Phosphorus

Contents

1 . Introduction :

Phosphorus is the chemical element that has the symbol **P** and atomic number 15. A multivalent nonmetal of the nitrogen group, phosphorus is commonly found in inorganic phosphate rocks. Elemental phosphorus exists in two major forms - white phosphorus and red phosphorus. Although the term "phosphorescence", meaning glow after illumination, derives from phosphorus, glow of phosphorus originates from oxidation of the white (but not red) phosphorus and should be called chemiluminescence.

Due to its high reactivity, phosphorus is never found as a free element in nature on Earth. The first form of phosphorus to be discovered (white phosphorus, discovered in 1669) emits a faint glow upon exposure to oxygen — hence its name given from Greek mythology, Φωσφόρος meaning " light - bearer " (Latin *Lucifer*) , referring to the " Morning Star ", the planet Venus.

Phosphorus is a component of DNA, RNA, ATP, and also the phospholipids which form all cell membranes. It is thus an essential element for all living cells. The most important commercial use of phosphorus-based chemicals is the production of fertilizers.

Phosphorus compounds are also widely used in explosives, nerve agents, friction matches, fireworks, pesticides, tooth paste and detergents.

Name , Symbol , Number	Phosphorus , P , 15
Element category	Nonmetal
Group , period , block	15 , 3 , p
Standard atomic weight	31 g · mol^{-1}
Electron configuration	[Ne] $3s^2$ $3p^3$
Electrons per shell	2, 8, 5
Density	(white) 1.823 g · cm^{-3} (red) ≈ 2.34 g · cm^{-3} (black) 2.69 g · cm^{-3}
Melting point	(white) 44.2 °C, (black) 610 °C
Sublimation point	(red) ≈ 416 °C, (purple) 620 °C
Boiling point	(white) 280.5 °C
Heat of fusion	(white) 0.66 kJ·mol^{-1}
Heat of vaporization	12.4 kJ·mol^{-1}
Specific heat capacity	(25 °C) (white) 23.824 J·mol^{-1}·K^{-1}
Oxidation states	5, 4, 3, 2 , 1 , -1, -2, -3 (mildly acidic oxide)
Electro negativity	2.19 (Pauling Scale)
Ionization energies	1st : 1011.8 kJ·mol^{-1} 2nd : 1907 kJ·mol^{-1} 3rd : 2914.1 kJ·mol^{-1}
Covalent radius	107 ± 3 pm

Van der Waals radius	180 pm
Magnetic ordering	diamagnetic
Thermal conductivity	(300 K) (white) 0.236, (black) 12.1 W·m^{-1}·K^{-1}
Bulk modulus	11 GPa

Main article: Isotopes of phosphorus

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

2 . Physical properties

2 . 1 . Glow from white phosphorus

Phosphorus was discovered by German alchemist Hennig Brand in 1674 or 1675. Working in Hamburg, Brand attempted to distil some kind of "life essence" from his urine, and in the process produced a white material that glowed in the dark. The phosphorus had in fact been produced from inorganic phosphate, which is a significant component of dissolved urine solids. White phosphorus is highly reactive and gives off a faint greenish glow upon uniting with oxygen. The glow observed by Brand was actually caused by the very slow burning of the phosphorus, but as he neither saw flame nor felt any heat he did not recognize it as burning.

It was known from early times that the glow would persist for a time in a stoppered jar but then cease. Robert Boyle in the 1680s ascribed it to "debilitation" of the air; in fact, it is oxygen being consumed. By the 18th century, it was known that in pure oxygen, phosphorus does not glow at all ; there is only a range of partial pressure at which it does. Heat can be applied to drive the reaction at higher pressures.

In 1974, the glow was explained by R. J. van Zee and A. U. Khan. A reaction with oxygen takes place at the surface of the solid (or liquid) phosphorus, forming the short - lived molecules HPO and P_2O_2 that both emit visible light. The reaction is slow and only very little of the intermediates are required to produce the luminescence, hence the extended time the glow continues in a stoppered jar.

Although the term phosphorescence is derived from phosphorus, the reaction which gives phosphorus its glow is properly called chemiluminescence (glowing due to a cold chemical reaction) , not phosphorescence (re - emitting light that previously fell onto a substance and excited it) .

Phosphorescence is the slow decay of a metastable electronic state to a lower energy state through emission of light. The decay is slow because the transition from the excited to the lower state requires a spin flip, making it classically forbidden. Often it involves a transition from an excited triplet state to a singlet ground state. The metastable excited state may have been populated by thermal excitations or some light source. Since phosphorescence is slow, it persists for some time after the exciting source is removed. In contrast, chemiluminescence occurs when the product molecules of a chemical reaction (HPO and P_2O_2 in this case) leave the reaction in an electronically excited state. These excited molecules then release their excess energy in the form of light. The frequency (colour) of the light emitted is proportional to the energy difference of the two electronic states involved .

2 . 2 . Allotropes of phosphorus

Phosphorus has several forms (allotropes) which have strikingly different properties. The two most common allotropes are white phosphorus and red phosphorus. Red phosphorus is an intermediate phase between white and violet phosphorus. Another form, scarlet phosphorus, is obtained by allowing a solution of white phosphorus in carbon disulfide to evaporate in sunlight. Black phosphorus, is obtained by heating white phosphorus under high pressures (about 12,000 atmospheres). In appearance, properties, and structure, it resembles graphite, being black and flaky, a conductor of electricity, and has puckered sheets of linked atoms. Another allotrope is diphosphorus; it contains a phosphorus dimer as a structural unit and is highly reactive .

White phosphorus has two forms, low - temperature β form and high-temperature α form. They both contain a phosphorus P_4 tetrahedron as a structural unit, 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 when it starts decomposing to P_2 molecules.[11] White phosphorus is the least stable, the most reactive, more volatile, less dense, and more toxic than the other allotropes. The toxicity of white phosphorus led to its discontinued use in matches. White phosphorus is thermodynamically unstable at normal condition and will gradually change to red phosphorus. This transformation, which is accelerated by light and heat, makes white phosphorus almost always contain some red phosphorus and therefore appear yellow. For this reason, it is also called yellow phosphorus. It glows greenish in the dark (when exposed to oxygen) , is highly flammable and pyrophoric (self - igniting) upon contact with air as well as toxic (causing severe liver damage on ingestion) . Because of 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 " (di) 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 .

The white allotrope can be produced using several different methods. In one process, calcium phosphate, which is derived from phosphate rock, is heated in an electric or fuel-fired furnace in the presence of carbon and silica. Elemental phosphorus is then liberated as a vapour and can be collected under phosphoric acid. This process is similar to the first synthesis of phosphorus from calcium phosphate in urine.

In the **red phosphorus**, one of the P_4 bonds is broken, and one additional bond is formed with a neighbouring tetrahedron resulting in a more chain-like structure. Red phosphorus may be formed by heating white phosphorus to 250 °C (482 °F) or by exposing white phosphorus to sunlight.[4] Phosphorus after this treatment exists as an amorphous network of atoms which reduces strain and gives greater stability; further heating results in the red phosphorus becoming crystalline. Therefore red phosphorus is not a certain allotrope, but rather an intermediate phase between the white and violet phosphorus, and most of its properties have a range of values. Red phosphorus does not catch fire in air at temperatures below 260 ° C, whereas white phosphorus ignites at about 30 ° C .

Violet phosphorus is a thermodynamic stable form of phosphorus which can be produced by day - long temper of red phosphorus above 550 °C. In 1865, Hittorf discovered that when phosphorus was recrystallized 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) .

Black phosphorus is the least reactive allotrope and the thermodynamic stable form below 550 °C . It is also known as β - metallic phosphorus and has a structure somewhat resembling that of graphite . High pressures are usually required to produce black phosphorus, but it can also be produced at ambient conditions using metal salts as catalysts .

The **diphosphorus** allotrope, P_2 , is stable only at high temperatures. The dimeric unit contains a triple bond and is analogous to N_2. The diphosphorus allotrope (P_2) can be obtained normally only under extreme conditions (for example, from P_4 at 1100 kelvin). Nevertheless, some advancements were obtained in generating the diatomic molecule in homogeneous solution, under normal conditions with the use by some transitional metal complexes (based on, for example, tungsten and niobium).

2 . 3 . Isotopes of phosphorus

Although twenty - three isotopes of phosphorus are known (all possibilities from ^{24}P up to ^{46}P), only ^{31}P, with spin 1/2, is stable and is therefore present at 100% abundance. The half-integer spin and high abundance of ^{31}P make it useful for nuclear magnetic resonance studies of biomolecules, particularly DNA.

Two radioactive isotopes of phosphorus have half-lives which make them useful for scientific experiments. ^{32}P has a half-life of 14.262 days and ^{33}P has a half-life of 25.34 days. Biomolecules can be "tagged" with a radioisotope to allow for the study of very dilute samples.

Radioactive isotopes of phosphorus include :

- ^{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. Because the high energy beta particles produced penetrate skin and corneas, and because any ^{32} P ingested, inhaled, or absorbed is readily incorporated into bone and nucleic acids, Occupational Safety and Health Administration in the United States, and similar institutions in other developed countries require that a lab coat, disposable gloves, and safety glasses or goggles be worn when working with ^{32} P, and that working directly over an open container be avoided in order to protect the eyes. Monitoring personal, clothing, and surface contamination is also required. In addition, due to the high energy of the beta particles, shielding this radiation with the normally used dense materials (*e.g.* lead), gives rise to secondary emission of X - rays via a process known as Bremsstrahlung, meaning braking radiation. Therefore shielding must be accomplished with low density materials, *e.g.* Plexiglas, Lucite, plastic, wood, or water.[20]
- ^{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.

3 . Chemical properties

- Hydrides : PH_3 , P_2H_4
- Halides : PBr_5 , PBr_3 , PCl_3 , PI_3
- Oxides : P_4O_6 , P_4O_{10}
- Sulfides : P_2S_5 , P_4S_3
- Acids : H_3PO_2 , H_3PO_4
- Phosphates : $(NH_4)_3PO_4$, $Ca_3(PO_4)_2$, $FePO_4$, $Fe_3(PO_4)_2$, Na_3PO_4 , $Ca\ (H_2PO_4)_2$, KH_2PO_4
- Phosphides : Ca_3P_2 , GaP, Zn_3P_2 , Cu_3P
- Organo phosphorus and organo phosphates : Lawesson's reagent, Parathion, Sarin, Soman, Tabun, Triphenyl phosphine, VX nerve gas

3 . 1 . Chemical bonding

Because phosphorus is just below nitrogen in the periodic table, the two elements share many of their bonding characteristics. For instance, phosphine, PH_3, is an analogue of ammonia, NH_3. Phosphorus, like nitrogen, is trivalent in this molecule.

The "trivalent" or simple 3 - bond view is the pre - quantum mechanical Lewis structure, which although somewhat of a simplification from a quantum chemical point of view, illustrates some of the distinguishing chemistry of the element. In quantum chemical valence bond theory, the valence electrons are seen to be in mixtures of four *s* and *p* atomic orbitals, so-called hybrids. In this view, the three unpaired electrons in the three 3*p* orbitals combine with the two electrons in the 3*s* orbital to form three electron pairs of opposite spin, available for the formation of three bonds. The remaining hybrid orbital contains two paired non-bonding electrons, which show as a lone pair in the Lewis structure.

The phosphorus cation is very similar to the nitrogen cation. In the same way that nitrogen forms the tetravalent ammonium ion, phosphorus can form the tetravalent phosphonium ion, and form salts such as phosphonium iodide $[PH_4]^+ [I^-]$.

Like other elements in the third or lower rows of the periodic table, phosphorus atoms can expand their valence to make penta- and hexavalent compounds. The phosphorus chloride molecule is an example. When the phosphorus ligands are not identical, the more electronegative ligands are located in the apical positions and the least electronegative ligands are located in the axial positions.

With strongly electronegative ions, in particular fluorine, hexavalency as in PF_6^- occurs as well. This octahedral ion is isoelectronic with SF_6. In the bonding the six octahedral sp^3d^2 hybrid atomic orbitals play an important role.

