Phosphorus

From Wikipedia, the free encyclopedia

Phosphorus is a chemical element with symbol **P** and atomic number 15. As an element, phosphorus exists in two major forms—white phosphorus and red phosphorus—but because it is highly reactive, phosphorus is never found as a free element on Earth. At 0.099%, phosphorus is the most abundant pnictogen in the Earth's crust. With few exceptions, minerals containing phosphorus are in the maximally oxidised state as inorganic phosphate rocks.

The first form of elemental phosphorus to be produced (white phosphorus, in 1669) emits a faint glow when exposed to oxygen – hence the name, taken from Greek mythology, Φωσφόρος meaning "light-bearer" (Latin *Lucifer*), referring to the "Morning Star", the planet Venus (or Mercury). The term "phosphorescence", meaning glow after illumination, originally derives from this property of phosphorus, although this word has since been used for a different physical process that produces a glow. The glow of phosphorus itself originates from oxidation of the white (but not red) phosphorus — a process now termed chemiluminescence. Together with nitrogen, arsenic, antimony, and bismuth, phosphorus is classified as a pnictogen.

Phosphorus is essential for life. Phosphates (compounds containing the phosphate ion, PO_4^{3-}) are a component of DNA, RNA, ATP, and the phospholipids, which form all cell membranes. Demonstrating the link between phosphorus and life, elemental phosphorus was first isolated from human urine, and bone ash was an important early phosphate source. Phosphate mines contain fossils, especially marine fossils, because phosphate is formed from the deposits of animal remains and excreta. Low phosphate levels are an important limit to growth in some aquatic systems. The vast majority of phosphorus compounds produced are consumed as fertilisers. Phosphate is needed to replace the phosphorus that plants remove from the soil, and its annual demand is rising nearly twice as fast as the growth of the human population. Other applications include the role of organophosphorus compounds in detergents, pesticides, and nerve agents.

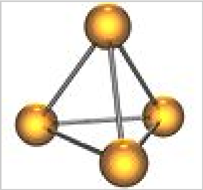
Phosphorus, $_{15}P$

waxy white (yellow cut), red (granules centre left, chunk centre right), and violet phosphorus

General properties	
Name, symbol	phosphorus, P
Appearance	colourless, waxy white, yellow, scarlet, red, violet, black
Phosphorus in the periodic table	
Atomic number (Z)	15
Group, block	group 15 (pnictogens), p-block
Period	period 3
Element category	polyatomic nonmetal
Standard atomic weight (±) (A_r)	30.973761998(5)[1]
Electron configuration	[Ne] $3s^2$ $3p^3$
per shell	2, 8, 5
Physical properties	
Phase	solid
Density near r.t.	white: 1.823 $g \cdot cm^{-3}$ red: ≈ 2.2–2.34 $g \cdot cm^{-3}$

Characteristics

Physical



P_4 molecule, as in white phosphorus

Phosphorus exists as several forms (allotropes) that exhibit strikingly different properties.[5] The two most common allotropes are **white phosphorus** and **red phosphorus**.

[6]

White phosphorus and related molecular forms

From the perspective of applications and chemical literature, the most important form of elemental phosphorus is white phosphorus, often abbreviated as **WP**. It is a soft and waxy solid which consists of tetrahedral P_4 molecules, in which each atom is bound to the other three atoms by a single bond. This P_4 tetrahedron is also present in liquid and gaseous phosphorus up to the temperature of 800 °C (1,470 °F) when it starts decomposing to P_2 molecules.[7] White phosphorus exists in two crystalline forms: α (alpha) and β (beta). At room temperature, the α-form is stable, which is more common and it has cubic crystal structure and at 195.2 K (−78.0 °C), it transforms into β-form, which has hexagonal crystal structure. These forms differ in terms of the relative orientations of the constituent P_4 tetrahedra.[8][9]

