 25). The average chain length depends on temperature, duration of fusion, and water vapor pressure of the melt. The melt temperatures are 600 – 800 °C, depending on the $Na_2O : P_2O_5$ ratio. The outflowing melt is chilled on water-cooled barrels or drums with formation of glassy clods, which are subsequently broken and ground.

In another process, fused phosphates are obtained directly from elemental phosphorus [129]. Phosphorus and caustic soda are sprayed by air into a spray tower lined with graphite bricks. Molten polyphosphate is formed in the phosphorus flame at 1500 – 1800 °C, accumulates at the tower bottom, and runs onto a cooled drum. About 30 % of the combusted phosphorus is entrained by the off-gas in the form of fused phosphate and small amounts of P_4O_{10}. These are

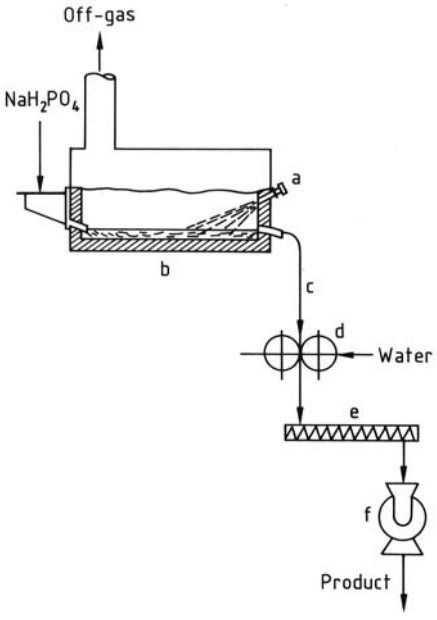


Figure 25. Production of fused phosphate [101]
a) Burner; b) Melting furnace; c) Melt; d) Cooling roller; e) Worm gear; f) Mill

converted to an aqueous solution of sodium phosphate in a downstream wash tower and returned to the combustion tower. The energy required for dehydration of caustic soda and wash solution as well as for production of the polyphosphate melt is supplied entirely by the heat of phosphorus combustion.

Water-soluble fused polyphosphates with the molar ratio $M^I : P < 1$ are qualified as acid polyphosphates with the general formula $[M^IH]_{n+2}P_nO_{3n+1}$.

High-molecular fused sodium acid polyphosphates are produced from sodium phosphate solution ($Na_2O:P_2O_5 = 0.5–0.7$) by drying and following condensation in an indirectly heated melting tank at a temperature range from 600 to 800°C and adherence of a high water vapor pressure [130–132].

The sodium acid polyphosphate concentration of P_2O_5 has a range from 75–79 % and a chain length (*n*) from 20–30. Compared to branched ultrametaphosphate, it is water soluble and has a pH < 2 in 1 % aqueous solution.

Tempering the sodium acid polyphosphate ($Na_2O : P_2O_5 = 0.5$) at 100°C–150°C at a specific water vapour pressure convert the long-chained polyphosphate to a crystalline sodium trihydrogendiphosphate ($NaH_3P_2O_7$) [133].

A posttreatment of the ground products by addition of Na_2CO_3 or $Na_4P_2O_7$ or by spray coating with alkaline solutions is recommended for decreasing the hygroscopicity [135].

Maddrell's Salt. Crystalline sodium polyphosphate with a chain length of ca. 2000 P units exists in two modifications: the high-temperature triclinic form (*d* 2.669) and the low-temperature form (*d* 2.52). Both are essentially insoluble in water. For application as a polishing compound in fluoridated toothpastes, it is important that formation of water-soluble trimetaphosphate during production is avoided by maintaining a low partial pressure of water vapor. Sodium dihydrogenphosphate is conveyed at a constant rate through a tunnel furnace while the generated water vapor is continuously drawn off [136]. In the Monsanto process, NaH_2PO_4 is compressed into pellets, which are then dehydrated in a rotary kiln at 300 – 460 °C in a hot air stream [137].

Kurrol's Sodium Salt. This crystalline, long-chain sodium polyphosphate is formed from Graham's salt by tempering at 580 – 590 °C: form A, *d* 2.58, monoclinic; form B, *d* 2.56, monoclinic. It has a fibrous structure similar to asbestos and is only sparingly soluble in water. Upon longer storage in water the fibers swell and slowly form a highly viscous solution.

3.3.6. Sodium Metaphosphates

Sodium tri- and tetrametaphosphate, $Na_3P_3O_9$ and $Na_4P_4O_{12}$, are the best known examples of cyclic sodium metaphosphates. In addition, metaphosphates with 5, 6, 7, and 8 phosphorus atoms have also been isolated from Graham's salt [138, 139].

Sodium trimetaphosphate can be prepared by cooling of a corresponding polyphosphate melt and subsequent tempering above 350 °C [140] or by condensation of sodium dihydrogen-phosphate with addition of a small amount of ammonium nitrate [141].

Sodium tetrametaphosphate can be prepared by reaction of the corresponding copper salt with Na_2S or by hydrolysis of hexagonal P_4O_{10} with caustic soda [142].

Sodium trimetaphosphate is used as a phosphorylating agent for ascorbic acid [211] to stabilize vitamin C mixtures against thermal decomposition.

In the construction industry, sodium trimetaphosphate is used to prevent the shrinkage of gypsum plaster boards (US Pat. 03/0154888) and as a setting retarder for gypsum plaster [134].

3.3.7. Uses of Condensed Sodium Phosphates

Water Treatment. Monophosphates form sparingly soluble precipitates with water hardeners and are therefore used as precipitation agents in water softening. However, the water softening effect of condensed phosphates is due to their ion-exchange capacity for cations. The water softening effect and the capability to mask heavy metal ions are utilized in various ways.

For instance, polyphosphates, especially fused phosphates, are used in the *textile industry* for bleaching, dyeing, and textile finishing. In these applications, additional advantages are attained by the other properties of phosphates, e.g., their dispersing capacity [143].

Fused phosphates are also used in *photography* to prevent spots and shadows caused by precipitation of water hardeners and heavy metal ions in the baths.

