Phosphorus

Red and white phosphorus. White phosphorus, one of the principal allotropes of solid phosphorus, is very reactive and must be handled with care because it produces severe burns when it comes in contact with skin. The sample shown here has a yellowish cast as a result of surface reactions with air. White phosphorus is usually stored under water. Red phosphorus, on the other hand, is much less reactive than white phosphorus and does not require special handling.

Phosphorus (atomic number 15, atomic mass 30.973761) was the first element whose discovery could be attributed to a specific person. It was discovered in 1669 by the German alchemist Hennig Brandt by the unsavory process of distilling putrefied urine. Although phosphorus constitutes less than 0.1% by mass of the earth's crust, all living organisms contain this element, and it is the sixth most abundant element in the human body. The energy requirements of essentially all biochemical reactions are supplied by phosphorus compounds. Plants require phosphorus as a nutrient, and most of the phosphorus compounds that are produced are used as fertilizers.

One of the most important compounds of phosphorus is phosphoric acid, $H_3PO_4(aq)$, a triprotic acid. Although the formulas of the other oxyacids of phosphorus are usually written as $H_3PO_2(aq)$ and $H_3PO_3(aq)$, we shall see that these acids are monoprotic and diprotic, respectively. Thus, the three oxyacids of phosphorus illustrate the idea of monoprotic and polyprotic acids presented in Chapter 20.

N-1. There Are Two Principal Allotropes of Solid Phosphorus

There are several allotropes of elemental solid phosphorus, the most important of which are **white phosphorus** and **red phosphorus** (Frontispiece). White phosphorus is a white, transparent, waxy crystalline solid that often appears pale yellow because of impurities. It is insoluble in water and alcohol but soluble in carbon disulfide. A characteristic property of white phosphorus is its high chemical reactivity. It ignites spontaneously in air at about 25°C. White phosphorus is very poisonous; the lethal dose is 50 to 100 milligrams. White phosphorus should always be kept under water and handled with forceps.

When white phosphorus is heated above 400°C for several hours in the absence of air, a form called red phosphorus is produced. Red phosphorus is a red to violet powder that is less reactive than white phosphorus. The chemical reactions that the red form undergoes are the same as those of the white form,

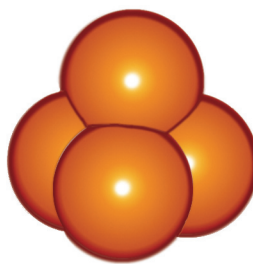> Recall that allotropes are forms of an element with different arrangements of the atoms.

Figure N.1 White phosphorus consists of tetrahedral P_4 molecules.

but they generally occur only at higher temperatures. For example, red phosphorus must be heated to 260°C before it burns in air. The toxicity of red phosphorus is much lower than that of white phosphorus.

White phosphorus consists of tetrahedral P_4 molecules (Figure N.1), whereas red phosphorus consists of large, random aggregates of phosphorus atoms. The structure of red phosphorus is called **amorphous**, which means that it has no definite shape. Butter is another example of an amorphous substance.

Most of the phosphorus that is produced is used to make phosphoric acid and other phosphorus compounds. Elemental phosphorus, however, is used in the manufacture of pyrotechnics, matches, rat poisons, incendiary shells, smoke bombs, and tracer bullets.

Phosphorus is not found as a free element in nature. The principal sources are calcium phosphate and the apatite ores (Figure N.2):

hydroxyapatite	$Ca_{10}(OH)_2(PO_4)_6(s)$
fluorapatite	$Ca_{10}F_2(PO_4)_6(s)$
chlorapatite	$Ca_{10}Cl_2(PO_4)_6(s)$

