

1. Details of Module and its Structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 03 (Class XII, Semester 01)
Module Name/Title	p-block Elements (Group 15 elements): Part 2
Module ID	lech_10702
Pre-requisites	Knowledge about electronic configuration of elements of this block and variation of Atomic size, Ionization Enthalpy, Electron Gain Enthalpy and Electronegativity within the groups in the block, shielding effect, chemical bonding
Objectives	After going through this module, the learners will be able to understand the following: <ol style="list-style-type: none">1. Allotropes of phosphorus,2. Hydride of phosphorus3. Halides of Phosphorus4. Oxoacids of phosphorus.
Keywords	Phosphorus, hydrides, halides, oxides, oxoacids, allotropes, group 15

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1. Introduction

Phosphorus is the second element in group 15 and has a valence electronic configuration of $3s^23p^3$ which is the configuration of stable half filled orbitals. Like nitrogen, phosphorus is a non metal. It has only one stable isotope ^{15}P . Though valence configuration of phosphorus is similar to nitrogen, the presence of vacant 3d orbitals in phosphorus helps it in achieving higher covalency and hence it forms compounds beyond those known for nitrogen. Differences in the properties of nitrogen and phosphorus are in the table 2.1.

Table 2.1 : Differences in nitrogen and phosphorus

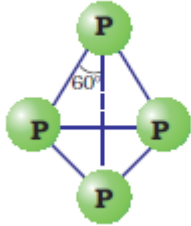
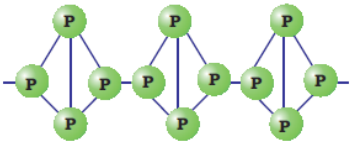
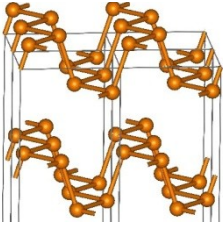
Nitrogen	Phosphorus
Nitrogen has maximum covalency of four	Phosphorus can expand its covalency beyond 4 upto six by utilizing vacant 3d orbitals in its valence shell
Nitrogen can form very stable $p\pi-p\pi$ multiple bonds with small 2p orbitals. It forms stable $\text{N}\equiv\text{N}$, $\text{N}=\text{N}$, $\text{N}=\text{C}$ and $\text{N}=\text{O}$ bonds.	Phosphorus tends to form $d\pi-p\pi$ multiple bonds by overlapping its vacant d orbitals with p orbitals of other atom. It forms stable $\text{P}=\text{O}$ bond
$\text{N}-\text{N}$ single bond is not stable because of lone pair lone pair repulsions between two nitrogen atoms	$\text{P}-\text{P}$ single bond with reduced lone pair lone pair repulsions is more stable than $\text{N}-\text{N}$ single bond.

2. Phosphorus- allotropes and their properties

Phosphorus exists in many allotropic modifications that reflect the variety of ways of achieving coordination, the important ones being white, red and black. The differences in three allotropes are enlisted in table 2.2.

Table 2.2. Allotropes of Phosphorus and their structure and properties

White Phosphorus	Red Phosphorus	Black phosphorus
White phosphorus is obtained	Red phosphorus is obtained by	Black phosphorus (α -form)