Fused phosphates are also used in place of monophosphates in the conditioning of *boiler feedwater*. Compared with monophosphates, polyphosphates have the advantage that, after addition to the feedwater, they initially keep the hardeners in solution. The hydrolytic degradation to monophosphates occurs only at elevated temperature in the boiler. Thus, the hardeners are precipitated there and can be discharged as sludge.

Another property of polyphosphates important in practice is their capability, even at very low concentrations, to prevent precipitation of calcium carbonate. This effect is utilized in the phosphate threshold treatment of tap water, e.g., in communal water conduits, in warm water facilities, or in industrial cooling water systems. The required amounts of phosphate, usually 2 – 5 g/m^3 of water, are much lower than the amount necessary for complexation of the hardeners. In this way, the precipitation of calcium carbonate can be completely prevented at moderate temperatures and water hardnesses and normal pH values. At elevated temperatures and higher water hardnesses, crystal growth is hindered to such an extent that no firmly adhering deposits can be formed. It is assumed that growth of the crystal nuclei is stopped or strongly retarded by adsorption of polyphosphate anions [144, 145].

It is important in the threshold process that the phosphate concentration does not exceed a certain limit because otherwise precipitation of sparingly soluble phosphates begins. These can only be redissolved at substantially higher concentration by complexation. Water-soluble, mostly long-chain fused phosphates such as Graham's salt are used in large waterworks. They are added to the water carrying system as a 2 – 5 % solution. Slow-dissolving, glassy calcium sodium polyphosphates are used mostly in smaller works and in private residences. They are charged in form of lumps to a lock installed in the main line or in a bypass, where they dissolve slowly in the passing water [101].

An additional advantage of the phosphate threshold treatment is the anticorrosion effect due to the formation of a firmly adhering, dense, protective layer of iron calcium phosphate. Phosphates also act as corrosion inhibitors for copper, zinc, and aluminum.

Detergents and Cleansers. (→ Cleansing Agents; → Laundry Detergents, 1. Introduction) are major applications of polyphosphates. Pentasodium triphosphate, mostly marketed under the name sodium tripolyphosphate (STPP), is by far the most important product. Many industrial cleansers contain 20 – 35 % pentasodium triphosphate as builder. On a much smaller scale, tetrasodium diphosphate is also used for these applications but its significance has declined steadily in the last 10 years. The higher condensed fused phosphates are also used, i.e., in specialty cleansers and personal hygiene preparations.

Triphosphate performs several functions in the laundry process. Primarily, it softens the water by masking alkaline earth metal ions and preventing their deposition on the fabric. In addition, triphosphate prevents precipitation in the washing machine, especially on the heating elements [146]. Furthermore, the pronounced dispersing capacity of triphosphate and its emulsion stabilizing effect are important in the laundry process. Condensed phosphates increase the surface activity of wash active substances and thus their detergency (synergistic effect).

To an increasing extent, $Na_5P_3O_{10}$ is also used in automatic dishwasher detergents, which contain 20 – 50 % pentasodium triphosphate. In this application, the triphosphate is used especially for its water softening and dispersing properties and for its advantageous pH range [147].

Food Industry. The versatile applicability of condensed phosphates in the production and processing of food is essentially due to their ion-exchange and colloid properties.

In the production of processed cheese, condensed phosphates are used as rectifying or melt salts. In the production process, calcium caseinate is converted by sodium polyphosphates to sodium caseinate and is peptized. A stable suspension is formed from this product together with milk fat, finely dispersed during melting, and the substances dissolved in the aqueous phase. Polyphosphates of medium chain length are preferred for this application. An important application of long-chain polyphosphates is their bacteriostatic effect in cheese products. To a small extent,

mono- and diphosphates are added as corrective and buffer salts [101].

Polyphosphates are also used in the production of concentrated milk products such as evaporated milk and milk powder, especially to prevent aggregation of the casein (heat coagulation) by deactivation of calcium ions.

Furthermore, the dispersing and calcium-binding properties of polyphosphates are utilized in the preparation of instant puddings, ice cream, skimmed milk products, and instant sauces. In end-products, they act as stabilizers for batters and as gelation regulators.

Polyphosphates are used for prevention of blood coagulation in the preparation of blood plasma from the blood of slaughtered animals in the Fibrisol process.

Polyphosphates effect disaggregation and peptization of muscular albumin. Thus, they act similarly to natural adenosine triphosphate, which is present in living organisms but not in meat. This effect of polyphosphates, especially of diphosphates, is utilized in the preparation of cooked sausage and boiled, cured meats to avoid loss of quality due to a change in the protein structure and the resulting loss of tissue water.

Baking Aids. Disodium dihydrogendiphosphate is widely used as an acid carrier in baking powders, especially in Europe. At moderate temperatures it does not react with $NaHCO_3$ contained in baking powder and thus permits the preparation or storage of large amounts of dough. The acidic diphosphate reacts with sodium hydrogencarbonate only during the baking process with evolution of carbon dioxide and formation of tasteless disodium monophosphate. In the United States, $Na_2H_2P_2O_7$ is used only for fine baked products; otherwise monocalcium phosphate, $Ca(H_2PO_4)_2 \cdot H_2O$, is used predominantly. Because of its high reactivity towards sodium hydrogencarbonate, monocalcium phosphate is often mixed with sodium aluminum sulfate, $NaAl(SO_4)_2$, which reacts only at baking temperature. In addition, it is added to flour as "bread improver" in bread baking [148].

Sodium aluminum phosphates of composition $NaH_{14}Al_3(PO_4)_8 \cdot 4\ H_2O$ and $Na_3H_{15}Al_2(PO_4)_8$ are now used in the United States as acid carriers in baking powders [148]. They are less reactive than monocalcium phosphate and develop their full effect as expanding agents only at baking heat. This is advantageous especially for the durability of prefinished mixtures.