These ores collectively are called phosphate rock. Large phosphate rock deposits occur in Russia, in Morocco, and in the United States in Florida, Tennessee, and Idaho. An electric furnace is used to obtain phosphorus from phosphate rock. The furnace is charged with powdered phosphate rock, sand, $SiO_2(s)$, and carbon in the form of coke. The source of heat is an electric current that produces temperatures of over 1000°C. A simplified version of the overall reaction that takes place is

$$2\,Ca_3(PO_4)_2(s) + 6\,SiO_2(s) + 10\,C(s) \rightarrow$$
phosphate rock   sand   coke

$$6\,CaSiO_3(l) + 10\,CO(g) + P_4(g)$$
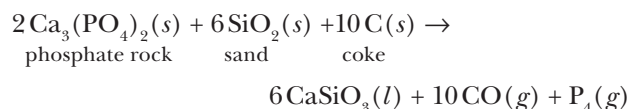
Figure N.2 The apatite minerals. *Left to right:* hydroxyapatite, $Ca_{10}(OH)_2(PO_4)_6(s)$; fluorapatite, $Ca_{10}F_2(PO_4)_6(s)$; and chlorapatite, $Ca_{10}Cl_2(PO_4)_6(s)$.

Liquid calcium silicate, $CaSiO_3(l)$, called slag, is tapped off from the bottom of the furnace, and the phosphorus vapor that is produced solidifies to white $P_4(s)$ when the mixture of $CO(g)$ and $P_4(g)$ is passed through water (carbon monoxide does not dissolve in water). The annual world production of elemental phosphorus is approximately one million metric tons.
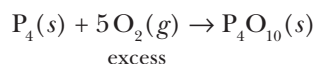
Although some phosphate rock is used to make elemental phosphorus, most phosphate rock is used in the production of fertilizers. Phosphorus is a required nutrient of all plants, and phosphorus compounds have long been used as fertilizer. In spite of its great abundance, phosphate rock cannot be used as a fertilizer because, as the name implies, it is insoluble in water. Consequently, plants are not able to assimilate the phosphorus from phosphate rock. To produce a water-soluble source of phosphorus, phosphate rock is reacted with sulfuric acid to produce a water-soluble product called **superphosphate**, $Ca(H_2PO_4)_2(s)$, one of the world's most important fertilizers.

N-2. Phosphorus Forms Several Oxyacids

White phosphorus reacts directly with oxygen to produce the oxides $P_4O_6(s)$, and $P_4O_{10}(s)$. With excess phosphorus present, $P_4O_6(s)$ is formed:

$$P_4(s) + 3\,O_2(g) \rightarrow P_4O_6(s)$$
$$\text{excess}$$
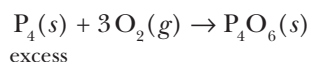
With excess oxygen present, $P_4O_{10}(s)$ is formed:

$$P_4(s) + 5\,O_2(g) \rightarrow P_4O_{10}(s)$$
$$\text{excess}$$

In practice, a mixture of oxides is formed in each case, but one oxide can be greatly favored over the other by controlling the relative amounts of phosphorus and oxygen.

Before the actual molecular formulas of these phosphorus oxides were known, the empirical formulas $P_2O_3(s)$ and $P_2O_5(s)$ were used. Consequently, $P_4O_6(s)$ and $P_4O_{10}(s)$ are still commonly called phosphorus trioxide and phosphorus pentoxide.

It is interesting to compare the molecular structures of P_4O_6 and P_4O_{10} (Figure N.3). The molecular structure of P_4O_6 is obtained from that of P_4 by inserting an oxygen atom between each pair of adjacent phosphorus atoms; there are six edges on a tetrahedron, and thus a total of six oxygen atoms are required. The molecular structure of P_4O_{10} is obtained from that of P_4O_6 by attaching an additional oxygen atom to each of the four phosphorus atoms.

The phosphorus oxides $P_4O_6(s)$ and $P_4O_{10}(s)$ react with cold water to form the phosphorus oxyacids: phosphorous acid, $H_3PO_3(aq)$, and phosphoric acid, $H_3PO_4(aq)$. The respective equations are:

$$P_4O_6(s) + 6\,H_2O(l) \rightarrow 4\,H_3PO_3(aq)$$

$$P_4O_{10}(s) + 6\,H_2O(l) \rightarrow 4\,H_3PO_4(aq)$$
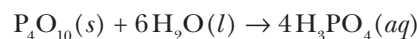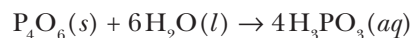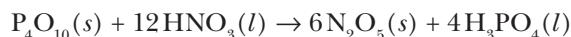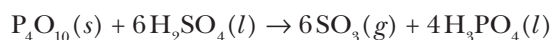
The reaction of $P_4O_{10}(s)$ with cold water is quite vigorous and can be explosive.