White phosphorus is the least stable, the most reactive, the most volatile, the least dense, and the most toxic of the allotropes. White phosphorus gradually changes to red phosphorus. This transformation is accelerated by light and heat, and samples of white phosphorus almost always contain some red phosphorus and accordingly appear yellow. For this reason, white phosphorus that is aged or otherwise impure (e.g. weapons-grade, not lab-grade WP) is also called **yellow phosphorus**. When exposed to oxygen, white phosphorus glows in the dark with a very faint tinge of green and blue. It is highly flammable and pyrophoric (self-igniting) upon contact with air. Owing to its pyrophoricity, white phosphorus is used as an additive in napalm. The odour of combustion of this form has a characteristic garlic smell, and samples are commonly coated with white

	violet: 2.36 g·cm^{-3} black: 2.69 g/cm^3
Heat of fusion	white: 0.66 kJ/mol
Heat of vaporisation	white: 51.9 kJ/mol
Molar heat capacity	white: 23.824 J/(mol·K)

Vapour pressure (white)

P (Pa)	**1**	**10**	**100**	**1 k**	**10 k**	**100 k**
at T (K)	279	307	342	388	453	549

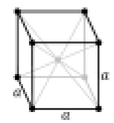
Vapour pressure (red, b.p. 431 °C)

P (Pa)	**1**	**10**	**100**	**1 k**	**10 k**	**100 k**
at T (K)	455	489	529	576	635	704

Atomic properties

Oxidation states	**5**, 4, **3**, 2, 1,[2] −1, −2, **−3** (a mildly acidic oxide)
Electronegativity	Pauling scale: 2.19
Ionisation energies	1st: 1011.8 kJ/mol 2nd: 1907 kJ/mol 3rd: 2914.1 kJ/mol (more)
Covalent radius	107±3 pm
Van der Waals radius	180 pm

Miscellanea

Crystal structure	body-centred cubic (bcc) 
Thermal conductivity	white: 0.236 W/(m·K) black: 12.1 W/(m·K)
Magnetic ordering	white, red, violet, black:

"phosphorus pentoxide", which consists of P_4O_{10} tetrahedra with oxygen inserted between the phosphorus atoms and at their vertices. White phosphorus is insoluble in water but soluble in carbon disulfide.[10]

Thermolysis (cracking) of P_4 at 1100 kelvin gives diphosphorus, P_2. This species is not stable as a solid or liquid. The dimeric unit contains a triple bond and is analogous to N_2. It can also be generated as a transient intermediate in solution by thermolysis of organophosphorus precursor reagents.[11] At still higher temperatures, P_2 dissociates into atomic P.[10]

	diamagnetic[3]
Bulk modulus	white: 5 GPa red: 11 GPa
CAS Number	white: 12185-10-3 red: 7723-14-0
History	
Discovery	Hennig Brand (1669)
Recognised as an element by	Antoine Lavoisier[4] (1777)

Most stable isotopes of phosphorus

iso	NA	half-life	DM	DE (MeV)	DP
^{31}P	100%	is stable with 16 neutrons			
^{32}P	trace	14.28 d	β^-	1.709	^{32}S
^{33}P	trace	25.3 d	β^-	0.249	^{33}S

Red phosphorus

Red phosphorus is polymeric in structure. It can be viewed as a derivative of P_4 wherein one P-P bond is broken, and one additional bond is formed with the neighbouring tetrahedron resulting in a chain-like structure. Red phosphorus may be formed by heating white phosphorus to 250 °C (482 °F) or by exposing white phosphorus to sunlight.[12] Phosphorus after this treatment is amorphous. Upon further heating, this material crystallises. In this sense, red phosphorus is not an allotrope, but rather an intermediate phase between the white and violet phosphorus, and most of its properties have a range of values. For example, freshly prepared, bright red phosphorus is highly reactive and ignites at about 300 °C (572 °F),[13] though it is more stable than white phosphorus, which ignites at about 30 °C (86 °F).[14] After prolonged heating or storage, the color darkens (see infobox images); the resulting product is more stable and does not spontaneously ignite in air.[15]