Leather Industry. In the production of leather, polyphosphates act in various ways. During the soaking of hides and skins, they prevent coagulation of blood and reduce the hardness of the water. In the liming step, the properties of a dispersing agent are necessary. The polyanions stabilize the lime slurry in the state of single solid particles, which are able to penetrate quicker. The result is a short and effective liming step. Another important function is the reaction with protein chains in the skin. It is comparable with a mild tanning process, so polyphosphates are used as pretanning agents [101]. These functions are important in the commonly used tannage with chromium salts and in classical vegetable tannage. In the latter process the iron-binding capacity is also essential, because the complexation of iron ions by polyphosphates prevents the formation of iron stains. During the complete beamhouse work, many washing steps are necessary. Addition of polyphosphates to the water prevents the formation of lime stains or lime shadows by complexing Ca ions.

Paint Industry. In the production of paints, especially emulsion paints, the main components water, pigments, fillers, and binder are stirred together to form a paint with good application properties. Manufacturers aim for high solids contents to give good covering power and for good storage stability of the paint. Both goals can be achieved by adding dispersing agents to the water in the first production step. Polyphosphates are well-known dispersing agents. Comparative tests show that Polyphosphates with chain lengths between $n = 6$ and $n = 10$ give the best results. The dispersing effect is due to adsorption of anionic phosphate molecules on the surface of the pigments and fillers, which eliminates the attractive forces between the particles [209]. In current emulsion paint formulations, a combination of polyphosphates and polyacrylates is used, because in addition to optimal dispersing and storage results advantages in scrubbing resistance can be obtained.

Construction Industry. Short-chain polyphosphates, especially the di- and triphosphates, are used as setting retarders for concrete and cement-based mortar. Addition of combinations

of tartraric or citric acid with long-chain polyphosphates to gypsum plaster results in optimum workability and plasticity. In cement-based self-leveling floor compounds, condensed phosphates increase the open time and the fluidity of the formulation.

Ceramics Industry. The production of large quantities of ceramic materials (e.g., tiles) requires very homogeneous raw materials. These so-called ceramic slips are formulations of different clays and additives and are prepared in a wet stage by mixing and grinding the components in ball mills. After homogenization the slips must be dried in spray towers to give granular materials. Normal ceramic slips have a solids content of 55 – 60 %. The energy consumption of the spray drier could be lowered by increasing the solids content. By adding small amounts (0.5 – 1.0 %) of polyphosphates to the slips during the ball mill process, solids contents of 70 % can be attained. The polyphosphate anions are adsorbed on the surface of the silicate particles and act as a deflocculant. Calculations show that the decreased energy demand in the spray drier is economically favorable for the overall process [210].

Other Uses. Polyphosphates are also used as dispersing agents and stabilizers in textile dyeing and printing, as well as in the paper industry for the prevention of resin excretions and for improving coatings and fillers [101]. They are also added to drilling muds in oil well drilling because of their emulsion stabilizing effect [101].

3.4. Other Phosphates

A range of inorganic phosphates, including zinc and chromium phosphates, are used as corrosion-inhibiting pigments; these are discussed elsewhere, → Metals, Surface Treatment. For phosphating of metal surfaces, see → Metals, Surface Treatment, Chap. 3..

3.4.1. Potassium Phosphates

Potassium Monophosphates. Potassium forms the following monophosphates:

KH_2PO_4
$KH_2PO_4 \cdot H_3PO_4$
$KH_2PO_4 \cdot 2\ K_2HPO_4 \cdot H_2O$
$KH_2PO_4 \cdot 3\ K_2HPO_4 \cdot 2\ H_2O$
K_2HPO_4
$K_2HPO_4 \cdot 3\ H_2O$
$K_2HPO_4 \cdot 6\ H_2O$
K_3PO_4
$K_3PO_4 \cdot 3\ H_2O$
$K_3PO_4 \cdot 7\ H_2O$
$K_3PO_4 \cdot 9\ H_2O$

Properties Generally, the potassium salts are more water soluble than the corresponding sodium monophosphates. Monopotassium dihydrogenphosphate, KH_2PO_4, is an exception; it is substantially less soluble than the other potassium monophosphates and monosodium phosphates. Figure 26 shows the solubilities of the potassium monophosphates.

The pH of 1 % aqueous solutions are 4.5 for KH_2PO_4, 9.1 for K_2HPO_4, and 11.8 for K_3PO_4. Like the corresponding rubidium and cesium salts, potassium dihydrogenphosphate forms ferroelectric crystals (T_C of KH_2PO_4, −151 °C). The alkali dihydrogenphosphates (K, Rb, Cs, NH_4) exhibit piezoelectric behavior [70].

Production Potassium monophosphates are usually produced by the same process as the

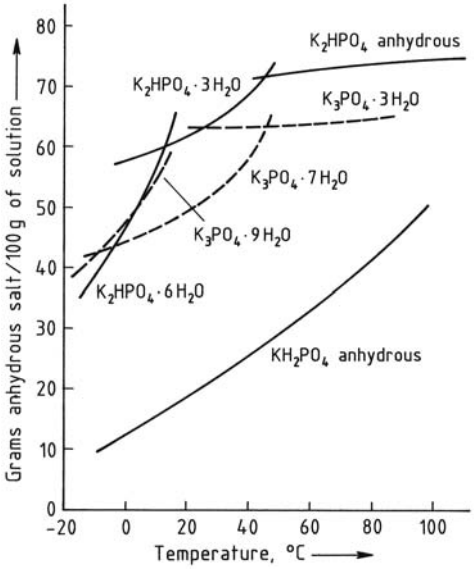


Figure 26. Solubility of potassium monophosphates [70]

corresponding sodium salts, i.e., from phosphoric acid and potassium hydroxide. For KH_2PO_4, the cheaper potassium chloride is also used instead of KOH [149]. Various methods have been suggested for quantitative removal of the hydrogen chloride formed: use of ion exchangers [150], long-chain tertiary amines [151], or distillation with octane [152]. The economics depend on the possibility of using the hydrogen chloride.