Before extensive computer calculations were feasible, it was generally assumed that the nearby *d* orbitals in the $n = 3$ shell were the obvious cause of the difference in binding between nitrogen and phosphorus (i.e., phosphorus had 3d orbitals available for 3s and 3p shell bonding electron hybridisation, but nitrogen did not). However, in the early eighties the German theoretical chemist Werner Kutzelnigg[21] found from an analysis of computer calculations that the difference in binding is more likely due to differences in character between the valence 2*p* and valence 3*p* orbitals of nitrogen and phosphorus, respectively. The 2*s* and 2*p* orbitals of first row atoms are localized in roughly the same region of space, while the 3*p* orbitals of phosphorus are much more extended in space. The violation of the octet rule observed in compounds of phosphorus is then due to the size of the phosphorus atom, and the corresponding reduction of steric hindrance between its ligands. In modern theoretical chemistry, Kutzelnigg's analysis is generally accepted.

The simple Lewis structure for the trigonal bipyramidal PCl_5 molecule contains five covalent bonds, implying a hypervalent molecule with ten valence electrons contrary to the octet rule.

An alternate description of the bonding, however, respects the octet rule by using 3 – centre – 4 - electron (3c - 4e) bonds. In this model the octet on the P atom corresponds to six electrons which form three Lewis (2c - 2e) bonds to the three equatorial Cl atoms, plus the two electrons in the 3 - centre Cl – P - Cl bonding molecular orbital for the two axial Cl electrons. The two electrons in the corresponding nonbonding molecular orbital are not included because this orbital is localized on the two Cl atoms and does not contribute to the electron density on the phosphorus atom. (However, it should always be remembered that the octet rule is not some universal rule of chemical bonding, and while many compounds obey it, there are many elements to which it does not apply) .

3 . 2 . Phosphine , diphosphine and phosphonium salts

Phosphine (PH_3) and arsine (AsH_3) are structural analogs with ammonia (NH_3) and form pyramidal structures with the phosphorus or arsenic atom in the center bound to three hydrogen atoms and one lone electron pair. Both are colourless, ill - smelling, toxic compounds. Phosphine is produced in a manner similar to the production of ammonia. Hydrolysis of calcium phosphide, Ca_3P_2, or calcium nitride, Ca_3N_2 produces phosphine or ammonia, respectively. Unlike ammonia, phosphine is unstable and it reacts instantly with air giving off phosphoric acid clouds. Arsine is even less stable. Although phosphine is less basic than ammonia, it can form some phosphonium salts (like PH_4I), analogs of ammonium salts, but these salts immediately decompose in water and do not yield phosphonium (PH_4^+) ions. Diphosphine (P_2H_4 or $H_2P\text{-}PH_2$) is an analog of hydrazine (N_2H_4) that is a colourless liquid which spontaneously ignites in air and can disproportionate into phosphine and complex hydrides.

3 . 3 . Halides

The trihalides PF_3, PCl_3, PBr_3 and PI_3 and the pentahalides, PCl_5 and PBr_5 are all known and mixed halides can also be formed. The trihalides can be formed simply by mixing the appropriate stoichiometric amounts of phosphorus and a halide. For safety reasons, however, PF_3 is typically made by reacting PCl_3 with AsF_5 and fractional distillation because the direct reaction of phosphorus with fluorine can be explosive. The pentahalides, PX_5, are synthesized by reacting excess halide with either elemental phosphorus or with the corresponding trihalide. Mixed phosphorus halides are unstable and decompose to form simple halides. Thus $5PF_3\ Br_2$ decomposes into $3PF_5$ and $2PBr_5$.

3 . 4 . Oxides and oxyacids

Phosphorus (III) oxide, P_4O_6 (also called tetra phosphorus hex oxide) and phosphorus (IV) oxide, P_4O_{10} (or tetra phosphorus decoxide) are acid anhydrides of phosphorus oxyacids and hence readily react with water. P_4O_{10} is a particularly good dehydrating agent that can even remove water from nitric acid, HNO_3. The structure of P_4O_6 is like that of P_4 with an oxygen atom inserted between each of the P - P bonds. The structure of P_4O_{10} is like that of P_4O_6 with the addition of one oxygen bond to each phosphorus atom via a double bond and protruding away from the tetrahedral structure.

Phosphorous oxyacids can have acidic protons bound to oxygen atoms and nonacidic protons which are bonded directly to the phosphorus atom. Although many oxyacids of phosphorus are formed, only six are important (see table), and three of them, hypophosphorous acid, phosphorous acid and phosphoric acid are particularly important ones.

Oxidation State	Formula	Name	Acidic Protons	Compounds
+ 1	$H_3\ PO_2$	Hypo phosphorous acid	1	acid, salts
+ 3	$H_3\ PO_3$	(ortho) phosphorous acid	2	acid, salts
+ 5	$(H\ PO_3)_n$	Meta phosphoric acids	n	salts (n=3,4)
+ 5	$H_5\ P_3O_{10}$	Tri phosphoric acid	3	salts
+ 5	$H_4\ P_2O_7$	Pyro phosphoric acid	4	acid, salts
+ 5	$H_3\ PO_4$	(ortho) phosphoric acid	3	acid, salts

4 . History and discovery :

The name *Phosphorus* in Ancient Greece was the name for the planet Venus and is derived from the Greek words (φως = light, φορέω = carry) which roughly translates as light - bringer or light carrier . (In Greek mythology, Hesperus (evening star) and Eosphorus (dawnbearer) are close homologues, and also associated with Phosphorus – the – planet) .

The first recorded production of elemental phosphorus was in 1674 or 1675 by the German alchemist Hennig Brand through a preparation of urine, which contains considerable quantities of dissolved phosphates from normal metabolism. Working in Hamburg, Brand attempted to create the fabled Philosopher's stone through the distillation of some salts by evaporating urine, and in the process produced a white material that glowed in the dark and burned brilliantly. His process originally involved letting urine stand for days until it gave off a terrible smell. Then he boiled it down to a paste, heated this paste to a high temperature, and led the vapours through water where he hoped they would condense to gold. Instead, he obtained a white, waxy substance that glowed in the dark. Brand had discovered phosphorus, the first element discovered since antiquity. We now know that Brand produced ammonium sodium hydrogen phosphate, (NH_4) $NaHPO_4$. While the quantities were essentially correct (it took about 1,100 L of urine to make about 60 g of phosphorus), it was unnecessary to allow the urine to rot. Later scientists would discover that fresh urine yielded the same amount of phosphorus.

Since that time, *phosphors* and *phosphorescence* were used loosely to describe substances that shine in the dark without burning. However, as mentioned above, even though the term phosphorescence was originally coined as a term by analogy with the glow from oxidation of elemental phosphorus, is now reserved for another fundamentally different process—re-emission of light after illumination.

Phosphorus was gradually recognized as a chemical element in its own right at the emergence of the atomic theory that gradually occurred in the late part of the 18th century and the early 19th century (see John Dalton for more history).

Brand at first tried to keep the method secret, but later sold the recipe for 200 thaler to D Krafft from Dresden,[4] who could now make it as well, and toured much of Europe with it, including England, where he met with Robert Boyle. The secret that it was made from urine leaked out and first Johann Kunckel (1630-1703) in Sweden (1678) and later Boyle in London (1680) also managed to make phosphorus. Boyle states that Krafft gave him no information as to the preparation of phosphorus other than that it was derived from "somewhat that belonged to the body of man". This gave Boyle a valuable clue, however, so that he, too, managed to make phosphorus and published the method of its manufacture. Later he improved Brand's process by using sand in the reaction (still using urine as base material),

$$4\ NaPO_3 + 2\ SiO_2 + 10\ C \rightarrow 2\ Na_2SiO_3 + 10\ CO + P_4$$

Robert Boyle was the first to use phosphorus to ignite sulfur-tipped wooden splints, forerunners of our modern matches, in 1680.

In 1769 Johan Gottlieb Gahn and Carl Wilhelm Scheele showed that calcium phosphate $Ca_3\ (PO_4)_2$ is found in bones and they obtained phosphorus from bone ash. Antoine Lavoisier recognized phosphorus as an element in 1777. Bone ash was the major source of phosphorus until the 1840s. Phosphate rock, a mineral containing calcium phosphate, was first used in 1850 and following the introduction of the electric arc furnace in 1890 this became the only source of phosphorus. Phosphorus, phosphates and phosphoric acid are still obtained from phosphate rock. Phosphate rock is a major feedstock in the fertilizer industry.

Early matches used white phosphorus in their composition, which was dangerous due to its toxicity. Murders, suicides and accidental poisonings resulted from its use. (An apocryphal tale tells of a woman attempting to murder her husband with white phosphorus in his food, which was detected by the stew giving off luminous steam) . In addition, exposure to the vapours gave match workers a necrosis of the bones of the jaw, the infamous "phossy jaw." When a safe process for manufacturing red phosphorus was discovered, with its far lower flammability and toxicity, laws were enacted, under the Berne Convention (1906), requiring its adoption as a safer alternative for match manufacture.

4 . 1 . Spelling and etymology

According to the Oxford English Dictionary the correct spelling of the element is **phosphorus**. The word **phosphorous** is the adjectival form of the P $^{3+}$ valence: so, just as sulfur forms sulfur**ous** and sulfur**ic** compounds, phosphor**us** forms phosphor**ous** compounds and P $^{5+}$ valency phosphor**ic** compounds .

5 . Occurrence

Due to its reactivity with air and many other oxygen- containing substances, phosphorus is not found free in nature but it is widely distributed in many different minerals.

Phosphate rock, which is partially made of apatite (an impure tri-calcium phosphate mineral) , is an important commercial source of this element. About 50 percent of the global phosphorus reserves are in the Arab nations.[23] Large deposits of apatite are located in China, Russia, Morocco, Florida, Idaho, Tennessee, Utah, and elsewhere. Albright and Wilson in the United Kingdom and their Niagara Falls plant, for instance, were using phosphate rock in the 1890s and 1900s from Connetable, Tennessee and Florida; by 1950 they were using phosphate rock mainly from Tennessee and North Africa.[13] In the early 1990s Albright and Wilson's purified wet phosphoric acid business was being adversely affected by phosphate rock sales by China and the entry of their long - standing Moroccan phosphate suppliers into the purified wet phosphoric acid business .

In 2007, at the current rate of consumption, the supply of phosphorus was estimated to run out in 345 years . However, scientists are now claiming that a " Peak Phosphorus " will occur in 30 years and that "At current rates, reserves will be depleted in the next 50 to 100 years ."

6 . Production

White phosphorus was first made commercially, for the match industry in the 19th century, by distilling off phosphorus vapour from precipitated phosphates, mixed with ground coal or charcoal, which was heated in an iron pot, in retort. The precipitated phosphates were made from ground - up bones that had been de - greased and treated with strong acids. Carbon monoxide and other flammable gases produced during the reduction process were burnt off in a flare stack.

This process became obsolete in the late 1890s when the electric arc furnace was adapted to reduce phosphate rock . Calcium phosphate (phosphate rock) , mostly mined in Florida and North Africa, can be heated to 1,200 - 1,500 °C with sand , which is mostly SiO_2, and coke (impure carbon) to produce vaporized tetraphosphorus, P_4, (mp. 44.2 C) which is subsequently condensed into a white powder under water to prevent oxidation. Even under water, white phosphorus is slowly converted to the more stable red phosphorus allotrope (mp. 597 C) . Both the white and red allotropes of phosphorus are insoluble in water.

The electric furnace method allowed production to increase to the point where phosphorus could be used in weapons of war.[7][13] In World War I it was used in incendiaries, smoke screens and tracer bullets . A special incendiary bullet was developed to shoot at hydrogen-filled Zeppelins over Britain (hydrogen being highly inflammable if it can be ignited) . During World War II, Molotov cocktails of benzene and phosphorus were distributed in Britain to specially selected civilians within the British resistance operation, for defence; and phosphorus incendiary bombs were used in war on a large scale. Burning phosphorus is difficult to extinguish and if it splashes onto human skin it has horrific effects .