Phosphorus pentoxide, $P_4O_{10}(s)$, is a powerful dehydrating agent capable of removing water from concentrated sulfuric acid, which is itself a strong dehydrating agent as we saw in Interchapter J. In a similar reaction, $N_2O_5(s)$ can be obtained by reacting $P_4O_{10}(s)$ with nitric acid. The equations for the two reactions are
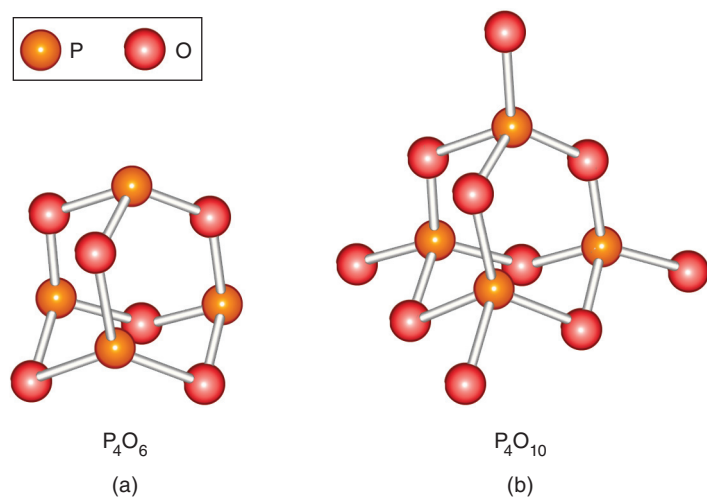
Figure N.3 Molecular structure of P_4O_6 and P_4O_{10}. (a) The P_4O_6 molecule can be viewed as arising from the tetrahedral P_4 molecule when an oxygen atom is inserted between each pair of adjacent phosphorus atoms. (b) The P_4O_{10} molecule can be viewed as arising from P_4O_6 when an oxygen atom is attached to each of the four phosphorus atoms. Notice that there are no phosphorus–phosphorus bonds in either P_4O_6 or P_4O_{10}.

$$P_4O_{10}(s) + 6\,H_2SO_4(l) \rightarrow 6\,SO_3(g) + 4\,H_3PO_4(l)$$

$$P_4O_{10}(s) + 12\,HNO_3(l) \rightarrow 6\,N_2O_5(s) + 4\,H_3PO_4(l)$$

Phosphorus pentoxide is used as a drying agent in desiccators and dry boxes to remove water vapor.

Hypophosphorous acid, $H_3PO_2(aq)$, is prepared by reacting $P_4(g)$ with a warm aqueous solution of $NaOH(aq)$, followed by addition of a strong acid:

$$P_4(g) + 3\,OH^-(aq) + 3\,H_2O(l) \rightarrow 3\,H_2PO_2^-(aq) + PH_3(g)$$

$$H_2PO_2^-(aq) + H^+(aq) \rightarrow H_3PO_2(aq)$$
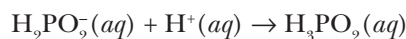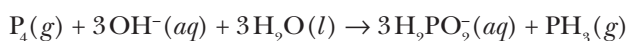
The Lewis formulas for the phosphate ion, PO_4^{3-}, the phosphite ion, HPO_3^{2-}, and the hypophosphite ion, $H_2PO_2^-$, are
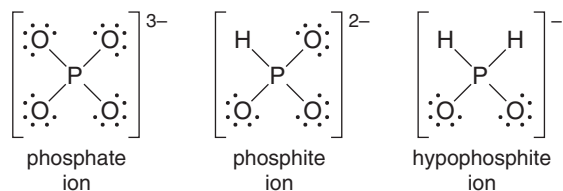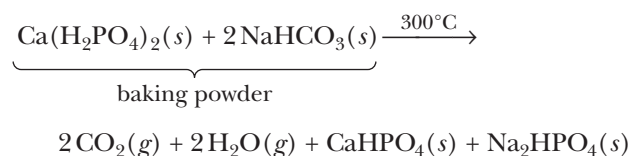

Using VSEPR theory (Chapter 8), we predict that these ions are tetrahedral.