Uses The potassium phosphates KH_2PO_4 and K_2HPO_4 are used in the food area for mineral enrichment of fruit juices and as stabilizers in milk products. Potassium dihydrogenphosphate is used as a nutrient salt for mushrooms and cormophytes. Crystals of KH_2PO_4 are used as piezoelectric vibrators [153]. Dipotassium phosphate is suitable as a buffer in the range pH 9, e. g., for pH adjustment of water – glycol mixtures in cooling systems of automotive engines in order to avoid corrosion [154]. Mono- and dipotassium phosphate are further processed to potassium polyphosphates.

Tetrapotassium Diphosphate. [*7320-34-5*], tetrapotassium pyrophosphate, $K_4P_2O_7$, M_r 330.35, crystallizes in the anhydrous form and the mono- and trihydrates. The anhydrous salt and the monohydrate are strongly hygroscopic. The solubility of $K_4P_2O_7$ in water is 187 g/100 g H_2O at 25 °C, and the pH of a 1 % aqueous solution is 10.3.

Tetrapotassium diphosphate is produced by the same methods as the corresponding sodium salt, i.e., by dehydration of K_2HPO_4 at 350 – 460 °C. Like the other alkali-metal polyphosphates, $K_4P_2O_7$ also has pronounced dispersive properties as well as the capacity to bind multivalent cations and to keep them in solution. Despite the higher price, tetrapotassium diphosphate is used preferentially as builder in liquid detergent formulations containing 20 – 25 % diphosphate and ca. 50 % water in addition to wash active substances. The reasons are the substantially higher water solubility compared with the sodium salts and the hydrolytic stability of the diphosphate anion.

Potassium diphosphate is also used as a stabilizer in foods and for the prevention of tartar formation. Use as a catalyst in the production of Buna is mentioned in some product information brochures.

Pentapotassium Triphosphate. [*13845-36-8*], potassium tripolyphosphate, $K_5P_3O_{10}$, M_r 448.43, *mp* 614.5 °C (decomp.), crystallizes in the anhydrous form and as the dihydrate. The anhydrous salt is strongly hygroscopic. Its solubility in water is ca. 200 g/100 g H_2O at 20 °C. The pH of a 1 % aqueous solution is 11.5. Like the corresponding sodium compound, pentapotassium triphosphate is produced from 2 mol of K_2HPO_4 and 1 mol of KH_2PO_4. It is used as a builder in liquid detergents.

Kurrol's Salt. [*29057-10-1*], (high-molecular potassium polyphosphate) $(KPO_3)_x$, M_r $(118.09)_x$, where x can vary from 400 to 20 000 depending on the conditions of preparation, *d* 2.26, *mp* 813 °C. Although it is a true polyphosphate with chain structure, the incorrect designation potassium metaphosphate is frequently still found in the literature. Kurrol's salt is insoluble in pure water. However, in the presence of other alkali-metal ions, especially Na^+, it dissolves to form a viscous gel.

Kurrol's salt is generally produced by heating KH_2PO_4 at 350 – 500 °C in a rotary kiln. In another process, $(KPO_3)_x$ is produced as a spray dried product from aqueous KH_2PO_4 solution in a hot gas stream at 330 – 390 °C [155]. Due to its good dispersing action, Kurrol's salt is used as an additive in soaps and cleansing agents.

3.4.2. Ammonium Phosphates

The most important application of ammonium phosphates is as fertilizers (→ Phosphate Fertilizers). Other applications are known, especially as flame retardants.

The following crystalline monophosphates exist in the $NH_3 - P_2O_5 - H_2O$ system [156]:

$NH_4H_2PO_4$	$(NH_4)_2HPO_4$
$NH_4H_2PO_4 \cdot H_3PO_4$	$(NH_4)_3PO_4 \cdot 3\ H_2O$
$NH_4H_2PO_4 \cdot H_3PO_4 \cdot H_2O$	$(NH_4)_3PO_4 \cdot 2\ (NH_4)_2HPO_4$

Only the mono- and diammonium phosphates are commercially important. The compound $(NH_4)_3PO_4$ and the double salt $(NH_4)_3PO_4 \cdot 2\ (NH_4)_2HPO_4$ are unstable at room temperature. They decompose with release of ammonia and formation of $(NH_4)_2HPO_4$.

Ammonium Dihydrogenphosphate. [*7722-76-1*], monoammonium phosphate, $NH_4H_2PO_4$, M_r 115.03, d 1.80, tetragonal, *mp* 190 °C; solubility in water, 36 g $NH_4H_2PO_4$/100 g H_2O at 20 °C, and 120 g at 80 °C; pH of a 1 % aqueous solution, 4.5. The crystals have piezoelectric properties. In contrast to the tri- and diammonium salts, monoammonium phosphate is very stable (pNH_3, 7 Pa at 125 °C) and melts at 190 °C without decomposition.

Single crystals of monoammonium phosphates are used, e.g., in underwater sounding equipment instead of quartz oscillators. Moreover, monoammonium phosphate has applications in ceramic binders and for the production of special fertilizers (→ Phosphate Fertilizers).

For production, see Diammonium Hydrogenphosphate.

Diammonium Hydrogenphosphate. [*7783-28-0*], diammonium phosphate, $(NH_4)_2HPO_4$, M_r 132.07, d 1.62, monoclinic, *mp* 155 °C (decomp.); solubility in water, 72 g $(NH_4)_2HPO_4$/100 g H_2O at 25 °C; pH of a 1 % aqueous solution, 8.0; pNH_3, 27 Pa at 50 °C and 1.21 kPa at 100 °C.

Ammonium monophosphates are produced by neutralization of phosphoric acid with ammonia. Crude or partially purified wet phosphoric acid is mostly used for fertilizer applications. However, pure thermal phosphoric acid is used preferentially for the production of commercial ammonium phosphates with an assay > 99 %. Commercial ammonium monophosphates are used for flame-retardant textile finishes (not washfast), as flame-retardant impregnating agents for wood, and as components of fire-extinguishing powders. Matches are impregnated with ammonium phosphate solutions to prevent smoldering. The flame-retardant effect of ammonium phosphates is due to their decomposition to phosphoric acid and ammonia. The generated phosphoric acid catalyzes carbonization of combustible material such as cellulose, so that the formation of readily combustible, gases (e.g., CO) is decreased. A film of condensed phosphoric acids or ultraphosphates is formed, which shields the substrate against heat and protects it from access of atmospheric oxygen [157].