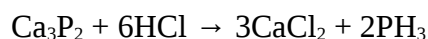
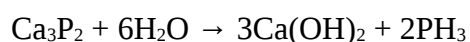
<p>when phosphate rock is heated with coke and sand in an electric furnace at 1773 K</p> $3\text{Ca}_3(\text{PO}_4)_2 + 6 \text{SiO}_2 \rightarrow 6 \text{CaSiO}_3 + \text{P}_4\text{O}_{10}$ $\text{P}_4\text{O}_{10} + 10\text{C} \rightarrow 10\text{CO} + \text{P}_4$	<p>heating white phosphorus in an inert atmosphere at 573K for several days</p>	<p>is formed when red phosphorus (β-form) is heated in a sealed tube at 803 K. Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure.</p>
<p>It consists of discrete tetrahedral P_4 molecule</p>	<p>It is polymeric, consisting of chains of P_4 tetrahedral linked together</p>	<p>Black phosphorus has layered structure in which each phosphorus atom is covalently bonded to three neighbouring phosphorus atom.</p>
<p>White phosphorus is less stable and therefore, most reactive allotrope of phosphorus. P_4 has a tetrahedral structure in which each of the vertices is occupied by phosphorus atoms. The molecule has a high angular strain as all P-P-P bond angles are only 60°.</p> 	<p>In red phosphorus, P_4 tetrahedrons link to each other to form polymeric structure. In this process some of the P-P bond angles in P_4 tetrahedrons cleave, relieving some of the angle strain and imparting stability to the polymer. Red P is less reactive than white phosphorus.</p> 	<p>Here all phosphorus atoms are linked to each other to give a highly polymerised layer like structure. No angle strain is present in the whole layer and the allotrope becomes thermodynamically the most stable form.</p>  <p>Image source: https://en.wikipedia.org/wiki/Phosphorus#/</p>
<p>White phosphorus is a translucent white waxy solid (α-form). It is poisonous, insoluble in water but soluble in carbon disulphide and</p>	<p>It is hard crystalline solid with iron grey lustre. It is non-poisonous in nature. It is insoluble in water as well as organic solvent such as CS_2</p>	<p>It has black metallic lustre</p>

glows in dark (chemiluminescence). It burns in air to produce dense white fumes of phosphorus pentaoxide.		
White phosphorus is stored under water to protect it from the air. It burns in air to produce dense white fumes of phosphorus pentaoxide.	Red phosphorus is quite stable in air.	Black phosphorus is stable in air and can be ignited only with difficulty.

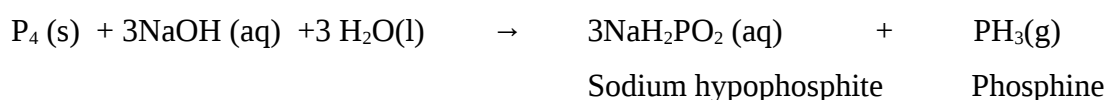
3. Hydride of Phosphorus – Phosphine (PH₃)

3.1. Preparation

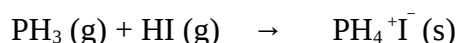
Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.



In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO₂.



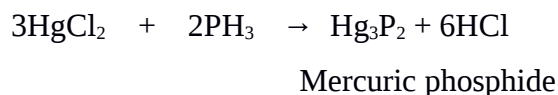
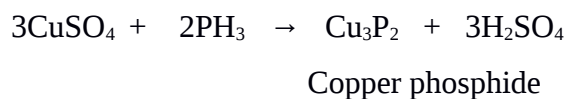
When pure, it is non flammable but becomes inflammable owing to the presence of P₂H₄ or P₄ vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH₄I) which on treating with KOH gives off phosphine.



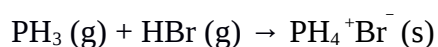
3.2. Properties

It is a colourless gas with rotten fish smell and is highly poisonous. It explodes in contact with traces of oxidising agents like HNO₃, Cl₂ and Br₂ vapours. It is only slightly soluble in water and is not associated like NH₃ because of decreased bond polarity. The solubility of

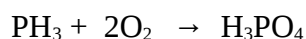
phosphene in organic solvents is high. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2 . When absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides (containing phosphorus in rare -3 oxidation state) are obtained.



Phosphene is very weakly basic though it gives phosphonium compounds with acids e.g.,



The pure gas oxidises in air at 150°C but when contaminated with diphosphine P_2H_4 , it is spontaneously flammable.

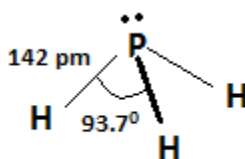


Phosphene is a strong reducing agent and reduces many metal salts to metals.