The hydrogen atoms attached to the phosphorus atom do not dissociate in aqueous solutions. Recall from Section 20-12 that an acid that can donate three acidic protons in solution is called a triprotic acid, one that can donate two acidic protons in solution is called a diprotic acid, and one that can donate only one acidic

proton in solution is called a monoprotic acid. Thus, phosphoric acid, $H_3PO_4(aq)$, is triprotic; phosphorous acid, $H_2(HPO_3)(aq)$, is diprotic; and hypophosphorous acid, $H(H_2PO_2)(aq)$, is monoprotic. As noted previously, the latter two formulas are generally written as $H_3PO_3(aq)$ and $H_3PO_2(aq)$, respectively. The structures of these three acids are shown in Figure N.4.

Almost 11.5 million metric tons of phosphoric acid are produced annually in the United States alone. It is produced industrially by the reaction of phosphate rock and sulfuric acid. Commercial phosphoric acid is sold as an 85% by mass (85 g of H_3PO_4 to 15 g of H_2O) solution, equivalent to 15 M. The solution is a colorless, syrupy liquid. The principal use of phosphoric acid is in the manufacture of fertilizers. It is also used extensively in the production of soft drinks, and many of its salts are used in the food industry. For example, the monosodium salt, $NaH_2PO_4(s)$, is used in a variety of foods to control acidity; and calcium dihydrogen phosphate, $Ca(H_2PO_4)_2(s)$, is the acidic ingredient in baking powder. The evolution of carbon dioxide that takes place when baking powder is heated can be represented as

$$\underbrace{Ca(H_2PO_4)_2(s) + 2\,NaHCO_3(s)}_{\text{baking powder}} \xrightarrow{300°C}$$

$$2\,CO_2(g) + 2\,H_2O(g) + CaHPO_4(s) + Na_2HPO_4(s)$$

The slowly evolving $CO_2(g)$ gets trapped in small gas pockets and thereby causes the cake or bread to rise.

| P	O	H
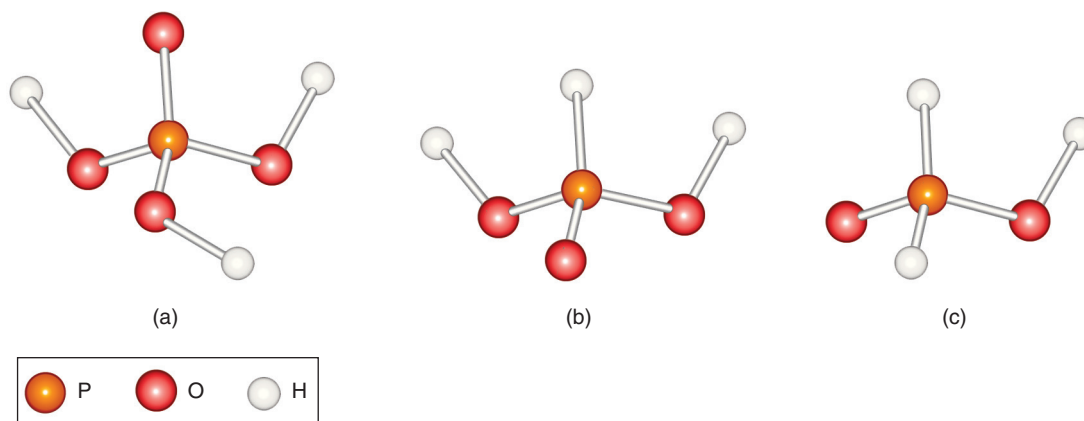
Figure N.4 The molecular structure of (a) phosphoric acid, $H_3PO_4(aq)$, (b) phosphorous acid, $H_3PO_3(aq)$, and (c) hypophosphorous acid, $H_3PO_2(aq)$. Note that all three hydrogen atoms of phosphoric acid are attached to oxygen atoms. One of the hydrogen atoms in phosphorous acid is attached directly to the phosphorus atom, and two of the hydrogen atoms in hypophosphorous acid are attached to the phosphorus atom. Only those hydrogen atoms attached to oxygen atoms are dissociable, so phosphoric acid is triprotic, phosphorous acid is diprotic, and hypophosphorous acid is monoprotic.