Ammonium Polyphosphates, $(NH_4)_{n+2}P_nO_{3n+1}$, cannot be produced from ammonium monophosphates by thermal condensation because the ammonia partial pressure is too high at the required temperatures. Short-chain ammonium polyphosphates are produced by neutralization of polyphosphoric acids with ammonia [158]. They are water soluble and used predominantly as components of liquid fertilizers (→ Phosphate Fertilizers, Chap. 1).

High-molecular ammonium polyphosphate with a minimum of water-soluble fractions is being used to an increasing extent in flame retardants. Five modifications with a chain length of $n > 50$ are described in the literature [159]. Form I or form II products are produced preferentially for commercial applications. The NH_3 partial pressure of form I is 0.053 kPa at 100 °C, 3.19 kPa at 200 °C, and 49.5 kPa at 300 °C [159]. In order to carry out the reaction at low temperatures, urea or similar compounds such as melamine are used as ammonia sources [159, 160].

$$x\,H_3PO_4 + x\,CO(NH_2)_2 \rightarrow (NH_4PO_3)_x + x\,CO_2 + x\,NH_3$$

In another process, phosphorus pentoxide is reacted with diammonium phosphate and ammonia in a mixing and kneading machine [161].

$$x/2\,P_4O_{10} + x(NH_4)_2HPO_4 + x\,NH_3 \rightarrow 3(NH_4PO_3)_x$$

The phosphorus pentoxide/diammonium phosphate/urea combination is also suitable for the production of high-molecular products [162].

$$x/2\,P_4O_{10} + x(NH_4)_2HPO_4 + x/2\,CO(NH_2)_2 + x/2\,H_2O \rightarrow 3(NH_4PO_3)_x + x/2\,CO_2$$

In this reaction, some product properties can already be influenced by the choice of starting materials. An ammonium polyphosphate with a high proportion of modification I and chain lengths of $n = 40$ to $n = 200$ is formed predominantly if urea is used as ammonia source. However, if gaseous ammonia is used, a modification II product with chain lengths of $n > 1000$ is obtained. The reasons for these reaction characteristics are related to the reaction rate. If urea is used, then ammonia supply is optimal provided that the components are thoroughly mixed. Accordingly, the reaction proceeds very quickly, and the kinetically favored product is formed. Thermodynamically stable ammonium polyphosphate of modification II is formed only if the reaction proceeds slowly such as in a kneading machine and at temperatures of 240 – 290 °C.

All manufacturing processes have to be carried out in an ammonia atmosphere so that the NH_3 partial pressure exceeds the decomposition pressure of ammonium polyphosphate.

Long-chain ammonium polyphosphates are used as fire-extinguishing agents [163], as flame retardants for paints and varnishes, for flame-retardant finishing of polyurethane foams [164], and in fireproof coatings on steel beams and wooden partitions [165].

3.4.3. Magnesium Phosphates

With the exception of magnesium-containing mixed phosphates used in feeds, magnesium phosphates have only minor commercial significance.

Magnesium Dihydrogenphosphate [*13092-66-5*], monomagnesium phosphate, $Mg(H_2PO_4)_2$, M_r 218.28, crystallizes in the anhydrous form and as the di- and tetrahydrate. On dissolution in water, partial hydrolysis occurs with formation of monophosphoric acid and crystalline magnesium hydrogenphosphate, $MgHPO_4 \cdot 3\ H_2O$. Acidic magnesium diphosphate is formed on heating to above 170 °C. It condenses at higher temperatures to give higher-molecular polyphosphates. The hydrated salts are obtained by dissolution of magnesium oxide, magnesium carbonate, or di- or trimagnesium phosphate in phosphoric acid and subsequent crystallization. The anhydrous compound is formed by dehydration at 100 – 170 °C.

Magnesium Hydrogenphosphate, dimagnesium phosphate, $MgHPO_4$, M_r 120.29. Only the trihydrate, $MgHPO_4 \cdot 3\ H_2O$, *d* 2.12, orthorombic, *mp* 205 °C (with loss of H_2O), is stable at 25 °C in the $MgO - H_2O - P_2O_5$ system. It is also the usual commercial product. In addition, the anhydrous salt and the mono- and heptahydrate are described in the literature. The trihydrate occurs as the natural mineral newberyite. It dissolves in dilute acids but is practically insoluble in water. It is produced by double decomposition of disodium phosphate with magnesium salts in aqueous solution or by neutralization of solutions of magnesium salts in phosphoric acid with caustic soda.

Magnesium hydrogenphosphate is used for mineral enhancement in foods for babies and athletes as well as in dietetic foods. It is also utilized as a feedstuff additive, in the ceramic industry, and as a stabilizer for $CaHPO_4 \cdot 2\ H_2O$ in toothpastes [166].

Trimagnesium Phosphate [*7757-87-1*], $Mg_3(PO_4)_2$, M_r 262.88, *mp* 1184 °C, crystallizes with 5, 8, and 22 H_2O. The octahydrate, *d* 2.19, monoclinic, occurs as the mineral bobbierite. $Mg_3(PO_4)_2 \cdot 22\ H_2O$, *d* 1.66, also crystallizes in the monoclinic form. The salts are practically insoluble in water but readily soluble in acids. The anhydrous salt is formed by heating the hydrates at 400 °C. Hydrated trimagnesium phosphate can be prepared from solutions of magnesium salts by addition of trisodium phosphate solution or phosphoric acid and caustic soda. It is used as anticaking agent for silicate-containing cleaning agents [167] and table salt and as a stabilizer for $CaHPO_4 \cdot 2\ H_2O$.

3.4.4. Calcium Phosphates

For production and use of calcium phosphates in fertilizers see → Phosphate Fertilizers. Pure calcium phosphates are used predominantly as feedstuff additives and as polishing compounds in toothpastes.