Today phosphorus production is larger than ever. It is used as a precursor for various chemicals , in particular the herbicide glyphosate sold under the brand name Roundup. Production of white phosphorus takes place at large facilities and it is transported heated in liquid form. Some major accidents have occurred during transportation, train derailments at Brownston, Nebraska and Miamisburg, Ohio led to large fires. The worst accident in recent times was an environmental one in 1968 when phosphorus spilled into the sea from a plant at Placentia Bay, Newfoundland.[31]

7 . Applications

Widely used compounds	Use
$Ca\ (H_2PO_4)_2 \bullet H_2O$	Baking powder & fertilizers
$CaHPO_4 \bullet 2H_2O$	Animal food additive, toothpowder
H_3PO_4	Manufacture of phosphate fertilizers
PCl_3	Manufacture of $POCl_3$ and pesticides
$POCl_3$	Manufacturing plasticizer
P_4S_{10}	Manufacturing of additives and pesticides
$Na_5P_3O_{10}$	Detergents

Phosphorus, being an essential plant nutrient, finds its major use as a constituent of fertilizers for agriculture and farm production in the form of concentrated phosphoric acids, which can consist of 70 % to 75 % P_2O_5. Global demand for fertilizers led to large increase in phosphate (PO_4^{3-}) production in the second half of the 20th century. Due to the essential nature of phosphorus to living organisms, the low solubility of natural phosphorus-containing compounds, and the slow natural cycle of phosphorus, the agricultural industry is heavily reliant on fertilizers which contain phosphate, mostly in the form of superphosphate of lime. Superphosphate of lime is a mixture of two phosphate salts, calcium dihydrogen phosphate $Ca(H_2PO_4)_2$ and calcium sulfate dihydrate $CaSO_4 \bullet 2H_2O$ produced by the reaction of sulfuric acid and water with calcium phosphate .

- Phosphorus is widely used to make organophosphorus compounds, through the intermediates phosphorus chlorides and two phosphorus sulfides: phosphorus pentasulfide, and phosphorus sesquisulfide . Organophosphorus compounds have many applications , including in plasticizers, flame retardants, pesticides, extraction agents, and water treatment.

- Phosphorus is also an important component in steel production, in the making of phosphor bronze, and in many other related products.
- Phosphates are utilized in the making of special glasses that are used for sodium lamps.
- Bone - ash, calcium phosphate, is used in the production of fine china.
- Sodium tripolyphosphate made from phosphoric acid is used in laundry detergents in some countries, but banned for this use in others.
- Phosphoric acid made from elemental phosphorus is used in food applications such as some soda beverages. The acid is also a starting point to make food grade phosphates . These include mono-calcium phosphate which is employed in baking powder and sodium tripolyphosphate and other sodium phosphates[13]. Among other uses these are used to improve the characteristics of processed meat and cheese. Others are used in toothpaste.[13] Trisodium phosphate is used in cleaning agents to soften water and for preventing pipe / boiler tube corrosion.
- White phosphorus, called " WP " (slang term " Willie Peter ") is used in military applications as incendiary bombs, for smoke-screening as smoke pots and smoke bombs, and in tracer ammunition. It is also a part of M34 White Phosphorus hand grenade. This grenade will cause severe burns, poisonings, and/or set fire to flammable material.
- Red phosphorus is essential for manufacturing matchbook strikers, flares, safety matches, pharmaceutical grade and street methamphetamine, and is used in cap gun caps.
- Phosphorus sesquisulfide is used in heads of strike-anywhere matches.
- In trace amounts, phosphorus is used as a dopant for N-type semiconductors.
- ^{32}P and ^{33}P are used as radioactive tracers in biochemical laboratories .

8 . Biological role

Phosphorus is a key element in all known forms of life. Inorganic phosphorus in the form of the phosphate PO_4^{3-} plays a major role in biological molecules such as DNA and RNA where it forms part of the structural framework of these molecules. Living cells also use phosphate to transport cellular energy via adenosine triphosphate (ATP). Nearly every cellular process that uses energy obtains it in the form of ATP. ATP is also important for phosphorylation, a key regulatory event in cells. Phospholipids are the main structural components of all cellular membranes. Calcium phosphate salts assist in stiffening bones .

Every cell has a membrane that separates it from its surrounding environment. Biological membranes are made from a phospholipid matrix and proteins, typically in the form of a bilayer. Phospholipids are derived from glycerol, such that two of the glycerol hydroxyl (OH) protons have been replaced with fatty acids as an ester, and the third hydroxyl proton has been replaced with phosphate bonded to another alcohol. [12]

An average adult human contains a little less than 1 kg of phosphorus, about 85 % of which is present in bones and teeth in the form of apatite, and the remainder inside cells in soft tissues. A well - fed adult in the industrialized world consumes and excretes about 1 - 3 g of phosphorus per day, with consumption in the form of inorganic phosphate and phosphorus-containing biomolecules such as nucleic acids and phospholipids; and excretion almost exclusively in the form of urine phosphate ion. Only about 0.1 % of body phosphate circulates in the blood, but this amount reflects the amount of phosphate available to soft tissue cells.

In medicine, low phosphate syndromes are caused by malnutrition, by failure to absorb phosphate, and by metabolic syndromes which draw phosphate from the blood (such as re-feeding after malnutrition) or pass too much of it into the urine. All are characterized by hypophosphatemia . which is a condition of low levels of soluble phosphate levels in the blood serum, and therefore inside cells. Symptoms of hypo phosphatemia include muscle and neurological dysfunction, and disruption of muscle and blood cells due to lack of ATP. Too much phosphate can lead to diarrhea and calcification (hardening) of organs and soft tissue, and can interfere with the body's ability to use iron, calcium, magnesium, and zinc .

Phosphorus is an essential macromineral for plants, which is studied extensively in edaphology in order to understand plant uptake from soil systems. In ecological terms, phosphorus is often a limiting factor in many environments; i.e. the availability of phosphorus governs the rate of growth of many organisms. In ecosystems an excess of phosphorus can be problematic, especially in aquatic systems, see eutrophication and algal blooms.

9 . Precautions

Organic compounds of phosphorus form a wide class of materials, some of which are extremely toxic. Fluorophosphate esters are among the most potent neurotoxins known. A wide range of organophosphorus compounds are used for their toxicity to certain organisms as pesticides (herbicides, insecticides, fungicides, etc.) and weaponised as nerve agents. Most inorganic phosphates are relatively nontoxic and essential nutrients. For environmentally adverse effects of phosphates see eutrophication and algal blooms . The white phosphorus allotrope should be kept under water at all times as it presents a significant fire hazard due to its extreme reactivity with atmospheric oxygen, and it should only be manipulated with forceps since contact with skin can cause severe burns. Chronic white phosphorus poisoning leads to necrosis of the jaw called "phossy jaw". Ingestion of white phosphorus may cause a medical condition known as "Smoking Stool Syndrome".

When the white form is exposed to sunlight or when it is heated in its own vapour to 250 °C, it is transmuted to the red form, which does not chemoluminesce in air. The red allotrope does not spontaneously ignite in air and is not as dangerous as the white form. Nevertheless, it should be handled with care because it reverts to white phosphorus in some temperature ranges and it also emits highly toxic fumes that consist of phosphorus oxides when it is heated . Upon exposure to elemental phosphorus, in the past it was suggested to wash the affected area with 2 % copper sulfate solution to form harmless compounds that can be washed away. According to the recent *US Navy's Treatment of Chemical Agent Casualties and Conventional Military Chemical Injuries: FM8-285: Part 2 Conventional Military Chemical Injuries*, "Cupric (copper (II) sulfate has been used by U.S. personnel in the past and is still being used by some nations. However, copper sulfate is toxic and its use will be discontinued. Copper sulfate may produce kidney and cerebral toxicity as well as intravascular hemolysis."

The manual suggests instead "a bicarbonate solution to neutralize phosphoric acid, which will then allow removal of visible white phosphorus. Particles often can be located by their emission of smoke when air strikes them, or by their phosphorescence in the dark. In dark surroundings, fragments are seen as luminescent spots." Then, "Promptly debride the burn if the patient's condition will permit removal of bits of WP which might be absorbed later and possibly produce systemic poisoning. DO NOT apply oily

66 - based ointments until it is certain that all WP has been removed. Following complete removal of the particles, treat the lesions as thermal burns ". As white phosphorus readily mixes with oils, any oily substances or ointments are not recommended until the area is thoroughly cleaned and all white phosphorus removed.

9 . 1 . US DEA List I status

Phosphorus can reduce elemental iodine to hydroiodic acid, which is a reagent effective for reducing ephedrine or pseudoephedrine to methamphetamine . For this reason, two allotropes of elemental phosphorus — red phosphorus and white phosphorus—were designated by the United States Drug Enforcement Administration as List I precursor chemicals under 21 CFR 1310.02 effective on November 17, 2001 . As a result, in the United States, handlers of red phosphorus or white phosphorus are subject to stringent regulatory controls pursuant to the Controlled Substances Act in order to reduce diversion of these substances for use in clandestine production of controlled substances .

White phosphorus

Contents

1 . Introduction :

White phosphorus (WP) is a flare - and smoke - producing agent and an incendiary agent that is made from a common allotrope of the chemical element phosphorus. The main utility of white phosphorus munitions is to create smokescreens to mask movement from the enemy, or to mask his fire. In contrast to other smoke - causing munitions, WP burns quickly causing an instant bank of smoke. As a result of this, WP munitions are very common -- particularly as smoke grenades for infantry; loaded in defensive grenade dischargers on tanks and other armored vehicles; or as part of the ammunition allotment for artillery or mortars.

However, white phosphorus has a secondary effect . While much less efficient than ordinary fragmentation effects in causing casualties, white phosphorus burns quite fiercely and can set cloth, fuel, ammunition and other combustibles on fire. It also can function as an anti - personnel weapon with the compound capable of causing serious burns or death. The agent is used in bombs, artillery, and mortars, short-range missiles which burst into burning flakes of phosphorus upon impact. White phosphorus is commonly referred to in military jargon as "WP". The slang term "Willy (ie) Pete" or "Willy(ie) Peter", dating from World War I and common at least through the Vietnam War, is still used by infantry and artillery servicemen to refer to white phosphorus.

White phosphorus weapons are controversial today because of their potential use against civilians. While the Chemical Weapons Convention does not designate WP as a chemical weapon, various groups consider it to be one. In recent years, the United States, Israel, Sri Lanka and Russia have used white phosphorus in combat.

The United States' use of white phosphorus in Iraq in the Iraq War has resulted in considerable controversy among critics of the war. Initial field reports referred to white phosphorus use against insurgents, but its use was officially denied until November 2005 , when the Department of Defense admitted[5] to the use of white phosphorus while stating that its use for producing obscuring smoke is legal and does not violate the CWC . A DoD spokesman has also admitted that WP "was used as an incendiary weapon against enemy combatants", though not against civilians.[7]

2 . History

WP is believed to have been first used by Fenian arsonists in the 19th century in the form of a solution of WP in carbon disulfide. When the carbon disulfide evaporated, the WP would burst into flames, and probably also ignite the highly flammable carbon disulfide fumes. This mixture was known as "Fenian fire" and allegedly was used by disgruntled itinerant workers in Australia to cause delayed destruction of shabby sleeping quarters.

In 1916, during an intense ideological struggle over conscription for the First World War, twelve members of the I.W.W., a radical union of workers who openly opposed conscription, were arrested and convicted for using or plotting to use incendiary materials, including phosphorus. It is believed that eight or nine men in this group, known as the Sydney Twelve, had been framed by the police. Most were released in 1920 after an inquiry.

2 . 1 . World War I and II

The British Army introduced the first factory - built WP grenades in late 1916. In World War II, white phosphorus mortar bombs, shells, rockets and grenades were used extensively by American, Commonwealth, and to a lesser extent Japanese forces, in both smoke - generating and antipersonnel roles. In 1940, when the invasion of Britain seemed imminent, the phosphorus firm of Albright and Wilson suggested that the British government use a material similar to Fenian fire in several expedient incendiary weapons. The only one fielded was the *Grenade, No. 76* or *Special Incendiary Phosphorus grenade*, which consisted of a glass bottle filled with a mixture similar to Fenian fire, plus some latex (*c.f.* Molotov cocktail, Greek fire). It came in two versions, one with a red cap intended to be thrown by hand, and a slightly stronger bottle with a green cap, intended to be launched from the North over projector (a crude 2.5 inch blackpowder grenade launcher). It must be noted that these were improvised anti-tank weapons, hastily fielded in 1940 when the British were awaiting a German invasion after losing the bulk of their modern armaments in France in May 1940. Instructions on each crate of SIP grenades included the observations, *inter alia* :

> Store bombs (preferably in cases) in cool places, under water if possible.
>
> Stringent precautions must be taken to avoid cracking bombs during handling.