3.3. Structure

Phosphene (Fig.2.1) has pyramidal geometry with three P-H bond pairs and one lone pair on phosphorus atom. The H-P-H bond angle is 93.7° .

Fig.2.1. Structure of phosphene



3.4. Uses

The spontaneous combustion of phosphine is technically used in *Holme's signals*. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal. It is also used in *smoke screens*.

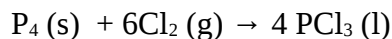
4. Halides of Phosphorus

Phosphorus reacts with halogens to form halides of two different compositions PX_3 and PX_5 . The most important halides are chlorides.

4.1. Phosphorus trichloride

4.1.1. Preparation

It is obtained by passing dry chlorine over heated white phosphorus.



It is also obtained by the action of thionyl chloride with white phosphorus.



Thionyl chloride

4.1.2. Properties

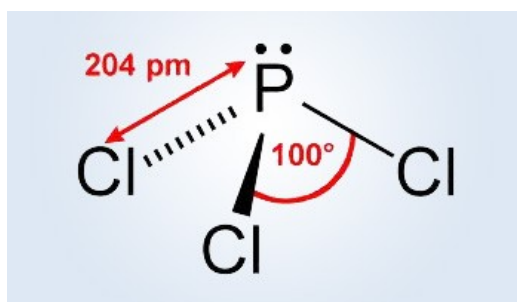
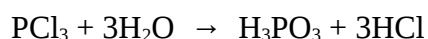


Fig. 2.2. Structure of phosphorus trichloride

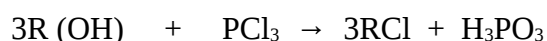
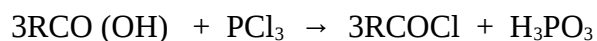
(Image source: https://en.wikipedia.org/wiki/Phosphorus_trichloride#/)

Phosphorus trichloride has a pyramidal shape (Fig.2.2) with sp^3 hybridisation of phosphorus atom. There are three bond pairs (P-Cl bond) and one non bonding electron pair on phosphorus atom. The Cl-P-Cl bond angle is 100° .

It is a colourless oily low boiling liquid (b.pt. 349 K) which undergoes a violent hydrolysis with water to give phosphorus acid.



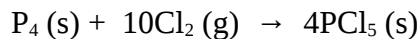
It reacts with organic compounds containing $-\text{OH}$ group and $-\text{COOH}$ group to give chlorinated derivatives.



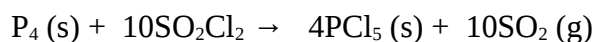
4.2. Phosphorus Pentachloride (PCl_5)

4.2.1. Preparation

Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

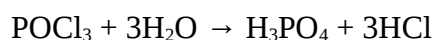
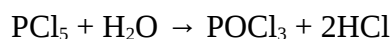


It can also be prepared by the action of SO_2Cl_2 (sulphuryl chloride) on white phosphorus.

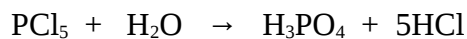


4.2.2. Properties

PCl_5 is moisture sensitive yellowish white powder. In moist air, it hydrolyses to phosphoryl chloride, POCl_3 which finally gets completely hydrolysed to phosphoric acid.



or



(excess)

When heated, it sublimes but decomposes on stronger heating into PCl_3 and Cl_2

Δ



- Like PCl_3 it also reacts with organic compounds containing $-\text{OH}$ and $-\text{COOH}$ group converting them to their chloro derivatives.



Ethanol

Chloroethane

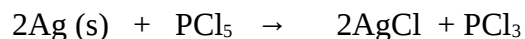


Acetic acid

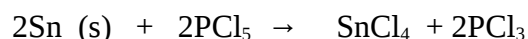
Acetyl chloride

- It oxidises and chlorinates finely divided metals also on heating to give corresponding chlorides.