Calcium Dihydrogenphosphate, monocalcium phosphate, $Ca(H_2PO_4)_2 \cdot H_2O$, M_r 252.09, *d* 2.22, triclinic, loses its water of crystallization starting at 109 °C, with formation of anhydrous $Ca(H_2PO_4)_2$ [*7758-23-8*], *d* 2.55, triclinic.

Monocalcium phosphate dissolves in water with precipitation of calcium hydrogenphosphate and formation of an aqueous phase with increased P_2O_5 content:

$$Ca(H_2PO_4)_2 \cdot H_2O \rightleftharpoons CaHPO_4 + H_3PO_4 + H_2O$$

Therefore, preparation of pure $Ca(H_2PO_4)_2 \cdot H_2O$ [*10031-30-8*] by crystallization from aqueous solution succeeds only in the presence of excess phosphoric acid [168]. Adhering phosphoric acid gives hygroscopic products which tend to decompose further by absorption of atmospheric moisture. Therefore, commercial products are made with an excess of CaO and contain up to 20 % calcium hydrogenphosphate.

Monocalcium phosphate is produced by neutralization of phosphoric acid with calcium oxide

or hydroxide [169]. Only thermal phosphoric acid is used for production of food-grade quality (e.g., for baking aids). Defluorinated wet phosphoric acid is used mostly for feed phosphate. The starting materials are reacted in vessels made of stainless steel by means of high-intensity agitators or in continuously operating mixers. Some of the water is evaporated by the heat of reaction. A pulpy to crumbly product is obtained, which is subsequently dried and ground.

Products with low bulk density are obtained from a slurry of the starting components by spray drying with hot air. Predominantly monohydrate is produced by these processes because the anhydrous salt is less stable towards atmospheric moisture.

A relatively water-stable, less reactive product is obtained by addition of small amounts of various metal salts, e.g., of potassium or aluminum [143].

The anhydrous salt is formed by carrying out the reaction at 140 °C. In a posttreatment step at 200 – 220 °C, the crystals become coated with a glassy, essentially water-stable, protective layer (anhydrous coated calcium phosphate, ACCP).

In the United States, monocalcium phosphate is used mainly as a leavening aid in the production of self-raising flour. Further applications are in mineral enrichment of foods, as a stabilizer for milk products, and as a feedstuff additive in place of calcium hydrogenphosphate.

For technical applications, monocalcium phosphate is used in gypsum plasters as a setting retarder.

Calcium Hydrogenphosphate. [*7757-93-9*], dicalcium phosphate, $CaHPO_4$, M_r 136.06, crystallizes in the anhydrous form, *d* 2.89, triclinic, and as the dihydrate, *d* 2.32, monoclinic. The dihydrate is slowly converted to the anhydrous salt at 36 °C (incongruent melting point). Substantially higher temperatures are required for production of the anhydrous salt. $CaHPO_4 \cdot 2\ H_2O$ dissolves in water with precipitation of hydroxyapatite, $Ca_5(PO_4)_3OH$, and formation of an aqueous phase with increased P_2O_5 content. However, its solubility is low (220 mg/L CaO and 530 mg/L P_2O_5 at 25 °C).

The dihydrate is produced by neutralization of phosphoric acid with calcium hydroxide, with cooling to avoid formation of anhydrous $CaHPO_4$. Thermal phosphoric acid is used as starting material in the production of $CaHPO_4 \cdot 2\ H_2O$ for use in toothpastes. However, feedstuff phosphates are produced predominantly from defluorinated wet phosphoric acid.

For defluorination, the acid is partially neutralized with calcium hydroxide or carbonate. The fluoride precipitates as calcium hexafluorosilicate together with phosphates of bi- or multivalent metal ions such as Fe and Al. The P_2O_5-containing precipitate is filtered and used for fertilizer production. Na_2SiF_6 or K_2SiF_6 can also be precipitated by addition of sodium or potassium salts. After subsequent addition of calcium hydroxide, the precipitated $CaHPO_4 \cdot 2\ H_2O$ is filtered, dried, and ground.

For a large decrease of the fluoride content, an additional defluorination can be carried out by adding SiO_2 in the form of bentonite [170].

In a more recent process, stoichiometric quantities of $CaCl_2$, NaOH, and H_3PO_4 are added simultaneously to an intensively agitated reactor [171]. In a variation of this process, $CaCl_2$ and NaOH are partially replaced by an aqueous suspension of calcium carbonate [172].

The water-adsorptive capacity of $CaHPO_4 \cdot 2\ H_2O$ also has a function in its application as a polishing compound in toothpastes. Highly adsorptive products can be prepared by adding H_3PO_4 to a suspension of $CaCO_3$ and homogenizing the reaction mixture at the drip spot with a disperser [173].

The anhydrous salt is produced by the same processes as are used for the dihydrate, but precipitation is carried out above 80 °C. Calcium hydrogenphosphate, in the form of its dihydrate and sometimes also as anhydrous salt, is used as a mineral supplement in feedstuff. The dihydrate is used as a component of toothpastes because of its advantageous polishing properties and low abrasiveness [174]. Stabilizers such as $MgCl_2$, $Mg_3(PO_4)_2$, $MgHPO_4 \cdot 2\ H_2O$, or $Na_4P_2O_7$ are added to prevent hardening of toothpastes prepared with $CaHPO_4$ due to dehydration during storage.

Calcium hydrogenphosphate is used in the food industry for mineral enrichment of various products, and in the pharmaceutical industry as a pelletizing aid and thickening agent. Use as fertilizer component for tropical soils is a special application of $CaHPO_4$.

Tricalcium Phosphate. [*7758-87-4*], $Ca_3(PO_4)_2$, M_r 310.20, *d* 3.14 (whitlockite, rhombohe-

dral); solubility in water 2.5 mg $Ca_3(PO_4)_2$/100 g H_2O at 25 °C. Two crystalline modifications are known, the high-temperature α- and the low-temperature β-form, transition temperature 1180 °C, *mp* 1730 °C. In production, hydroxyapatite, $Ca_5(PO_4)_3OH$, is formed by complete neutralization of phosphoric acid with slaked lime and subsequent filtration, drying, and grinding. The Ca/P ratio depends on the process conditions. Pure $Ca_3(PO_4)_2$ with a Ca/P ratio of 1.5 can be obtained from hydroxyapatite by calcination above 900 °C. However, commercial tricalcium phosphate consists mostly of hydroxyapatite.