It was generally regarded as overly dangerous to its own operators. They were never deployed in combat.

At the start of the Normandy campaign, 20 % of American 81 mm mortar rounds were WP. At least five American Medal of Honor citations mention their recipients using white phosphorus grenades to clear enemy positions. In the 1944 liberation of Cherbourg alone, a single U.S. mortar battalion, the 87th, fired 11,899 white phosphorus rounds into the city.

The U.S. Army and Marines used WP shells in 107 - mm [4.2 Inch] mortars. WP was widely credited by Allied soldiers for breaking up German infantry attacks and creating havoc among enemy troop concentrations during the latter part of the war. American servicemen in the Pacific and otherwise (to this day) were known to call the thrown bottles "Willie Pete" grenades. The origin of the term has been thought to be derived from the British military's phonetic alphabet.

Incendiary bombs were used extensively by the German, British and US air forces against civilian populations and targets of military significance in civilian areas (London, Hamburg, Dresden, Area bombing etc). Late in the war, some of these bombs used white phosphorus (about 1 - 200 grams) in place of magnesium as the igniter for their flammable mixtures. The use of incendiary weapons against civilians was banned (by signatory countries) in the 1980 Convention on Certain Conventional Weapons Protocol III. The USA signed Protocols I and II on March 24, 1995 (and the amended article II on May 24 , 1999) and later Protocols III, IV, and V, on January 21, 2009.

3 . Others

WP munitions were used extensively in Korea, Vietnam and later by Russian forces in Chechnya. According to GlobalSecurity.org, during the December 1994 battle for Grozny in Chechnya, every fourth or fifth Russian artillery or mortar round fired was a smoke or white phosphorus round. [9]

In Iraq, the Saddam Hussein regime used white phosphorus, as well as chemical weapons that are scheduled in the Chemical Weapons Convention, in the Halabja poison gas attack during the Iran – Iraq War in 1988, according to the ANSA news agency .

Another news report said "US intelligence" called WP a chemical weapon in a declassified Pentagon report from February 1991:

> " Iraqi forces loyal to President Saddam may have possibly used white phosphorus chemical weapons against Kurdish rebels and the populace in Erbil and Dohuk. The WP chemical was delivered by artillery rounds and helicopter gunships."

3 . 1 . Use in Iraq (2004)

Use of WP against enemy areas in Fallujah were reported as early as April 2004:

> The boom kicked dust around the pit as they ran through the drill again and again, sending a mixture of burning white phosphorus and high explosives they call "shake 'n' bake" into a cluster of buildings where insurgents have been spotted all week . However, an U.S. official release of December 2004 denied any WP use :
>
> *U.S. forces have used [phosphorus shells] very sparingly in Fallujah, for illumination purposes. They were fired into the air to illuminate enemy positions at night, not at enemy fighters* .

This U.S. Department of State website carried an addendum in November 2005, replacing the previous statement with the comment:

> We have learned that some of the information we were provided [in the above paragraph] is incorrect. White phosphorus shells, which produce smoke, were used in Fallujah not for illumination but for screening purposes, i.e., obscuring troop movements and, according to an article in *Field Artillery* magazine , "as a potent psychological weapon against the insurgents in trench lines and spider holes…." The article states that U.S. forces used white phosphorus rounds to flush out enemy fighters so that they could then be killed with high explosive rounds.

The specific aspect of use against humans was highlighted[16] after the documentary film *Fallujah, The Hidden Massacre* by Sigfrido Ranucci was aired on Italy's RaiNews24 and released on the internet.[10] In the film, Giuliana Sgrena quotes city refugees testimonies from Fallujah about the reported danger of weapons effects:

> In particular, some women had tried to enter their homes, and they had found a certain dust spread all over the house. The Americans themselves had told them to clean the houses with detergents, because that dust was very dangerous. In fact, they had some effect on their bodies, leading to some very strange things."

The film also shows U.S. soldiers on film admitting to WP use against insurgents. U.S. officials continued to deny the use of white phosphorus for antipersonnel purposes; U.S. ambassador to UK Robert Holmes Tuttle stated in November 2005, that U.S. forces "do not use napalm or white phosphorus as weapons".[17]

How ever, within a week of ambassador Tuttle's statement, on November 15, Pentagon spokesman Lieutenant-Colonel Barry Venable confirmed to the BBC that WP had been used as an antipersonnel weapon, and was quoted as stating: "It has been used as an incendiary weapon against enemy combatants". In particular,

> Venable pointed out that WP was effective against enemy forces in covered positions that were protected from high explosives. "One technique is to fire a white phosphorus round into the position because the combined effects of the fire and smoke—and in some case the terror brought about by the explosion on the ground—will drive them out of the holes so that you can kill them with high explosives.

WP use is legal for purposes such as illumination and obscuring smoke, and the Chemical Weapons Convention does not list WP in its schedules of chemical weapons.

The March 2005 edition of the U.S. Army magazine *Field Artillery*, contained an article on using white phosphorus as an "effective munition" for flushing out insurgents during the Fallujah attack of November 2004:

> "WP proved to be an effective and versatile munition. We used it for screening missions at two breeches and, later in the fight, as a potent psychological weapon against the insurgents in trench lines and spider holes when we could not get effects on them with HE (High Explosive) Rounds. We fired ‘shake and bake’ missions at the insurgents, using WP to flush them out and HE to take them out ."

On November 30, 2005, General Peter Pace defended use of WP, declaring that WP munitions were a " legitimate tool of the military ", used to illuminate targets and create smokescreens, and that there were better weapons for killing people:

> It is well within the law of war to use those weapons as they're being used, for marking and for screening... A bullet goes through skin even faster than white phosphorus does " .

On June 22, 2007 *New York Times* correspondent Michael R. Gordon was interviewed on National Public Radio in a story called "Baquba Residents Displaced by Insurgents" by Melissa Block and Michele Norris. In this interview, Gordon was asked about civilian casualties in Baquba, Iraq. He responded by saying "Yeah, there have been civilian casualties. I was just talking to our photographer and he had seen people who are hurt by phosphorus shells." The photographer was not identified in the interview and the report was not corroborated.

3 . 2 . 2006 Israel - Lebanon conflict

During the 2006 Israel -Lebanon conflict , Israel stated that it had used phosphorus shells "against military targets in open ground" in south Lebanon. Israel stated that its use of the white phosphorus bombs was permitted under international conventions. President of Lebanon Émile Lahoud claimed that phosphorus shells were used against civilians in Lebanon . The first Lebanese official complaint about the use of phosphorus came from Information Minister Ghazi Aridi .

3 . 3 . Gaza War

Human rights groups say that Israel used white phosphorus munition during the 2009 conflict in Gaza .

Several reports indicate that white phosphorus shells were used by Israel in the 2008 – 2009 Israel–Gaza conflict. Human Rights Watch claims shells exploded over populated civilian areas, including a crowded refugee camp and a United Nations school where civilians were seeking refuge . Additionally, Human Rights Watch has claimed that White phosphorus injuries are suspected in the cases of ten burn victims.

Human Rights Watch said its experts in the region had witnessed the use of white phosphorus. Kenneth Roth, the organization's executive director, added: "This is a chemical compound that burns structures and burns people. It should not be used in populated areas."

Amnesty International said a fact-finding team found "indisputable evidence of the widespread use of white phosphorus" in crowded residential areas of Gaza City and elsewhere in the territory. Donatella Rovera, the head of an Amnesty fact-finding mission to southern Israel and Gaza, said: "Israeli forces used white phosphorus and other weapons supplied by the USA to carry out serious violations of international humanitarian law, including war crimes."[32]

On January 14, the news paper Haaretz reported that Hamas had fired a White Phosphorus mortar shell which exploded in an open area in the Eshkol area in the western Negev of southern Israel. No injuries or damage were reported.

On 15 January, the United Nations compound, housing numerous refugees in Gaza City, was reportedly struck by Israeli White phosphorus artillery shells, setting fire to pallets of relief materials and igniting several large fuel storage tanks. A UN spokesperson indicated that there were difficulties in attempting to extinguish the fires and stated "You can’t put it [White phosphorus] out with traditional methods such as fire extinguishers. You need sand but we do not have any sand in the compound." Senior Israeli defense officials maintain that the shelling was in response to Israeli military personnel being fired upon by Hamas fighters who were in proximity to the UN headquarters. The Israeli army is investigating improper use of WP in this conflict, particularly in one incident in which 20 WP shells were fired in a built - up area of Beit Lahiya.

On 17 January, Peter Herby, head of the International Committee of the Red Cross Arms Unit , confirmed the use of white phosphorous weapons by Israel in Gaza, outlined the rules applicable to phosphorous weapons and explained the ICRC's approach to the issue.

On January 20, Paul Wood of the BBC reports from Gaza on what appears to be white phosphorus use near the vicinity of civilian areas. Amnesty team weapon expert Christopher Cobb-Smith, who witnessed the shelling during the conflict, reported "we saw streets and alleyways littered with evidence of the use of white phosphorus, including still - burning wedges and the remnants of the shells and canisters fired by the Israeli army."

On January 26, the Israel's Ministry of Defence confirmed speculations about the use of white phosphorous in the Israeli-Gaza conflict .

On March 25, 2009, USA Based Human Rights Organization Human Rights Watch published a 71 page report titled Rain of Fire, *Israel's Unlawful Use of White Phosphorus in Gaza* and claimed the Israel's usage of the weapon was illegal.

This 71-page report provides witness accounts of the devastating effects that white phosphorus munitions had on civilians and civilian property in Gaza. Human Rights Watch researchers in Gaza immediately after hostilities ended found spent shells, canister liners, and dozens of burnt felt wedges containing white phosphorus on city streets, apartment roofs, residential courtyards, and at a United Nations school. The report also presents ballistics evidence, photographs, and satellite imagery, as well as documents from the Israeli military and government.

3 . 4 . Use in Afghanistan (2009)

There are confirmed cases of white phosphorous burns on bodies of civilians wounded in Afganistan US - Taliban clashes near Bagram. U.S. accuses Taliban of use of these weapons in 38 cases.[42] However, no independent report confirmed use of phosphorous by Taliban. The only forces known to use such weapons before is U.S . - NATO coalition .

4 . Smoke - screening properties

Weight – for - weight, phosphorus is the most effective smoke-screening agent known, for two reasons: first, it absorbs most of the screening mass from the surrounding atmosphere and secondly, the smoke particles are an aerosol, a mist of liquid droplets which are close to the ideal range of sizes for Mie scattering of visible light. This effect has been likened to three dimensional textured privacy glass—the smoke cloud does not simply obstruct an image, but thoroughly scrambles both visual and infrared radiation, interfering with infra - red optics and weapon-tracking systems, serving as a protection for military forces from guided weapons such as anti-tank missiles.

When phosphorus burns in air, it first forms phosphorus pent oxide (which exists as tetra phosphorus decoxide except at very high temperatures) :

$$P_4 + 5\ O_2 \rightarrow 2P_2O_5$$

However phosphorus pentoxide is extremely hygroscopic and quickly absorbs even minute traces of moisture to form liquid droplets of phosphoric acid :

$$P_4O_{10} + 6\ H_2O \rightarrow 4\ H_3PO_4$$

(also forms poly phosphoric acids such as pyro phosphoric acid , $H_4P_2O_7$)

Since an atom of phosphorus has an atomic mass of 31 but a molecule of phosphoric acid has a molecular mass of 98, the cloud is already 68 % by mass derived from the atmosphere (i.e. 3.2 kilograms of smoke for every kilogram of WP you started with); however, it may absorb more because phosphoric acid and its variants are hygroscopic. Given time, the droplets will continue to absorb more water, growing larger and more dilute until they reach equilibrium with the local water vapour pressure. In practice, the droplets quickly reach a range of sizes suitable for scattering visible light and then start to dissipate from wind or convection.

