

phosphorus

Phosphorus

atomic number	15	30.973762	atomic weight
symbol	P		acid-base properties of higher-valence oxides
electron configuration	[Ne]3s ² 3p ³		crystal structure
name	phosphorus		physical state at 20 °C (68 °F)

 Other nonmetals	 Solid
 Cubic	 Weakly acidic

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phosphorus

phosphorus (P),
nonmetallic
chemical
element
of the
nitrogen

family (Group 15 [Va] of the periodic table) that at room temperature is a colourless, semitransparent, soft, waxy solid that glows in the dark.

Element Properties

atomic number 15

atomic weight 30.9738

melting point (white) 44.1 °C (111.4 °F)

boiling point (white) 280 °C (536 °F)

density (white) 1.82 gram/cm³ at 20 °C (68 °F)

oxidation states −3, +3, +5

electron configuration 1s²2s²2p⁶3s²3p³

History

Arabian alchemists of the 12th century may have isolated elemental phosphorus by accident, but the records are unclear. Phosphorus appears to have been discovered in 1669 by Hennig Brand, a German merchant whose hobby was alchemy. Brand allowed 50 buckets of urine to stand until they putrified and “bred worms.” He then boiled the urine down to a paste and heated it with sand, thereby distilling elemental phosphorus from the mixture. Brand reported his discovery in a letter to Gottfried Wilhelm Leibniz, and, thereafter, demonstrations of this element and its ability to glow in the dark, or “phosphoresce,” excited public interest.

Phosphorus, however, remained a chemical curiosity until about a century later when it proved to be a component of bones. Digestion of bones with nitric or sulfuric acid formed phosphoric

TABLE OF CONTENTS

- Introduction
- History
- Occurrence and distribution
- Commercial production and uses
- Properties and reactions
- Principal compounds
- Analytical chemistry
- Biological and physiological significance

acid, from which phosphorus could be distilled by heating with charcoal. In the late 1800s James Burgess Readman of Edinburgh developed an electric furnace method for producing the element from phosphate rock, which is essentially the method employed today.

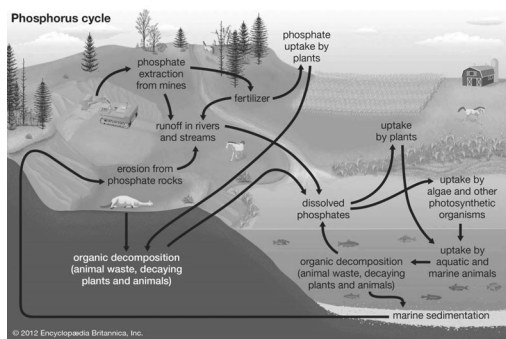
Occurrence and distribution

Phosphorus is a very widely distributed element—12th most abundant in Earth's crust, to which it contributes about 0.10 weight percent. Its cosmic abundance is about one atom per 100 atoms of silicon, the standard. Its high chemical reactivity assures that it does not occur in the free state (except in a few meteorites). Phosphorus always occurs as the phosphate ion. The principal combined forms in nature are the phosphate salts. About 550 different minerals have been found to contain phosphorus, but, of these, the principal source of phosphorus is the apatite series in which calcium ions exist along with phosphate ions and variable amounts of fluoride, chloride, or hydroxide ions, according to the formula $[\text{Ca}_{10}(\text{PO}_4)_6(\text{F}, \text{Cl}, \text{or OH})_2]$. Other important phosphorus-bearing minerals are wavellite and vivianite. Commonly, such metal atoms as magnesium, manganese, strontium, and lead substitute for calcium in the mineral, and silicate, sulfate, vanadate, and similar anions substitute for phosphate ions. Very large sedimentary deposits of fluoroapatite are found in many parts of Earth. The phosphate of bone and tooth enamel is hydroxyapatite. (The principle of lessening tooth decay by fluoridation depends upon the conversion of hydroxyapatite to the harder, more decay-resistant, fluoroapatite.)

The chief commercial source is phosphorite, or phosphate rock, an impure massive form of carbonate-bearing apatite. Estimates of the total phosphate rock in Earth's crust average about 65,000,000,000 tons, of which Morocco and Western Sahara contain about 80 percent. This estimate includes only ore that is sufficiently rich in phosphate for conversion to useful products by present methods. Vast quantities of material lower in phosphorus content also exist.

The only naturally occurring isotope of phosphorus is that of mass 31. The other isotopes from mass 24 to mass 46 have been synthesized by appropriate nuclear reactions. All of these are radioactive with relatively short half-lives. The isotope of mass 32 has a half-life of 14.268 days and has proven extremely useful in tracer studies involving the absorption and movement of phosphorus in living organisms.

Commercial production and uses



phosphorus cycle

Phosphorus, which cycles primarily through the terrestrial and aquatic environments, is one of the most-important elements influencing the growth of plants.

wasted on its journey from mining to being eaten by humans, and the wasted phosphorus ends up in waterways where it can cause algal blooms. Another concern is that increased phosphorus usage will deplete the nonrenewable supply of phosphate rock.