Tricalcium phosphate is added to various substances such as table salt, sugar, and fertilizers as anticaking agent in amounts of 1 – 2 %. It is used in toothpastes containing calcium hydrogenphosphate for adjustment of the polishing strength.

Tricalcium phosphate and calcium halophosphates such as $Ca_5(PO_4)_3(F,Cl)$ are used in the manufacture of luminescent materials.

Dicalcium Diphosphate [*7790-76-3*], calcium pyrophosphate, $Ca_2P_2O_7$, M_r 254.11, *d* 3.09, orthorhombic, *mp* 1353 °C, is practically insoluble in water but soluble in acids. It is produced by thermal dehydration of $CaHPO_4$ or $CaHPO_4 \cdot 2\ H_2O$ at 700 – 900 °C. Dicalcium diphosphate is used as a polishing compound in fluoridated toothpastes because of its low solubility and its inertness towards fluoride ions [175].

Calcium Triphosphate [*26158-70-3*], calcium tripolyphosphate, $Ca_5(P_3O_{10})_2$, M_r 706.47, is practically insoluble in water. It is produced as the octahydrate from calcium chloride solutions by precipitation with pentasodium triphosphate. It is added to hygroscopic salts such as table salt for preservation of the pourability and as a stabilizer for $CaHPO_4 \cdot 2\ H_2O$ [176].

3.4.5. Boron Phosphate

Boron phosphate [*13308-51-5*], BPO_4, M_r 105.79, *d* 2.80, tetragonal, is a white, crystalline solid that sublimes at 1450 °C without decomposition. In addition to the anhydrous product, hydrates with 3, 4, and 6 H_2O have also been reported. The hydrates dissolve readily in water with hydrolysis to give the corresponding acids. The anhydrous salt also hydrolyzes but at a much slower rate. Under ambient conditions, BPO_4 has a cristobalite structure consisting of alternating BO_4 and PO_4 tetrahedra linked via common oxygen atoms to form a three-dimensional network.

Boron phosphate is produced by reaction of boric acid with 85 % phosphoric acid and subsequent dehydration at up to 1000 °C [177]. A product with very large specific surface area is obtained by heating tri-*n*-propyl borate with phosphoric acid at 120 – 130 °C [178]. Addition of aluminum hydroxide in combination with ethylenediamine and ethyl acetate or of the combination aluminum oxide chloride/urea has the same effect [179].

Boron phosphate is used in organic chemistry as a catalyst in various syntheses, especially in hydration, dehydration, isomerization, and amination reactions [180], and in the ceramic industry as a carrier for boric acid and phosphate.

3.4.6. Aluminum Phosphates

The following aluminum monophosphates are known in the $Al_2O_3 – P_2O_5 – H_2O$ system: $Al(H_2PO_4)_3 \cdot n\ H_2O$, $Al_2(HPO_4)_3 \cdot n\ H_2O$, and $AlPO_4 \cdot n\ H_2O$. Acidic salts of composition $Al(H_2PO_4) \cdot (HPO_4) \cdot n\ H_2O$ are also known.

Aluminum Dihydrogenphosphate [*13530-50-2*], monoaluminum phosphate, $Al(H_2PO_4)_3$, M_r 317.96, water soluble, exists in the anhydrous form (hexagonal) and as the trihydrate. The trihydrate is obtained by reaction of aluminum hydroxide with phosphoric acid and subsequent crystallization. On heating to 200 °C, acidic aluminum triphosphate $(AlH_2P_3O_{10}) \times 2\ H_2O$ is formed, which condenses above 200 °C to give cyclic hexametaphosphate (cyclic metaphosphate Type B) $Al_2P_6O_{18}$ and (> 650°C) cyclic tetrametaphosphate (cyclic metaphosphate Type A) $Al_4(P_4O_{12})_3$. At temperatures above 900°C, berlinite $AlPO_4$ is obtained [181, 182].

Aluminum Phosphate [*7784-30-7*], $AlPO_4$, M_r 121.95, *d* 2.57, *mp* 1850 ± 50 °C, crystallizes in the anhydrous form as hexagonal berlinite. Cubic and orthorhombic modifications are also known. It also crystallizes as a dihydrate (variscite,

orthorombic); a monoclinic modification also exists. It is practically insoluble in water and sparingly soluble in acids. It dissolves in alkalies with formation of aluminates. $AlPO_4$ is isotypic with SiO_2 and forms polymorphous modifications with quartz, tridymite, and cristobalite structures.

Aluminum phosphates are produced by addition of alkali metal phosphates to solutions of aluminum salts or by treating aluminum hydroxide with phosphoric acid.

Aluminum dihydrogenphosphate is used as binder for highly fireproof materials [170].

Aluminum metaphosphates are used in the enamel industry in heat-resistant glasses, as component of optical glasses, and as hardeners for water glass putties [172].

Aluminum phosphate [*7784-30-7*], $AlPO_4$, is used in the manufacture of molecular sieves and optical glasses, in ceramics, in the enamel industry, as an anticorrosion powder in coatings and antacidicum for pharmaceutical preparations.