Because of the great weight efficiency of WP smoke, it is particularly suited for applications where weight is highly restricted, such as hand grenades and mortar bombs. An additional advantage for hand smoke grenades — which are more likely to be used in an emergency — is that the WP smoke clouds form in a fraction of a second. Because WP is also pyrophoric , most munitions of this type have a simple burster charge to split open the casing and spray fragments of WP through the air, where they ignite spontaneously and leave a trail of rapidly thickening smoke behind each particle. The appearance of this cloud forming is easily recognized ; one sees a shower of burning particles spraying outward, followed closely by distinctive streamers of white smoke, which rapidly coalesce into a fluffy, very pure white cloud (unless illuminated by a coloured light source) .

Various disadvantages of WP are discussed below, but one which is particular to smoke-screening is "pillaring". Because the WP smoke is formed from fairly hot combustion, the gasses in the cloud are hot, and tend to rise. Consequently the smoke screen tends to rise off the ground relatively quickly and form aerial "pillars" of smoke which are of little use for screening. Tactically this may be counteracted by using WP to get a screen quickly, but then following up with emission type screening agents for a more persistent screen. Some countries have begun using red phosphorus instead. Red phosphorus ("RP") burns cooler than WP and eliminates a few other disadvantages as well, but offers exactly the same weight efficiency. Other approaches include WP soaked felt pads (which also burn more slowly, and pose a reduced risk of incendiarism) and PWP, or plasticised white phosphorus.

5 . Effects on humans

White phosphorus can cause injuries and death in three ways: by burning deep into tissue, by being inhaled as a smoke, and by being ingested. Extensive exposure by burning and ingestion is fatal.

5 . 1 . By burning

Injuries from white phosphorus .

Incandescent particles of WP cast off by a WP weapon's initial explosion can produce extensive, deep second and third degree burns. One reason why this occurs is the tendency of the element to stick to the skin. Phosphorus burns carry a greater risk of mortality than other forms of burns due to the absorption of phosphorus into the body through the burned area, resulting in liver, heart and kidney damage, and in some cases multiple organ failure . These weapons are particularly dangerous to exposed people because white phosphorus continues to burn unless deprived of oxygen or until it is completely consumed. In some cases, burns are limited to areas of exposed skin because the smaller WP particles do not burn completely through personal clothing before being consumed.

5 . 2 . By inhalation of smoke

Burning WP produces a hot, dense, white smoke consisting mostly of phosphorus pent oxide. Most forms of the smoke are not hazardous in the likely concentrations produced by a battlefield smoke shell. Exposure to heavy smoke concentrations of any kind for an extended period (particularly if near the source of emission) does have the potential to cause illness or even death.

WP smoke irritates the eyes, mucous membranes of the nose, and respiratory tract in moderate concentrations, while higher concentrations may produce severe burns. However, no casualties have been recorded from the effects of WP smoke alone in combat operations and there are no confirmed deaths resulting from exposure to phosphorus smoke.

The Agency for Toxic Substances and Disease Registry has set an acute inhalation Minimum Risk Level (MRL) for white phosphorus smoke of 0.02 mg / m³, the same as fuel oil fumes. By contrast, the chemical weapon mustard gas is 30 times more potent: 0.0007 mg / m³ .

5 . 3 . By oral ingestion

The accepted lethal dose when white phosphorus is ingested orally is 1 mg per kg of body weight, although the ingestion of as little as 15 mg has resulted in death. It may also cause liver, heart or kidney damage. There are reports of individuals with a history of oral ingestion who have passed phosphorus - laden stool ("smoking stool syndrome")

6 . Arms control status and military regulations

Article 1 of Protocol III of the Convention on Certain Conventional Weapons defines an incendiary weapon as 'any weapon or munitions which is primarily designed to set fire to objects or to cause burn injury to persons through the action of flame, heat, or combination thereof, produced by a chemical reaction of a substance delivered on the target'. The same protocol also prohibits the use of incendiary weapons against civilians (already forbidden by the Geneva Conventions) or in civilian areas.

However, the use against military targets outside civilian areas is not explicitly banned by any treaty. There is a debate on whether white phosphorus should be considered a chemical weapon and thus be outlawed by the Chemical Weapons Convention (CWC) which went into effect in April 1997. The convention is meant to prohibit weapons that are "dependent on the use of the toxic properties of chemicals as a method of warfare " (Article II, Definitions, 9) .

The convention defines a "toxic chemical" as a chemical "which through its chemical action on life processes can cause death, temporary incapacitation or permanent harm to humans or animals" (CWC, II) . An annex lists chemicals that fall under this definition and WP is not listed in the Schedules of chemical weapons or precursors.

In an 2005 interview with RAI, Peter Kaiser, spokesman for the Organisation for the Prohibition of Chemical Weapons (an organization overseeing the CWC and reporting directly to the UN General Assembly), questioned whether the weapon should fall under the convention's provisions:

> No it's not forbidden by the CWC if it is used within the context of a military application which does not require or does not intend to use the toxic properties of white phosphorus. White phosphorus is normally used to produce smoke, to camouflage movement.
>
> If that is the purpose for which the white phosphorus is used, then that is considered under the convention legitimate use.
>
> If on the other hand the toxic properties of white phosphorus are specifically intended to be used as a weapon, that of course is prohibited, because the way the convention is structured or the way it is in fact applied, any chemicals used against humans or animals that cause harm or death through the toxic properties of the chemical are considered chemical weapons".

Kaiser was a staff spokesman for the Organization for the Prohibition of Chemical Weapons . The OPCW, using member votes, creates Schedules of chemical weapons or dual-use chemicals of concern and white phosphorus is not in any of these schedules.

The Convention on Certain Conventional Weapons, not the Chemical Weapons Convention, goes on, in its Protocol III, to prohibit the use of all air - delivered incendiary weapons against civilian populations, or for indiscriminate incendiary attacks against military forces co - located with civilians . However, that protocol also specifically excludes weapons whose incendiary effects are secondary, such as smoke grenades. This has often been read as excluding white phosphorus munitions from this protocol, as well. Several countries, including the United States and Israel, are not signatories to Protocol III .

The legal position however, is not the only consideration in any war. For instance, concerning the U.S. use of WP in Iraq , the British Liberal Democrat foreign affairs spokesman Sir Menzies Campbell, said :

> "The use of this weapon may technically have been legal, but its effects are such that it will hand a propaganda victory to the insurgency. The denial of use followed by the admission will simply convince the doubters that there was something to hide".

6 . 1 . Military regulations

Within the US Army, there appears to be conflicting advice on the use of WP against humans. According to the field manual on the Rule of Land Warfare, "The use of weapons which employ fire, such as tracer ammunition, flamethrowers, napalm and other incendiary agents, against targets requiring their use is not violative of international law." However, the *ST 100-3 Battle Book*, a student text published by the US Command and General Staff College at Fort Leavenworth states that "It is against the law of land warfare to employ WP against personnel targets."[57] At the same time, other field manuals discuss the use of white phosphorus against personnel.

Though white phosphorus is still used in modern armed conflict, it is regulated by international humanitarian law, or the law of war.

Phosphorus acids

Phosphorus acids are oxo acids of phosphorus. There are a large number of these and some cannot be isolated and are only known through their salts. Examples include :

- H_3PO_2 ; Hypo phosphorous acid, $H_2PO(OH)$, monobasic acid , contains P in oxidation state +1
- H_3PO_3 ; Phosphorous acid , HPO $(OH)_2$, dibasic acid, contains P in oxidation state + 3
- H_3PO_4 ; Phosphoric acid , PO $(OH)_3$, tribasic acid, contains P in oxidation state +5
- H_3PO_5 ; Peroxomono phosphoric acid , $OP(OH)_2$ OOH , tri basic acid, contains P in oxidation state +5
- $H_4P_2O_6$; Hypo phosphoric acid , $(OH)_2P(O)-P(O)(OH)_2$, tetra basic acid, contains P in formal oxidation state +4
- $H_4P_2O_7$; pyro phosphoric acid, $(OH)_2(O)P-O-P(O)(OH)_2$, tetra basic acid , contains P in formal oxidation state +5

In addition there are a range of poly phosphoric acids such as

- $H_5P_3O_{10}$; Tri phosphoric acid

as well as acids with mixed oxidation states e.g.

- $H_4P_2O_6$; H (OH) (O) P - O - P (O) $(OH)_2$, containing P in oxidation state +3 and +5

Hypo Phosphorous Acid

Contents

1 . Introduction :

Hypo phosphorous acid is a phosphorus oxo acid and a powerful reducing agent with molecular formula H_3PO_2. Inorganic chemists refer to the free acid by this name (also as " HPA ") although its IUPAC name is dihydridohydroxidooxidophosphorus, or the acceptable name of **phosphinic acid**. It is a colorless low-melting compound, which is soluble in water , dioxane, and alcohols. The formula for hypo phosphorous acid is generally written H_3 PO_2, but a more descriptive presentation is HOP (O) H_2 which highlights its monoprotic character. Salts derived from this acid are called **phosphinates** (hypo phosphites) .

HOP (O) H_2 exists in equilibrium with the minor tautomer HP (OH) $_2$. Some times the minor tautomer is called hypo phosphorous acid and the major tautomer is called phosphinic acid.

Molecular Formula	H_3PO_2
Molar Mass	66 g / mol
Appearance	Colorless, deliquescent crystals or oily liquid
Density	1.493 g / cm^3
Melting Point	26.5 ° C , 300 K , 80 ° F
Boiling Point	130 ° C decomp.
Solubility in Water	Miscible
Solubility	Very soluble in alcohol , ether
Flash Point	Non - flammable

2 . Preparation and availability

The acid is prepared industrially via a two step process. Hypophosphite salts of the alkali and alkaline earth metals result from treatment of white phosphorus with hot aqueous solution of the appropriate hydroxide, e.g. Ca $(OH)_2$.

$$P_4 + 3OH^- + 3H_2O \rightarrow 3H_2PO_2^- + PH_3$$

The free acid may be prepared by the action of a strong acid on these hypophosphite salts.

$$H_2PO_2^- + H^+ \rightarrow H_3PO_2$$

Alternatively, H_3PO_2 arises by the oxidation of phosphine with iodine in water.

$$PH_3 + 2I_2 + 2H_2O \rightarrow H_3PO_2 + 4I^- + 4H^+$$

HPA is usually supplied as a 50% aqueous solution.

3 . Uses

Hypo phosphorous acid is used in the formulation of pharmaceuticals, discoloration of polymers, water treatment, retrieval of precious or non - ferrous metals. Its main use is for electro less plating; i.e. deposition of select metal films from solution on a sensitized surface. In organic chemistry, H_3PO_2 best known for their use in the reduction of arenediazonium salts, converting Ar N_2^+ to Ar – H . When diazotized in a concentrated solution of hypo phosphorous acid, an amine substituent can be removed from arenes , selectively over alkyl amines.

3 . 1 . DEA List I chemical status

Because hypo phosphorous acid can reduce elemental iodine to form hydro iodic acid, which is a reagent effective for reducing ephedrine or pseudoephedrine to methamphetamine , the United States Drug Enforcement Administration designated hypo phosphorous acid (and its salts) as a List I precursor chemical effective November 16, 2001 . Accordingly, handlers of hypo phosphorous acid or its salts in the United States are subject to stringent regulatory controls including registration, recordkeeping, reporting, and import/export requirements pursuant to the .

4 . Inorganic and organic derivatives

Numerous derivatives are known in which the two hydrogen atoms directly bound to phosphorus are replaced by organic groups. These derivatives are known as **phosphinic acids**, and their salts as **phosphinates** . For example, formaldehyde and H_3PO_2 react to give ($HOCH_2$)$_2$ PO_2H . The reaction is akin to the addition of thiols and HCN to aldehydes. Similarly, it adds to Michael acceptors, for example with acryl amide it gives $H(HO)P(O)CH_2CH_2C(O)NH_2$.

Few metal complexes have been prepared from H_3PO_2, one example is $Ni(O_2PH_2)_2$.

Phosphorous acid

Contents

1 . Introduction :

Phosphorous acid is the compound described by the formula H_3PO_3. It can be formulated as HP (O) $(OH)_2$ and therefore contains phosphorus in oxidation state +3. It is one of the oxo acids of phosphorus, other important members being phosphoric acid (H_3PO_4) and hypo phosphorous acid (H_3PO_2). Note that only the reduced phosphorus compounds are spelled with an "ous" ending. Other names for this acid are ortho phosphorous acid and di hydroxy phosphine oxide.