Only about 5 percent of the phosphorus consumed per year in the United States is used in the elemental form. Pyrotechnic applications of the element include tracers, incendiaries, fireworks, and matches. Some is used as an alloying agent, some is used to kill rodents, and the rest is employed in chemical synthesis. A large amount is converted to sulfides used in matches and in the manufacture of insecticides and oil additives. Most of the remainder is converted to halides or oxides for subsequent use in synthesizing organic phosphorus compounds.

Properties and reactions

The electron configuration of the phosphorus atom can be represented by $1s^2 2s^2 2p^6 3s^2 3p^3$. The outer shell arrangement therefore resembles that of nitrogen, with three half-filled orbitals each capable of forming a single covalent bond and an additional lone-pair of electrons. Depending on the electronegativity of the elements with which it combines, phosphorus can therefore exhibit oxidation states of +3 or −3, just as does nitrogen. The principal differences between nitrogen and phosphorus are that the latter is of considerably lower electronegativity and has larger atoms, with outer *d* orbitals available. For these reasons, the similarities between nitrogen and phosphorus chemistry are largely formal ones, tending to conceal the actual, wide differences. The outer *d* orbitals in phosphorus permit an expansion of the octet,

The principal technique for converting phosphate rock to usable materials involves acidulation of the crushed rock—with either sulfuric or phosphoric acids—to form crude calcium hydrogen phosphates that, being water-soluble, are valuable additions to fertilizer. Most of the output is burned to phosphoric anhydride and subsequently treated with water to form phosphoric acid, H_3PO_4 . About 95 percent of the phosphate rock mined in the United States is used to make fertilizer or food supplements for animals. Concerns have arisen about phosphorus use, however. Most of the phosphorus is

which leads to the +5 state, with five actual covalent bonds being formed in compounds, a condition impossible for nitrogen to achieve.

The first striking difference in chemistry of the two elements is that elemental phosphorus exists under ordinary conditions in any of 10 modifications, or allotropic forms, all of which are solid; the three major allotropes are white, red, and black. Phosphorus molecules of formula P_2 , structurally analogous to N_2 molecules and evidently also triply bonded, exist only at very high temperatures. These P_2 molecules do not persist at lower temperatures—below about 1,200 °C (2,200 °F)—because of the fact that three single bonds in phosphorus, in contrast to the situation with nitrogen, are energetically favoured over one triple bond. On cooling, the triply bonded P_2 molecules condense to form tetrahedral P_4 molecules, in which each atom is joined to three others by single bonds. White phosphorus has two allotropes: the alpha form, which is stable at ordinary temperatures, has a cubic crystal structure; the beta form, which is stable below -78 °C (-108 °F), has a hexagonal crystal structure. Because of the relatively weak intermolecular attractions (van der Waals forces) between the separate P_4 molecules, the solid melts easily at 44.1 °C (111.4 °F) and boils at about 280 °C (536 °F). Formation of tetrahedra requires bond angles of 60° instead of the preferred 90°–109° angles, so that white phosphorus is a relatively unstable, or metastable, form. It changes spontaneously, but slowly, at temperatures around 200 °C (390 °F) or higher, to a polymeric form called “red phosphorus.” This substance is amorphous when formed at lower temperatures, but it can become crystalline, with a melting point of about 590° C (1,090 °F). At higher temperatures and pressures, or with the aid of a catalyst, at ordinary pressures and a temperature of about 200 °C, phosphorus is converted to a flaky black crystalline form, which somewhat resembles graphite. This may prove to be the most stable form of phosphorus, despite the relative difficulty in its preparation. In both the red and the black forms, each phosphorus atom forms three single bonds, which are spread apart sufficiently to be relatively strain free.

Consistent with the metastable condition of the white modification, and the crowding of its covalent bonds, this form is far more reactive chemically than the others. It is highly toxic, reacts vigorously with most reagents, and inflames in air at only 35° C (95 °F), so it must be stored under water or other inert liquid. White phosphorus dissolves readily in solvents such as carbon disulfide, in which it maintains the composition P_4 . White phosphorus has been used

for military purposes as a source of smoke and to fill incendiary shells and grenades. In contrast, red phosphorus is insoluble and relatively inert, although large quantities of the usual commercial form can ignite spontaneously in air and react with water to form phosphine and phosphorus oxyacids. Red phosphorus is used in preparing the striking surface for safety matches. Black phosphorus is more inert and is capable of conducting electricity. Both these polymeric forms are insoluble and are very much less volatile than white phosphorus.

Principal compounds

Phosphorus is used almost entirely in the form of compounds, usually in the oxidation states of +3, +5, and -3. Unlike nitrogen and various other members of the family, phosphorus tends to exhibit a preference for the +5 state.