3.5. Economic Aspects

Tables 12–15, and 16 list regional and world demand for phosphates in various applications. The following abbreviations are used:

MSP = monosodium phosphate
DSP = disodium phosphate
TSP = trisodium phosphate
TSPP = tetrasodium pyrophosphate
TKPP = tetrapotassium pyrophosphate
STPP = sodium tri(poly)phosphate
SHMP = sodium hexametaphosphate
MCP = monocalcium phosphate
DCP = dicalcium phosphate
DAP = diammonium phosphate
TCP = tricalcium phosphate
SAPP = acidic sodium pyrophosphate
SAlP = sodium aluminum phosphate
IMP = Maddrell's salt (insoluble)
SMFP = sodium monofluorophosphate
APP = ammonium polyphosphate
ZnP = zinc phosphates
AlP = aluminum phosphates

4. Toxicology

Phosphoric Acid. Analogous to phosphorus pentoxide, phosphoric acid does not possess any

Table 12. Phosphate demand for soaps and detergents (in 10^3 t P_2O_5)*

Region	1999	2000	2002	2004	2006**
Europe	405	412	389	419	458
America	381	390	403	428	460
Asia	405	427	460	510	568
World	1444	1500	1540	1680	1836

* Main phosphates: STPP (95 %), TSP, TKPP.
** Estimated.

Table 13. Phosphate demand for the food, beverage, and baking industry (in 10^3 t P_2O_5)*

Region	1999	2000	2002	2004	2006**
Europe	66	68	70	73	76
America	141	146	152	162	172
Asia	34	36	39	44	48
World	251	260	272	291	309

* Main phosphates: STPP, SHMP, TSP, SAPP, SAlP, MCP, DSP, H_3PO_4.
** Estimated.

Table 14. Phosphate demand for water treatment (in 10^3 t P_2O_5)*

Region	1999	2000	2002	2004	2006**
Europe	45	46	46	48	49
America	47	49	49	52	54
Asia	40	41	43	46	48
World	143	146	149	156	164

* Main phosphates: Glassy phosphates, SHMP, STPP, TSPP, MSP, DSP.
** Estimated.

Table 15. Phosphate demand for toothpastes (in 10^3 t P_2O_5)*

Region	1999	2000	2002	2004	2006**
Europe	8	8	8	8	8
America	20	20	21	22	24
Asia	21	22	25	27	30
World	54	56	59	63	68

* Main phosphates: DCP, IMP, SMFP.
** Estimated.

Table 16. Phosphates for other uses* (in 10^3 t P_2O_5)**

Region	1999	2000	2002	2004	2006***
Europe	83	86	86	91	96
America	103	106	108	114	121
Asia	40	43	46	51	56
World	237	247	252	269	287

* Ceramics, leather, anticaking, setting retarders, flame retardants, paper, anticorrosion pigments, textiles, rubber manufacture, activated carbon, fermentation, antifreeze.
** Main phosphates: Glassy phosphates, STPP, TCP, APP, DAP, ZnP, AlP, H_3PO_4.
*** Estimated.

specific toxic effects. Phosphoric acid irritates the eyes, respiratory tract, and mucous membranes. Aqueous solutions containing phosphoric acid in concentrations > 10% are irritating, solutions with concentrations > 25% are corrosive. After swallowing larger quantities, nausea, vomiting, diarrhea, hematemesis, and hypovolemic shock occur. Ingestion of concentrated solutions causes burns of the mucosa of the mouth, esophagus, and stomach. Additionally, hyperphosphatemia, hypocalcemia and acidosis may be present [185, 186]. Washing of the skin with warm water, irrigation of the eyes with warm water or physiological saline solution is recommended in case of contamination. First aid after ingestion consists of support of respiration and treatment of shock by intravenous replacement of lost fluid volume [186]. The systemic toxicity of phosphoric acid is low. No effect on growth and reproduction was observed in three generations of rats that received 0.75% phosphoric acid in the diet for 90 weeks. No pathological findings attributable to the administration of phosphoric acid were observed in this study. Dental attrition was somewhat higher than in controls [187]. Phosphoric acid was not mutagenic in the Ames test [188]. Phosphoric acid can be used in concentrations of 500 – 1000 mg/L in beverages. No changes which could indicate any detrimental effect on metabolism could be established in voluntary subjects who took 2000 – 4000 mg/kg per day orally for 10 d or 3900 mg/kg per day for 14 d [189]. The TLV-TWA value for phosphoric acid is 1 mg/m^3 [190].

Phosphates and Polyphosphates. A summary of the toxicological properties of phosphates and polyphosphates is given in [191, 192]. There was no evidence for genotoxicity of inorganic phosphates in various test systems. Embryo-fetal toxicity studies in rats, mice, rabbits, and hamsters did not reveal any evidence of teratogenicity. The toxicological profiles phosphates and polyphosphates are largely similar, provided no toxic cations are present. Hyperphosphatemia, secondary hyperparathyreoidism, skeletal changes (deformations, bone loss), and calcification were observed in animal studies after administration of high phosphate dosages. In subchronic and chronic feeding studies with rats, primarily nephrocalcinosis occurred, whereby this species is particularly sensitive to acids that form calcium chelates or complexes. The effective dosages overlap in the different studies; the lowest concentration which caused nephrocalcinosis was 10 g per kg of feed. In view of these results, it was concluded that the oral intake of 70 mg of phosphate (as phosphorus) per kilogram of body weight per day is tolerable in humans (70 mg is the MTDI, maximum tolerable daily intake) [192].

Hypocalcemia, hyperphosphatemia, and dehydration have been reported in studies where sodium phosphate/biphosphate was administered as an enema [193]. Sodium hexametaphosphate, which is used for softening water, can cause serious, or even fatal poisoning when taken orally. The most prominent symptoms are massive shock, irregular pulse, eventually bradycardia, and severe hypocalcemia with tetanic symptoms. Lavaging the stomach with chalk and repeated intravenous injection of calcium gluconate are recommended as therapy [194].

Chlorinated trisodium phosphate, which is used in various cleaning compounds, has a low acute and subchronic toxicity in rats and mice. Toxic effects after chronic administration were observed in rats and were attributable to local irritation/corrosion, which led to termination of the two-year carcinogenicity bioassay. The compound was not carcinogenic after administration for two years to mice. Like sodium hypochlorite, it is a weak base-pair substitution mutagen in bacteria [195].

Sodium monofluorophosphate is used in dentifrices [196] and for treatment of osteoporosis in postmenopausal women [197]. Toxic effects after administration of higher doses (fluorosis) are related to fluoride [198].

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