HP (O) $(OH)_2$ is the product of the hydrolysis of its acid anhydride, P_4O_6 :

$$P_4O_6 + 6\ H_2O \rightarrow 4\ HP(O)(OH)_2$$

Other Names	Phosphonic Acid
Molecular formula	H_3PO_3
Molar mass	82 g / mol
Appearance	white solid deliquescent
Density	1.651 g / cm^3 (21 ° C)
Melting Point	73.6 ° C

Boiling Point	200 ° C (decomp)
Solubility in Water	310 g / 100 mL
Solubility	Soluble in alcohol

2 . Tautomerization

H_3PO_3 is better described with the structural formula HP (O) $(OH)_2$. This species exists in equilibrium with a minor tautomer P $(OH)_3$. (IUPAC recommendations, 2005, are that the latter is called phosphorous acid , whereas the di hydroxy form is called phosphonic acid.) The P $(OH)_3$ tautomer has recently , (2004) , been stabilized as a ligand bonded to molybdenum . Many of the reduced phosphorus acids are subject to similarly complicated equilibria involving shifts of H between O and P.

3 . Structure

In the solid state, $HP(O)(OH)_2$ is tetrahedral with one shorter P = O bond of 148 pm and two longer P - O (H) bonds of 154 pm .

4 . Preparation

Although commercially available, the acid is most commonly prepared by hydrolysis of phosphorus trichloride with water or steam:

$$PCl_3 + 3\ H_2O \rightarrow HP\ (O)\ (OH)_2 + 3\ HCl$$

Potassium phosphite is a convenient precursor to phosphorous acid :

$$K_2HPO_3 + 2\ H\ Cl \rightarrow 2\ K\ Cl + H_3PO_3$$

In practice aqueous potassium phosphite is treated with excess hydrochloric acid. By concentrating the solution and precipitations with alcohols, the pure acid can be separated from the salt.

5 . Acid - base properties

Phosphorous acid is a di protic acid, since the hydrogen bonded directly to the central phosphorus atom is not readily ionizable. Chemistry examinations often test students' appreciation of the fact that all three hydrogen atoms are *not* acidic under aqueous conditions, in contrast with phosphoric acid. $HP(O)_2(OH)^-$ is a moderately strong acid.

$$HP(O)(OH)_2 \rightarrow HP(O)_2(OH)^- + H^+ \quad pK_a = 1.3^{[4]}$$
$$HP(O)_2(OH)^- \rightarrow HPO_3^{2-} + H^+ \quad pK_a = 6.7$$

The $HP(O)_2(OH)^-$ species is called the hydrogen phosphite ion, and the HPO_3^{2-} the phosphite ion . (Note that the IUPAC recommendations are di hydrogen phosphite and hydrogen phosphite respectively)

The IUPAC (mostly organic) name is **phosphonic acid**. This nomenclature is commonly reserved for substituted derivatives, that is, organic group bonded to phosphorus, not simply an ester. For example, $(CH_3)PO(OH)_2$ is "methyl phosphonic acid", which may of course form "methyl phosphonate" esters.

Both phosphorous acid and its deprotonated forms are good reducing agents, although not necessarily quick to react. They are oxidized to phosphoric acid or its salts. It reduces solutions of noble metal cations to the metals.

6 . Uses

6 . 1 . Conversion to phosphine

Phosphine PH_3 , being a flammable and toxic gas, is inconvenient to store. Fortunately this useful species is readily prepared by thermal decomposition of phosphorous acid, at 205 - 210 °C :

$$4\ HP(O)(OH)_2 \rightarrow PH_3 + 3\ H_3PO_4$$

6 . 2 . In Agriculture

A large quantity of phosphorous acid is used as phosphatic fertilizer. Pure phosphorous acid is also used for preparing phosphite salts, such as mono potassium phosphite or aluminum phosphonite . These salts, as well as aqueous solutions of pure phosphorous acid, have shown effectiveness in controlling a variety of microbial plant diseases—in particular, treatment using either trunk injection or foliar containing phosphorous acid salts is indicated in response to infections by *phytophthora* and *pythium* - type plant pathogens (both within class *oomycetes*, known as water molds), such as dieback/root rot and downy mildew. Anti - microbial products containing salts of phosphorous acid are marketed in Australia as 'Yates Anti - Rot' and in the United States of America, for example, aluminum salts of phosphorous acid (known generically as 'Fosetyl -Al') are sold under the trade name 'Aliette'. Phosphorus acid and its salts, unlike phosphoric acid, are highly toxic and should be handled carefully. Only about 1 g of phosphorus acid are lethal to an adult human .

6 . 3 As a Chemical Reagent

Phosphorous acid is used in chemical reactions as a reducing agent that is somewhat less vigorous than the related hypo phosphorous acid .

Phosphoric acid

Contents

1 . Introduction :

Phosphoric acid, also known as **ortho phosphoric acid** or **phosphoric (V) acid**, is a mineral (inorganic) acid having the chemical formula H_3PO_4. Ortho phosphoric acid molecules can combine with themselves to form a variety of compounds which are also referred to as **phosphoric acids**, but in a more general way. The term *phosphoric acid* can also refer to a chemical or reagent consisting of ortho phosphoric acid .

Other Names	Ortho Phosphoric Acid
Molecular Formula	H_3PO_4
Molar Mass	98 g / mol
Appearance	White solid or colourless, viscous liquid (> 42 ° C)
Density	1.685 g / ml (liquid)

Melting Point	42.35 °C (anhydrous) 29.32 (hemihydrate)
Boiling Point	158 °C (decomp)
Solubility in Water	548 g / 100 mL
Acidity (pK_a)	2.12 , 7.21 , 12.67
Viscosity	2.4 – 9.4 cP (85 % aq. soln.)
EU Classification	Corrosive (**C**)

2 . Ortho phosphoric acid chemistry

Pure anhydrous phosphoric acid is a white solid that melts at 42.35 ° C to form a colorless, viscous liquid.

Most people and even chemists refer to ortho phosphoric acid as *phosphoric acid*, which is the IUPAC name for this compound. The prefix *ortho* is used to distinguish the acid from other phosphoric acids, called poly phosphoric acids. Ortho phosphoric acid is a non - toxic, inorganic, rather weak tri protic acid, which, when pure, is a solid at room temperature and pressure. The chemical structure of orthophosphoric acid is shown above in the data table. Orthophosphoric acid is a very polar molecule; therefore it is highly soluble in water. The oxidation state of phosphorus (P) in ortho- and other phosphoric acids is +5; the oxidation state of all the oxygen atoms (O) is -2 and all the hydrogen atoms (H) is +1. Tri protic means that an orthophosphoric acid molecule can dissociate up to three times, giving up an H^+ each time, which typically combines with a water molecule, H_2O, as shown in these reactions:

$$H_3PO_{4\,(s)} + H_2O_{\,(l)} \quad H_3O^+{}_{(aq)} + H_2PO_4^-{}_{(aq)} \qquad K_{a1} = 7.5 \times 10^{-3}$$

$$H_2PO_4^-{}_{(aq)} + H_2O_{\,(l)} \quad H_3O^+{}_{(aq)} + HPO_4^{2-}{}_{(aq)} \qquad K_{a2} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}{}_{(aq)} + H_2O_{\,(l)} \quad H_3O^+{}_{(aq)} + PO_4^{3-}{}_{(aq)} \qquad K_{a3} = 2.14 \times 10^{-13}$$

The anion after the first dissociation, $H_2PO_4^-$, is the *di hydrogen phosphate* anion. The anion after the second dissociation, HPO_4^{2-}, is the *hydrogen phosphate* anion. The anion after the third dissociation,

PO_4^{3-}, is the **phosphate** or **orthophosphate** anion. For each of the dissociation reactions shown above, there is a separate acid dissociation constant, called K_{a1}, K_{a2}, and K_{a3} given at 25°C. Associated with these three dissociation constants are corresponding $pK_{a1} = 2.12$, $pK_{a2} = 7.21$, and $pK_{a3} = 12.67$ values at 25° C. Even though all three hydrogen (H) atoms are equivalent on an orthophosphoric acid molecule, the successive K_a values differ since it is energetically less favorable to lose another H^+ if one (or more) has already been lost and the molecule/ion is more negatively - charged.

Because the triprotic dissociation of ortho phosphoric acid, the fact that its conjugate bases (the phosphates mentioned above) cover a wide pH range, and, because phosphoric acid / phosphate solutions are, in general, non-toxic, mixtures of these types of phosphates are often used as buffering agents or to make buffer solutions, where the desired pH depends on the proportions of the phosphates in the mixtures. Similarly, the non-toxic, anion salts of tri protic organic citric acid are also often used to make buffers. Phosphates are found pervasively in biology, especially in the compounds derived from phosphorylated sugars, such as DNA, RNA, and adenosine tri phosphate (ATP). There is a separate article on phosphate as an anion or its salts.

Upon heating ortho phosphoric acid, condensation of the phosphoric units can be induced by driving off the water formed from condensation. When one molecule of water has been removed for each two molecules of phosphoric acid, the result is pyro phosphoric acid ($H_4P_2O_7$) . When an average of one molecule of water per phosphoric unit has been driven off, the resulting substance is a glassy solid having an empirical formula of $\mathbf{HPO_3}$ and is called **meta phosphoric acid** . Meta phosphoric acid is a singly anhydrous version of orthophosphoic acid and is sometimes used as a water - or moisture - absorbing reagent. Further dehydrating is very difficult, and can be accomplished only by means of an extremely strong desiccant (and not by heating alone). It produces *phosphoric anhydride,* which has an empirical formula P_2O_5, although an actual molecule has a chemical formula of P_4O_{10}. Phosphoric anhydride is a solid, which is very strongly moisture-absorbing and is used as a desiccant.

2 . 1 . pH and composition of a phosphoric acid aqueous solution :

For a given total acid concentration [A] = $[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$ ([A] is the total number of moles of pure H_3PO_4 which have been used to prepare 1 liter of solution) , the composition of an aqueous solution of phosphoric acid can be calculated using the equilibrium equations associated with the three reactions described above together with the $[H^+]\,[OH^-] = 10^{-14}$ relation and the electrical neutrality equation. Possible concentrations of polyphosphoric molecules and ions is neglected. The system may be reduced to a fifth degree equation for $[H^+]$ which can be solved numerically, yielding :

[A] (mol/L)	pH	$[H_3PO_4]/[A]$ (%)	$[H_2PO_4^-]/[A]$ (%)	$[HPO_4^{2-}]/[A]$ (%)	$[PO_4^{3-}]$ / [A] (%)
1	1.08	91.7	8.29	6.20×10^{-6}	1.60×10^{-17}
10^{-1}	1.62	76.1	23.9	6.20×10^{-5}	5.55×10^{-16}
10^{-2}	2.25	43.1	56.9	6.20×10^{-4}	2.33×10^{-14}
10^{-3}	3.05	10.6	89.3	6.20×10^{-3}	1.48×10^{-12}
10^{-4}	4.01	1.30	98.6	6.19×10^{-2}	1.34×10^{-10}
10^{-5}	5.00	0.133	99.3	0.612	1.30×10^{-8}
10^{-6}	5.97	1.34×10^{-2}	94.5	5.50	1.11×10^{-6}
10^{-7}	6.74	1.80×10^{-3}	74.5	25.5	3.02×10^{-5}
10^{-10}	7.00	8.24×10^{-4}	61.7	38.3	8.18×10^{-5}

For large acid concentrations, the solution is mainly composed of H_3PO_4. For [A] = 10^{-2} , the pH is closed to pK_{a1}, giving an equimolar mixture of H_3PO_4 and $H_2PO_4^-$. For [A] below 10^{-3}, the solution is mainly composed of $H_2PO_4^-$ with $[HPO_4^{2-}]$ becoming non negligible for very dilute solutions. $[PO_4^{3-}]$ is always negligible.