When phosphoric acid is heated gently, pyrophosphoric acid, $H_4P_2O_7(aq)$, (*pyro-* means heat) is obtained as a result of the elimination of a water molecule from a pair of phosphoric acid molecules:

elimination of water

pyrophosphoric acid, $H_4P_2O_7$
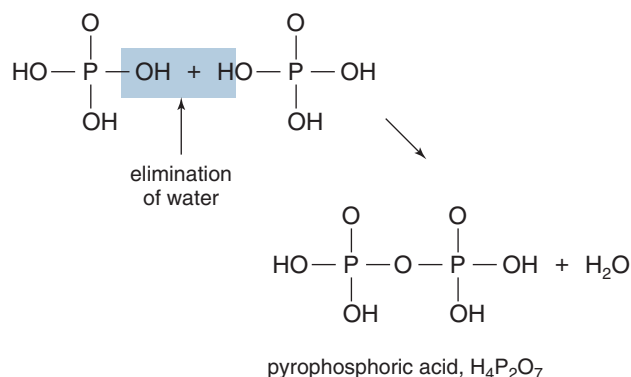
Pyrophosphoric acid, which is also called diphosphoric acid, is a viscous, syrupy liquid that tends to solidify on long standing. In aqueous solution, it slowly reverts to phosphoric acid.

Longer chains of phosphate groups can be formed. The compound sodium triphosphate, $Na_5P_3O_{10}(s)$, used to be the primary phosphate ingredient of detergents. Its role was to break up and suspend dirt and stains by forming water-soluble complexes with metal ions. (The formation of complexes is discussed in Chapter 26.) In the 1960s almost all detergents contained phosphates, sometimes as much as 50% by mass. It was discovered, however, that the phosphates

triphosphate ion
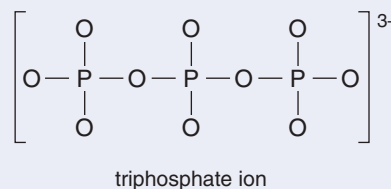
led to a serious water pollution problem. The enormous quantity of phosphates discharged into rivers and lakes served as a nutrient for the rampant growth of algae and other organisms. When these organisms died, much of the oxygen dissolved in the water was consumed in the decay process, thus depleting the water's oxygen supply and destroying the ecological balance. This process is called eutrophication. As a result of legislation in the 1970s, phosphates have been eliminated from detergents, or at least their levels have been reduced markedly.

N-3. Phosphorus Forms a Number of Binary Compounds

Phosphorus reacts directly with reactive metals, such as sodium and calcium, to form phosphides; for example,

$$12\,Na(s) + P_4(s) \rightarrow 4\,Na_3P(s)$$
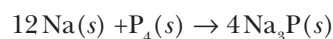
Most metal phosphides react vigorously with water to produce phosphine, $PH_3(g)$:

$$Ca_3P_2(s) + 6 H_2O(l) \rightarrow 2 PH_3(g) + 3 Ca(OH)_2(aq)$$

Phosphine has a trigonal pyramidal structure with an H–P–H bond angle of 93.7°. It is a colorless, extremely toxic gas with an offensive odor like that of rotten fish. Phosphine reacts violently with oxygen and the halogens. Unlike ammonia, phosphine does not act as a base toward water, and few phosphonium (PH_4^+) salts are stable. Phosphine can also be prepared by the reaction of white phosphorus with a strong base. The equation for the reaction is

$$P_4(s) + 3 NaOH(aq) + 3 H_2O(l) \rightarrow$$
$$PH_3(g) + 3 NaH_2PO_2(aq)$$
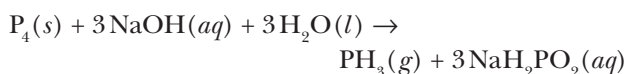
Phosphorus reacts directly with the halogens to form halides (Figure N.5). If an excess of phosphorus is used, then the trihalide is formed. For example,

$$\underset{\text{excess}}{P_4(s)} + 6 Cl_2(g) \rightarrow 4 PCl_3(l)$$
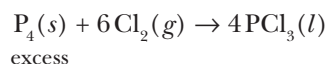
Phosphorus trichloride reacts with chlorine to give phosphorus pentachloride:

$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$$

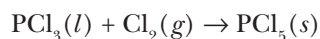
Figure N.5 The reaction between phosphorus and bromine.