Of considerable economic significance is phosphine, or hydrogen phosphide, PH_3 . This gaseous compound is produced either by the action of a strong base (or hot water) on white phosphorus or by the hydrolysis of a metal phosphide. Phosphine is used mainly as a starting material in the synthesis of various organic phosphorus compounds, as a doping agent for solid-state electronics components, and as a fumigant.

Among the most commercially important phosphorus compounds are the oxides and acids. Much of the industrially produced white phosphorus is burned to form phosphorus pentoxide, P_4O_{10} . Sometimes called phosphoric anhydride, or diphosphorus pentoxide, this compound can be obtained in the form of a soft white powder or colourless crystalline solid. It is widely used in chemical analysis as a dehydrating agent and in organic synthesis as a condensing agent. Large quantities are treated with water to make orthophosphoric acid (H_3PO_4), commonly called phosphoric acid, which has diverse industrial applications, including the production of phosphates, salts that contain the phosphate ion (PO_4^{3-}), the hydrogen phosphate ion (HPO_4^{2-}), or the dihydrogen phosphate ion (H_2PO_4^-). Such salts are used as leavening agents in baking, as abrasives in toothpaste, and sometimes as additives to detergents. Another salt, prepared by the action of phosphoric acid on phosphate rock, is calcium dihydrogen phosphate, or superphosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, the most widely used phosphate fertilizer.

With the halogen elements phosphorus forms various halides; PX_3 (in which X is F, Cl, Br, or I) and PX_5 (in which X is F, Cl, or Br) are the two simple series. Interestingly, the solids PCl_5

and PBr_5 contain PX_4^+ cations and PX_6^- anions rather than PX_5 molecules. These halides are used to synthesize organic phosphorus chemicals. Phosphorus reacts with sulfur to form several sulfides that are used in the manufacture of organic chemicals and matches. It reacts with many metals and metalloids to form phosphides.

Phosphorus atoms can bond with oxygen atoms to form ester groups. These can bond with carbon atoms, yielding a large number of organic phosphorus chemicals. These are found in many important biological processes. The phosphoglycerides, for example, are required for fermentation. The adenosine phosphates are essential in photosynthesis and for muscle action; adenosine triphosphate (ATP) plays a central role in metabolism and is found in the cells of all living things. Industrially important organic phosphorus compounds include plasticizers and gasoline additives. Certain highly toxic forms are employed in insecticides of the parathion type. Poisonous organic derivatives of phosphorus have been used as nerve gas, a key weapon of chemical warfare.

Analytical chemistry

Elemental phosphorus can be detected by its phosphorescence. It can also be converted to phosphine with boiling sodium hydroxide solution or with zinc and sulfuric acid; the phosphine is identified by means of test paper containing either silver nitrate or mercuric chloride, both of which are reduced to the free metal by phosphine, thereby darkening the paper. Phosphorus vapour also readily darkens silver nitrate test paper. Phosphorus is determined quantitatively by oxidation to phosphate, followed by any of several standard procedures. Phosphate, for example, may be precipitated as the magnesium ammonium salt, MgNH_4PO_4 , converted by ignition to magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$, and weighed. Alternatively, phosphate may be precipitated as ammonium phosphomolybdate; this can be weighed as such, converted to magnesium pyrophosphate and weighed, or titrated directly with sodium hydroxide solution.

Biological and physiological significance

Phosphorus is an important constituent of bones and teeth, and it is essential to the growth of living organisms. In organisms the element usually appears as phosphate. In its other forms phosphorus is likely to prove very toxic. White phosphorus attacks the skin and, when ingested, causes a necrosis of the jawbone, called “phossy jaw.” Certain organic esters of phosphoric acid, used as lubricating-oil additives, have been found to cause permanent

paralysis when accidentally ingested. Phosphine is extremely toxic, as are its organic derivatives. Some of the most toxic substances known to man, collectively termed nerve gas, are organic derivatives of phosphorus.

Phosphorus is present in the fluids within cells of living tissues as the phosphate ion, PO_4^{3-} , one of the most important mineral constituents for cellular activity. The genes, which direct heredity and other cellular functions and are found in the nucleus of each cell, are molecules of DNA (deoxyribonucleic acid), which all contain phosphorus. Cells store the energy obtained from nutrients in molecules of adenosine triphosphate (ATP). Calcium phosphate is the principal inorganic constituent of teeth and bones.

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phosphate

phosphate, any of numerous chemical compounds related to phosphoric acid (H_3PO_4). One group of these derivatives is composed of salts containing the phosphate ion (PO_4^{3-}), the hydrogen phosphate ion (HPO_4^{2-}), or the dihydrogen phosphate ion (H_2PO_4^-), and positively charged ions such as those of sodium or calcium; a second group is composed of esters, in which the hydrogen atoms of phosphoric acid have been replaced by organic combining groups such as ethyl (C_2H_5) or phenyl (C_6H_5).

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