3 . Chemical reagent

Pure 75 – 85 % aqueous solutions (the most common) are clear, colour less , odour less , non-volatile, rather viscous, syrupy liquids, but still pourable. Phosphoric acid is very commonly used as an aqueous solution of 85 % phosphoric acid or H_3PO_4. Because it is a concentrated acid, an 85 % solution can be corrosive, although nontoxic when diluted. Because of the high percentage of phosphoric acid in this reagent, at least some of the orthophosphoric acid is condensed into poly phosphoric acids in a temperature-dependent equilibrium, but, for the sake of labeling and simplicity, the 85 % represents $H_3\ PO_4$ as if it were all ortho phosphoric acid. Other percentages are possible too, even above 100 %, where the phosphoric acids and water would be in an unspecified equilibrium, but the overall elemental mole content would be considered specified. When aqueous solutions of phosphoric acid and / or phosphate are dilute, they are in or will reach an equilibrium after a while where practically all the phosphoric/phosphate units are in the ortho - form.

3 . 1 . Preparation of hydrogen halides

Phosphoric acid reacts with halides to form the corresponding hydrogen halide gas (steamy fumes are observed on warming the reaction mixture). This is a common practice for the laboratory preparation of hydrogen halides :

$$NaCl\ (s) + H_3PO_4\ (l) \rightarrow NaH_2PO_4\ (s) + HCl\ (g)$$
$$NaBr\ (s) + H_3PO_4\ (l) \rightarrow NaH_2PO_4\ (s) + HBr\ (g)$$
$$NaI\ (s) + H_3PO_4\ (l) \rightarrow NaH_2PO_4\ (s) + HI\ (g)$$

3 . 2 . Rust removal

Phosphoric acid may be used by direct application to rusted iron, steel tools, or surfaces to convert iron (III) oxide (rust) to a water-soluble phosphate compound. It is usually available as a greenish liquid, suitable for dipping (acid bath) , but is more generally used as a component in a gel, commonly called **naval jelly**. It is sometimes sold under other names, such as "rust remover" or "rust killer." As a thick gel, it may be applied to sloping, vertical, or even overhead surfaces.

After treatment, the reddish-brown iron oxide will be converted to a black iron phosphate compound coating that may be scrubbed off. Multiple applications of phosphoric acid may be required to remove all rust. The resultant black compound can provide further corrosion resistance (such protection is some what provided by the superficially similar Parkerizing and blued electrochemical conversion coating processes) .

Following application and removal of rust using phosphoric acid compounds, the metal should be oiled (if to be used bare, as in a tool) or appropriately painted, by using a multiple coat process of primer, intermediate, and finish coats.

Care must be taken to avoid acid burns of the skin and especially the eyes, but the residue is easily diluted with water. When sufficiently diluted, it can even be nutritious to plant life, containing the essential nutrients phosphorus and iron. It should not be directly introduced into surface water such as creeks or into drains, however.

3 . 3 . Processed food use

Food - grade phosphoric acid (often labeled as E number **E338**) is used to acidify foods and beverages such as various colas, but not without controversy regarding its health effects. It provides a tangy or sour taste and, being a mass - produced chemical, is available cheaply and in large quantities. The low cost and bulk availability is unlike more expensive natural seasonings that give comparable flavors, such as citric acid which is obtainable from lemons and limes. (However most citric acid in the food industry is not extracted from citrus fruit, but fermented by *Aspergillus niger* mold from scrap molasses, waste starch hydrolysates and phosphoric acid) .

3 . 3 . 1 . Biological effects on bone calcium and kidney health :

Phosphoric acid, used in many soft drinks (primarily cola) , has been linked to lower bone density in epidemiological studies. For example, a study using dual-energy X - ray absorptiometry rather than a questionnaire about breakage , provides reasonable evidence to support the theory that drinking cola results in lower bone density. This study was published in the American Journal of Clinical Nutrition. A total of 1672 women and 1148 men were studied between 1996 and 2001. Dietary information was collected using a food frequency questionnaire that had specific questions about the number of servings of cola and other carbonated beverages and that also made a differentiation between regular, caffeine-free, and diet drinks. The paper cites significant statistical evidence to show that women who consume cola daily have lower bone density. Total phosphorus intake was not significantly higher in daily cola consumers than in non consumers ; however, the calcium-to-phosphorus ratios were lower. The study also suggests that further research is needed to confirm the findings.

On the other hand, a study funded by Pepsi suggests that low intake of phosphorus leads to lower bone density. The study does not examine the effect of phosphoric acid, which binds with magnesium and calcium in the digestive tract to form salts that are not absorbed but rather studies general phosphorus intake .

However, a well-controlled clinical study by Heaney and Rafferty using calcium-balance methods found no impact of carbonated soft drinks containing phosphoric acid on calcium excretion.[4] The study compared the impact of water, milk, and various soft drinks (two with caffeine and two without; two with phosphoric acid and two with citric acid) on the calcium balance of 20 - to 40 – year - old women who customarily consumed ~ 3 or more cups (680 ml) of a carbonated soft drink per day. They found that, relative to water, only milk and the two caffeine-containing soft drinks increased urinary calcium, and that the calcium loss associated with the caffeinated soft drink consumption was about equal to that previously found for caffeine alone. Phosphoric acid without caffeine had no impact on urine calcium, nor did it augment the urinary calcium loss related to caffeine. Because studies have shown that the effect of caffeine is compensated for by reduced calcium losses later in the day , Heaney and Rafferty concluded that the net effect of carbonated beverages – including those with caffeine and phosphoric acid - is negligible, and that the skeletal effects of carbonated soft drink consumption are likely due primarily to milk displacement.

Other chemicals such as caffeine (also a significant component of popular common cola drinks) were also suspected as possible contributors to low bone density, due to the known effect of caffeine on calciuria. One other study, involving 30 women over the course of a week, suggests that phosphoric acid in colas has no such effect, and postulates that caffeine has only a temporary effect, which is later reversed. The authors of this study conclude that the skeletal effects of carbonated beverage consumption are likely due primarily to milk displacement . (Another possible confounding factor may be an association between high soft drink consumption and sedentary lifestyle) .

Cola consumption has also been linked to chronic kidney disease and kidney stones through medical research. This study differentiated between the effects of cola (generally contains phosphoric acid), non - cola carbonated beverages (substitute citric acid) and coffee (control for caffeine), and found that drinking 2 or more colas per day more than doubled the incidence of kidney disease.

3 . 4 . Medical use

Phosphoric acid is used in dentistry and orthodontics as an etching solution, to clean and roughen the surfaces of teeth where dental appliances or fillings will be placed. Phosphoric acid is also an ingredient in over – the -counter anti-nausea medications that also contain high levels of sugar (glucose and fructose). It should not be used by diabetics without consultation with a doctor. This acid is also used in many teeth whiteners to eliminate plaque that may be on the teeth before application.

4 . Preparation

Phosphoric acid can be prepared by three routes - the Thermal Process, the Wet Process and the dry Kiln Process.

4 . 1 . Thermal phosphoric acid

This very pure phosphoric acid is obtained by burning elemental phosphorus to produce phosphorus pentoxide and dissolving the product in dilute phosphoric acid. This produces a very pure phosphoric acid, since most impurities present in the rock have been removed when extracting phosphorus from the rock in a furnace. The end result is food - grade, thermal phosphoric acid; however, for critical applications, additional processing to remove arsenic compounds may be needed.

4 . 2 . Wet phosphoric acid

Wet process phosphoric acid is prepared by adding sulfuric acid to tri calcium phosphate rock .The simplified reaction is :

$$3\ H_2SO_4 + Ca_3(PO_4)_2 + 6\ H_2O \leftrightarrow 2\ H_3PO_4 + 3\ CaSO_4.2H_2O$$

Wet - process acid can be purified by removing fluorine to produce animal - grade phosphoric acid, or by solvent extraction and arsenic removal to produce food - grade phosphoric acid.

4 . 3 . Kiln Phosphoric Acid

Kiln phosphoric acid (KPA) process technology is the most recent technology. Called the “Improved Hard Process”, this technology will both make low grade phosphate rock reserves commercially viable and will increase the P_2O_5 recovery from existing phosphate reserves. This will significantly extend the commercial viability of phosphate reserves.

5 . Other applications

- Phosphoric acid is used as the electrolyte in phosphoric-acid fuel cells. It is also used as an external standard for phosphorus -31 Nuclear magnetic resonance (NMR) .
- Phosphoric acid is used as a cleaner by construction trades to remove mineral deposits, cementitious smears, and hard water stains. It is also used as a chelate in some household cleaners aimed at similar cleaning tasks.

- Hot phosphoric acid is used in micro fabrication to etch silicon nitride (Si_3N_4) . It is highly selective in etching Si_3N_4 instead of SiO_2, silicon dioxide.
- Phosphoric acid is used as a flux by hobbyists (such as model railroaders) as an aid to soldering.
- Phosphoric acid is also used in hydroponics pH solutions to lower the pH of nutrient solutions. While other types of acids can be used, phosphorus is a nutrient used by plants, especially during flowering, making phosphoric acid particularly desirable. General Hydroponics pH Down liquid solution contains phosphoric acid in addition to citric acid and ammonium bisulfate with buffers to maintain a stable pH in the nutrient reservoir.
- Phosphoric acid is used as a pH adjuster in cosmetics and skin - care products .
- Phosphoric acid is used as a chemical oxidizing agent for activated carbon production .
- Phosphoric acid is also used for High Pressure Liquid Chromatography.
- Phosphoric acid can be used as an additive to stabilize acidic aqueous solutions within a wanted and specified pH range
- Phosphoric acid is the key ingredient that gives the bite taste in widely consumed Coke and Pepsi sodas.

Phosphoric acids and phosphates

Contents :

1 . Ortho phosphoric acid

The simplest compound of a series of **phosphoric acids** is sometimes called by its common name, **ortho phosphoric acid**, but more often called by its IUPAC name, simply **phosphoric acid**, by both non - technical people and even many chemists. The chemical formula of ortho phosphoric acid is H_3PO_4 and its chemical structure is shown in the illustration below. There is a separate article on this most important compound in the series under Phosphoric Acid. However, two or more ortho phosphoric acid molecules can be joined by condensation into larger molecules by elimination of water. This way, a series of **poly phosphoric acids** can be obtained.

Ortho phosphoric acid H_3PO_4

Pyro phosphoric acid $H_4P_2O_7$

Tri poly phosphoric acid $H_5P_3O_{10}$

Tetra poly phosphoric acid $H_6P_4O_{13}$

Tri meta phosphoric acid $H_3P_3O_9$

Phosphoric anhydride P_4O_{10}

2 . **Ortho phosphate**

Ortho phosphoric acid has three hydrogen atoms bonded to oxygen atoms in its structure. All three hydrogens are acidic to varying degrees and can be lost from the molecule as H^+ ions (alternatively referred to as protons). When all three H^+ ions are lost from ortho phosphoric acid, an **ortho phosphate** ion (PO_4^{3-}) is formed. Orthophosphate is the simplest in a series of phosphates, and is usually just called **phosphate** by both non-technical people and many chemists alike; see a separate article on phosphate for details.

Because ortho phosphoric acid can undergo as many as three dissociations or ionizations (losses of H^+ ions) , it has three acid dissociation constants called K_{a1}, K_{a2}, and K_{a3}. Another way to provide acid dissociation constant data is to list pK_{a1} , pK_{a2} , and pK_{a3} instead. Orthophosphate is in a sense the triple conjugate base of phosphoric acid and has three related basicity constants, K_{b1} , K_{b2} , and K_{b3} , which likewise have corresponding pK_{b1} , pK_{b2} , and pK_{b3} values.

3 . Poly phosphoric acids

When two ortho phosphoric acid molecules are condensed into one molecule, **pyro phosphoric acid** ($H_4P_2O_7$) is obtained as follows:

$$2\ H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

The chemical structure of pyrophosphoric acid is also shown in the illustration. There is also a separate article on Pyro phosphoric acid. Three ortho phosphoric acid molecules can condense in a row to obtain **tri poly phosphoric acid** $H_5P_3O_{10}$, which is also shown in the illustration. This condensation process can continue with additional orthophosphoric acid units to obtain **tetra poly phosphoric acid** $H_6P_4O_{13}$, and so on. Note that each extra phosphoric unit adds 1 extra H (hydrogen) atom, 1 extra P (phosphorus) atom, and 3 extra O (oxygen) atoms. The " back bone " chain of these types of molecules consists of alternating P and O atoms covalently bonded together. Poly phosphoric acid molecules can have dozens of such phosphoric units bonded in a row. A general formula for such poly-acid compounds is HO (PO_2 OH) $_x$ H, where x = number of phosphoric units in the molecule. The four oxygen atoms bonded to each phosphorus atom are in a tetrahedral configuration with the phosphorus in the center of the tetrahedron and the oxygens in each of the four corners.