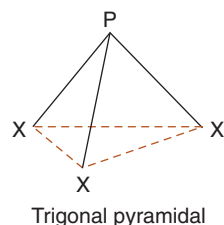Figure N.6 The phosphorus trihalides, PX_3, have a trigonal pyramidal molecular structure in the gas phase.

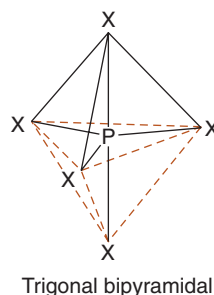Trigonal pyramidal

Figure N.7 The phosphorus pentahalides, PX_5, have a trigonal bipyramidal molecular structure in the gas phase.

Trigonal bipyramidal

Recall from Chapter 8 that phosphorus trihalide molecules in the gas phase have a trigonal pyramidal structure (Figure N.6) and that phosphorus pentahalide molecules in the gas phase have a trigonal bipyramidal structure (Figure N.7). In the solid phase, however, X-ray diffraction studies have shown that $PCl_5(s)$ exists as PCl_4^+ and PCl_6^- ion pairs.

Phosphorus halides react vigorously with water:

$$PCl_3(l) + 3 H_2O(l) \rightarrow H_3PO_3(aq) + 3 HCl(aq)$$

$$PCl_5(s) + 4 H_2O(l) \rightarrow H_3PO_4(aq) + 5 HCl(aq)$$
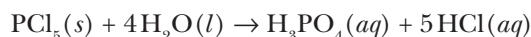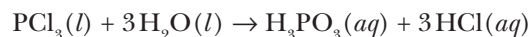
When phosphorus is heated with sulfur, the yellow crystalline compound tetraphosphorus trisulfide, $P_4S_3(s)$, is formed. Matches that can be ignited by striking on any rough surface contain a tip composed of the yellow $P_4S_3(s)$ on top of a red portion that contains lead dioxide, $PbO_2(s)$, together with antimony sulfide, $Sb_2S_3(s)$ (Figure N.8). Friction causes the $P_4S_3(s)$ to ignite in air, and the heat produced then initiates a reaction between antimony sulfide and lead dioxide, which produces a flame.

Safety matches consist of a mixture of potassium chlorate, $KClO_3(s)$, and antimony sulfide, $Sb_2S_3(s)$. The match is ignited by striking it on a special rough surface composed of a mixture of red phosphorus, glue, and abrasive. The red phosphorus is ignited by friction and in turn ignites the reaction mixture in the match head.

Figure N.8 Phosphorus in the form of $P_4S_3(s)$ is one of the principal components of "strike-anywhere" matches.

## N-4. Many Phosphorus Compounds Are Important Biologically

Ordinary tooth enamel is hydroxyapatite, $Ca_{10}(OH)_2(PO_4)_6(s)$. If low concentrations of fluoride ion are added to the diets of children, then a substantial amount of the tooth enamel formed will consist of fluorapatite, $Ca_{10}F_2(PO_4)_6(s)$, which is much harder and less affected by acidic substances than hydroxyapatite. Consequently, fluorapatite is more resistant to tooth decay than is hydroxyapatite. Small quantities of fluoride are added to most municipal water supplies, and the incidence of tooth decay among children has decreased markedly over the past few decades.

The energy requirements for many biochemical reactions are supplied by a substance called **adenosine triphosphate**, or simply **ATP** (Figure N.9). The chain of three phosphate groups in ATP makes it an energy-rich molecule. Under physiological conditions, the reaction of one mole of ATP with water to produce adenosine diphosphate (ADP) and a hydrogen phosphate ion releases −31 kilojoules of energy. This energy is used by all living species to drive biochemical reactions. We can represent the reaction of ATP with water schematically by

$$ATP(aq) + H_2O(l) \rightarrow ADP(aq) + HPO_4^{2-}(aq)$$
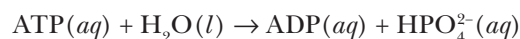
Adenosine diphosphate is converted into ATP by the biochemical oxidation of food molecules. The ATP is then available to supply energy for muscular activity, synthesis of proteins and other biochemical molecules, production of nerve signals, and other biological activity. In other words, ATP is a biological fuel. The formation and utilization of ATP occur on the average within about one minute of each other. The amount of ATP used by the human body is truly remarkable: at rest over a 24-hour period about 40 kilograms of ATP are utilized. For strenuous exercise, the rate of utilization of ATP can reach 5 kilograms in 10 minutes.