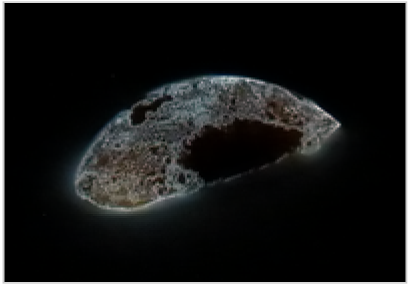
White phosphorus

Violet phosphorus

Violet phosphorus is a form of phosphorus that can be produced by day-long annealing of red phosphorus above 550 °C. In 1865, Hittorf discovered that when phosphorus was recrystallised from molten lead, a red/purple form is obtained. Therefore, this form is sometimes known as "Hittorf's phosphorus" (or violet or α-metallic phosphorus).[16]

Black phosphorus

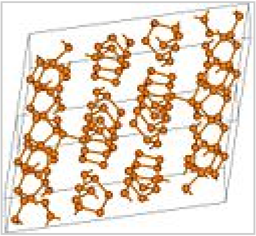
Black phosphorus is the least reactive allotrope and the thermodynamically stable form below 550 °C (1,022 °F). It is also known as β-metallic phosphorus and has a structure somewhat resembling that of graphite.[17][18]



White phosphorus exposed to air glows in the darkness

Black phosphorus is obtained by heating white phosphorus under high pressures (about 12,000 standard atmospheres or 1.2 gigapascals). It can also be produced at ambient conditions using metal salts, e.g. mercury, as catalysts.[19] In appearance, properties, and structure, it resembles graphite, being black and flaky, a conductor of electricity, and has puckered sheets of linked atoms.[20]

Other forms



Crystal structure of red phosphorus

Another form, scarlet phosphorus, is obtained by allowing a solution of white phosphorus in carbon disulfide to evaporate in sunlight.

Another allotrope is diphosphorus; it contains a phosphorus dimer as a structural unit and is highly reactive.[16]

Isotopes

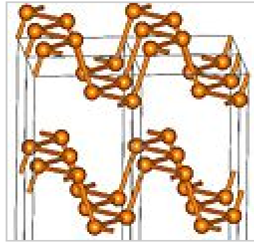
Twenty-three isotopes of phosphorus are known,[21] including all possibilities from ^{24}P up to ^{46}P. Only ^{31}P is stable and is therefore present at 100% abundance. The half-integer nuclear spin and high abundance of ^{31}P make phosphorus-31 NMR spectroscopy a very useful analytical tool in studies of phosphorus-containing samples.

Red phosphorus

Two radioactive isotopes of phosphorus have half lives suitable for biological scientific experiments. These are:

- ^{32}P, a beta-emitter (1.71 MeV) with a half-life of 14.3 days, which is used routinely in life-science laboratories, primarily to produce radiolabeled DNA and RNA probes, *e.g.* for use in Northern blots or Southern blots.
- ^{33}P, a beta-emitter (0.25 MeV) with a half-life of 25.4 days. It is used in life-science laboratories in applications in which lower energy beta emissions are advantageous such as DNA sequencing.

The high energy beta particles from ^{32}P penetrate skin and corneas and any ^{32}P ingested, inhaled, or absorbed is readily incorporated into bone and nucleic acids. For these reasons, Occupational Safety and Health Administration in the United States, and similar institutions in other developed countries require personnel working with ^{32}P to wear lab coats, disposable gloves, and safety glasses or goggles to protect the eyes, and avoid working directly over open containers. Monitoring personal, clothing, and surface contamination is also required. Shielding requires special consideration. The high energy of the beta particles gives rise to secondary emission of X-rays via Bremsstrahlung (braking radiation) in dense shielding materials such as lead. Therefore, the radiation must be shielded with low density materials such as acrylic or other plastic, water, or (when transparency is not required), even wood.[22]



Crystal structure of black phosphorus

Source

- Wikipedia: Phosphorus