4 . Poly phosphates

In a pyro phosphoric acid molecule, there are four hydrogens bonded to oxygens , and one, two, three, or all four can be lost as H^+ ions. When all four are lost from pyro phosphoric acid, a **pyro phosphate** ion is formed. Because pyro phosphoric acids can undergo four dissociations, there are four K_a values for it, as well as four corresponding pK_a values. Similarly, pyrophosphate is a base with four K_b and, of course, four pK_b values for regaining the H^+ ions in reverse order.

The situation with higher order poly phosphoric acids and polyphosphates continues in a similar way. Tri poly phosphoric acid can lose up to five H^+ ions to form a **tri poly phosphate** ion, tetra poly phosphoric acid can lose up to six H^+ ions to form **tetra poly phosphate**, etc. As more dissociations per molecule are possible, the intervals between individual pK_a and pK_b values now start becoming smaller on the pH scale.

As the poly phosphoric molecules grow increasingly larger and more complex, practically any number of the somewhat acidic -OH groups in them can dissociate to become negatively charged oxygens, forming numerous combinations of multiple-charged poly phosphoric / poly phosphate anions. Generally in an aqueous solution, the degree or percentage of dissociation depends on the pH of the solution.

Ortho - , pyro - , and tri poly phosphate compounds have been commonly used in detergents (i. e. Cleaners) formulations. For example, see Sodium tri poly phosphate. Sometimes pyrophosphate, tri poly phosphate , tetra poly phosphate, etc. are called **di phosphate**, **tri phosphate**, **tetra phosphate**, etc. , especially when they are part of phosphate esters in biochemistry.

5 . Cyclo - or Meta phosphoric acids and meta phosphates

The phosphoric acid units can be bonded together in rings (cyclic structures) forming **meta phosphoric acid** molecules. The simplest such compound is **tri meta phosphoric acid** or **cyclo – tri phosphoric acid** having the formula $H_3P_3O_9$. Its structure is shown in the illustration . Since the ends are condensed, its formula has one less H_2O (water) than tri poly phosphoric acid. A general formula for such cyclic compounds is (HPO_3)$_x$ where x = number of phosphoric units in the molecule.

When these meta phosphoric acids lose their hydrogens as H^+, cyclic anions called **meta phosphates** are formed. An example of a compound with such an anion is sodium hexa meta phosphate ($Na_6P_6O_{18}$) used as a sequestrant and a food additive.

6 . Branched polyphosphates

The third - OH group on an ortho phosphoric acid unit can also be used for condensation with other phosphoric groups to form branches in the polyphosphoric/polyphosphate chains. The ultimate example of cyclic and branching condensation would be the cyclic four - phosphate unit double-branched to form the phosphoric anhydride P_4O_{10} ; see illustration.

7 . Hydrolysis of poly phosphoric / poly phosphates

These phosphoric acids series are generally water-soluble considering the polarity of the molecules. Ammonium and alkali phosphates are also quite soluble in water. The alkaline earth salts start becoming less soluble and phosphate salts of various other metals are even less soluble. In aqueous solutions (solutions of water) , water gradually (over the course of hours) hydrolyzes poly phosphates into smaller phosphates and finally into ortho - phosphate, given enough water. Higher temperature or acidic conditions can speed up the hydrolysis reactions considerably .

Conversely, poly phosphoric acids or poly phosphates are often formed by dehydrating a phosphoric acid solution ; in other words, removing water from it often by heating and evaporating the water off.

8 . Phosphate and phosphite esters

General Chemical Structure of an ortho - (or mono -) phosph**a**te ester .
Here any R can be H , or some other organic radical

The - OH groups in phosphoric acids can also condense with the hydroxyl groups of alcohols to form phosphate esters. Since ortho phosphoric acid has three -OH groups, it can esterify with one, two, or three alcohol molecules to form a mono- , di- , or tri ester. See the general structure image of an ortho - (or mono-) phosphate ester below on the left, where any of the **R** groups can be a hydrogen or an organic radical. Pyro- (or di-) phosphate esters and tri poly - (or tri -) phosphate esters, etc. are also possible. Any - OH groups on the phosphates in these ester molecules may lose H^+ ions to form anions, again depending on the pH in a solution. In the biochemistry of living organisms, there are many kinds of (mono) phosphate, di phosphate , and tri phosphate compounds (essentially esters), many of which play a significant role in metabolism such as adenosine di phosphate (ADP) and tri phosphate (ATP).

General Chemical Structure of a Phosph**i**te Ester .
Here any R can be H , or some other organic radical

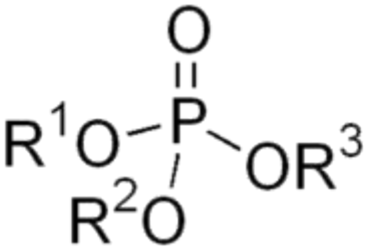
Similarly, phosphorous acid can bond with alcohol molecules to form a phosphite ester. See the general structure image below on the right. The two dots on the P represent the lone electron pair of the phosphorus atom.

Phosphate & Phosphate Rock

1 – Introduction :

A **phosphate**, an inorganic chemical, is a salt of phosphoric acid. Inorganic phosphates are mined to obtain phosphorus for use in agriculture and industry . In organic chemistry, a phosphate, or organophosphate, is an ester of phosphoric acid. Organic phosphates are important in biochemistry and biogeochemistry.

2 - Chemical properties :



The general chemical structure of a phosphate

The phosphate ion is a polyatomic ion with the empirical formula PO_4^{3-} and a molar mass of 94.973 g/mol; it consists of one central phosphorus atom surrounded by four identical oxygen atoms in a tetrahedral arrangement. The phosphate ion carries a negative three formal charge and is the conjugate base of the hydrogen phosphate ion, HPO_4^{2-}, which is the conjugate base of $H_2PO_4^{-}$, the di hydrogen phosphate ion, which in turn is the conjugate base of H_3PO_4, phosphoric acid. It is a hypervalent molecule (the phosphorus atom has 10 electrons in its valence shell). Phosphate is also an organophosphorus compound with the formula $OP(OR)_3$ A phosphate salt forms when a positively - charged ion attaches to the negatively-charged oxygen atoms of the ion, forming an ionic compound. Many phosphates are not soluble in water at standard temperature and pressure. The sodium , potassium , rubidium , cesium and ammonium phosphates are all water soluble. Most other phosphates are only slightly soluble or are insoluble in water. As a rule, the hydrogen phosphates and the di hydrogen phosphates are slightly more soluble than the corresponding phosphates. The pyro phosphates are mostly water soluble.

In dilute aqueous solution, phosphate exists in four forms. In strongly-basic conditions, the phosphate ion (PO_4^{3-}) predominates, whereas in weakly-basic conditions, the hydrogen phosphate ion (HPO_4^{2-}) is prevalent. In weakly-acid conditions, the di hydrogen phosphate ion ($H_2PO_4^-$) is most common. In strongly-acid conditions, aqueous phosphoric acid (H_3PO_4) is the main form.

$$H_3PO_4H_2PO_4^-HPO_4^{2-}PO_4^{3-}$$

More precisely, considering the following three equilibrium reactions :

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

the corresponding constants at 25°C (in mol / L) are :

$$K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \simeq 6.92 \times 10^{-3} \quad (pK_{a1}\ 2.16)$$

$$K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \simeq 6.17 \times 10^{-8} \quad (pK_{a2}\ 7.21)$$

$$K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \simeq 4.79 \times 10^{-13} \quad (pK_{a3}\ 12.32)$$

For a strongly-basic pH (pH=13), we find

$$\frac{[H_2PO_4^-]}{[H_3PO_4]} \simeq 7.5 \times 10^{10} \ , \ \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \simeq 6.2 \times 10^5 \ , \ \frac{[PO_4^{3-}]}{[HPO_4^{2-}]} \simeq 2.14$$

showing that only PO_4^{3-} and HPO_4^{2-} are in significant amounts.

For a neutral pH (for example the cytosol pH =7.0), we find

$$\frac{[H_2PO_4^-]}{[H_3PO_4]} \simeq 7.5 \times 10^4 \ , \ \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \simeq 0.62 \ , \ \frac{[PO_4^{3-}]}{[HPO_4^{2-}]} \simeq 2.14 \times 10^{-6}$$

so that only $H_2PO_4^-$ and HPO_4^{2-} ions are in significant amounts (62 % $H_2PO_4^-$, 38 % HPO_4^{2-}) . Note that in the extracellular fluid (pH = 7.4), this proportion is inverted (61 % HPO_4^{2-}, 39% $H_2PO_4^-$).

For a strongly - acid pH (pH = 1) , we find

$$\frac{[H_2PO_4^-]}{[H_3PO_4]} \simeq 0.075 \ , \ \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \simeq 6.2 \times 10^{-7} \ , \ \frac{[PO_4^{3-}]}{[HPO_4^{2-}]} \simeq 2.14 \times 10^{-12}$$

showing that H_3PO_4 is dominant with respect to $H_2PO_4^-$. HPO_4^{2-} and PO_4^{3-} are practically absent.

Phosphate can form many polymeric ions such as di phosphate (also pyro phosphate) , $P_2O_7^{4-}$, and tri phosphate, $P_3O_{10}^{5-}$. The various meta phosphate ions have an empirical formula of PO_3^- and are found in many compounds.

Phosphate deposits can contain significant amounts of naturally occurring uranium. Uptake of these substances by plants can lead to high uranium concentrations in crops.

3 - Cellular function :

Phosphate is useful in animal cells as a buffering agent. Phosphate salts that are commonly used for preparing buffer solutions at cell pHs include Na_2HPO_4 , NaH_2PO_4 , and the corresponding potassium salts.

4 - Mining of Phosphate rock :

Phosphate rock or **phosphorite** is a general description applied to several kinds of rock which contain significant concentrations of phosphate minerals, which are minerals that contain the phosphate ion in their chemical structure.

Many kinds of rock contain mineral components containing phosphate or other phosphorus compounds in small amounts. However, rocks which contain phosphate in quantity and concentration which are economic to mine as ore for their phosphate content are not particularly common. The two main sources for phosphate are guano, formed from bird droppings, and rocks containing concentrations of the calcium phosphate mineral, apatite.

The United States is the world's leading producer and consumer of phosphate rock, which is used to manufacture phosphate fertilizer and industrial products.

China, the United States and Morocco are the world's largest miners of phosphate rock, each producing about a quarter of the total world production. Other countries with significant production include Brazil, Russia, Jordan and Tunisia. Historically, large amounts of phosphates were obtained from guano deposits on small islands such as Christmas Island, but these sources are now largely depleted.

Phosphate rock is mined, beneficiated, and either solubilized to produce wet - process phosphoric acid, or smelted to produce elemental phosphoric acid or smelted to produce elemental phosphorus. Phosphoric acid is reacted with phosphate rock to produce the fertilizer triple super phosphate or with anhydrous ammonia to produce the ammonium phosphate fertilizers. Elemental phosphorus is the base for furnace-grade phosphoric acid, phosphorus pentasulfide, phosphorus pent oxide, and phosphorus tri chloride. Approximately 90 % of phosphate rock production is used for fertilizer and animal feed supplements and the balance for industrial chemicals.

For general use in the fertilizer industry, phosphate rock or its concentrates preferably have levels of 30 % phosphorus pent oxide (P_2O_5), reasonable amounts of calcium carbonate (5%), and <4% combined iron and aluminium oxides. Worldwide, the resources of high - grade ore are declining, and the beneficiation of lower grade ores by washing, flotation and calcining is becoming more widespread.

5 - See also

- Organo phosphorus compounds
- Phosphate conversion coating
- Phosphine - PR_3

- Phosphine oxide - OPR_3
- Phosphinite - $P(OR)R_2$
- Phosphonite - $P(OR)_2R$
- Phosphite - $P(OR)_3$
- Phosphinate - $OP(OR)R_2$
- Phosphonate - $OP(OR)_2R$
- Phosphate - $OP(OR)_3$, such as tri phenyl phosphate
- Polyphosphate - P_n