Many organic phosphates are potent insecticides that are also toxic to humans. These insecticides act by blocking the transmission of electrical signals in the respiratory system, thereby causing paralysis and death by suffocation. Fortunately, such poisons do not last for long in the environment because they are destroyed over a period of several days by reaction with water. An important example of an organophosphorus insecticide is malathion, which has been used
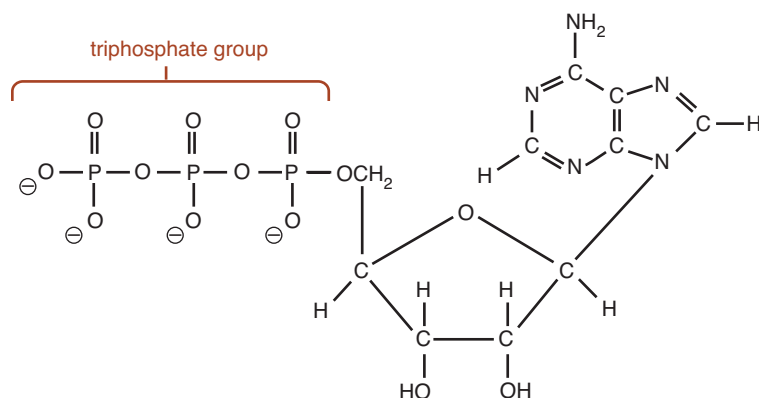
Figure N.9 The Lewis formula of ATP. ADP is similar but has two phosphate groups joined together instead of three.

to combat the Mediterranean fruit fly infestation in California and mosquitoes carrying the West Nile virus in various urban communities around the United States. Malathion is toxic to humans, but only at fairly large doses. An enzyme in human gastric juice decomposes malathion (insects lack this enzyme); thus, malathion is most toxic to humans when it is absorbed directly into the bloodstream, as, for example, when it comes into contact with a cut in the skin.

Some commercially important compounds of phosphorus are given in Table N.1.

TABLE N.1 Some important compounds of phosphorus

Compound	Uses
phosphorus pentasulfide, $P_2S_{10}(s)$	safety matches; oil additive
phosphorus pentoxide, $P_4O_{10}(s)$	dehydrating agent
phosphoric acid, $H_3PO_4(aq)$	fertilizers; soaps and detergents; soft drinks; soil stabilizer
sodium phosphates: $NaH_2PO_4(s)$, $Na_2HPO_4(s)$, and $Na_3PO_4(s)$	synthetic detergents; water softeners; leavening agents
calcium phosphates: $CaHPO_4(s)$ and $Ca(H_2PO_4)_2(s)$	fertilizers; poultry and animal feeds

QUESTIONS

N-1. Discuss the difference in reactivity between white phosphorus and red phosphorus.

N-2. What is the molecular structure of $P_4(s)$?

N-3. What is the general formula for an apatite mineral?

N-4. What is phosphate rock? What is its most important use?

N-5. Why can't phosphate rock be used directly as a fertilizer?

N-6. Describe the molecular structures of $P_4O_6(s)$ and $P_4O_{10}(s)$.

N-7. Describe the molecular structures of $H_3PO_2(l)$, $H_3PO_3(l)$, and $H_3PO_4(l)$. How many dissociable protons are there per mole of phosphorous acid? Of hypophosphorous acid?

N-8. Describe the action of baking powder.

N-9. Discuss the process of eutrophication.

N-10. Compare ammonia and phosphine as bases.

N-11. Describe two ways to prepare phosphine.

N-12. Discuss the difference between safety matches and strike-anywhere matches.

N-13. What is a desiccant? Give an example of one.

TERMS YOU SHOULD KNOW

white phosphorus *N1*
red phosphorus *N1*
amorphous *N1*
superphosphate *N2*
adenosine triphosphate (ATP) *N6*