Δ



Δ



4.2.3. Structure

PCl_5 has a trigonal bipyramidal geometry (Fig.2.3) with sp^3d hybridisation on phosphorus atom. Equatorial P-Cl bonds are shorter than the axial P-Cl bonds. Two different Cl-P-Cl bond angles observed in the molecule are 90° (involving one axial and one equatorial Cl atom) and 120° (involving both equatorial Cl atoms).

PCl_5 is molecular in the gaseous phase, ionic in the crystalline phase, $[\text{PCl}_4]^+[\text{PCl}_6]^-$ and either molecular or ionically dissociated in solution depending on the nature of the solvent. In $[\text{PCl}_4]^+[\text{PCl}_6]^-$, the cation $[\text{PCl}_4]^+$ is tetrahedral and the anion, $[\text{PCl}_6]^-$ is octahedral.

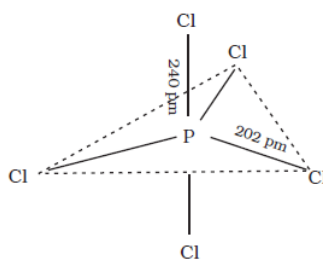
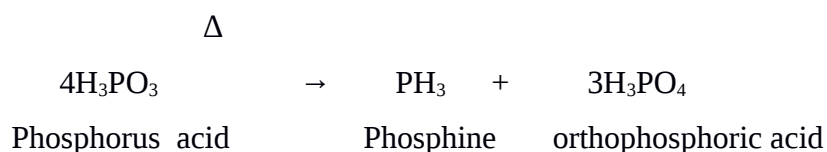


Fig.2.3. Phosphorus pentachloride

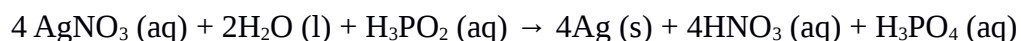
5. Oxoacids of Phosphorus

All the oxoacids of phosphorus contain at least one P=O bond and at least one P-OH bond. Some oxoacids of phosphorus also contain P-P bond or P-H bond but not both in the same acid. They are generally present in oxoacids which contain P in oxidation state less than +5.

The oxoacids in +3 oxidation state undergo disproportionation reaction on heating



The acids containing P-H bond have strong reducing properties. Thus, hypophosphorous acid, H_3PO_2 , is a good reducing agent as it contains two P-H bonds and reduces AgNO_3 to metallic silver.



H_3PO_3 also acts as a reducing agent though weaker than H_3PO_2 because it contains only one P-H bond as compared to two in H_3PO_2 .

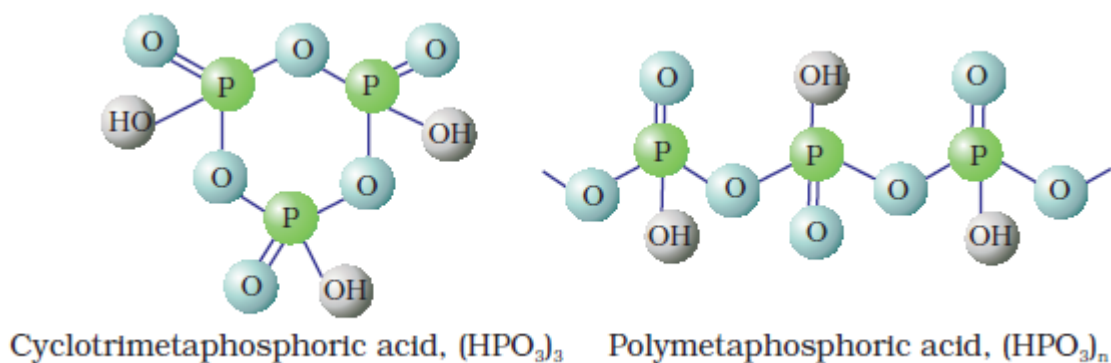
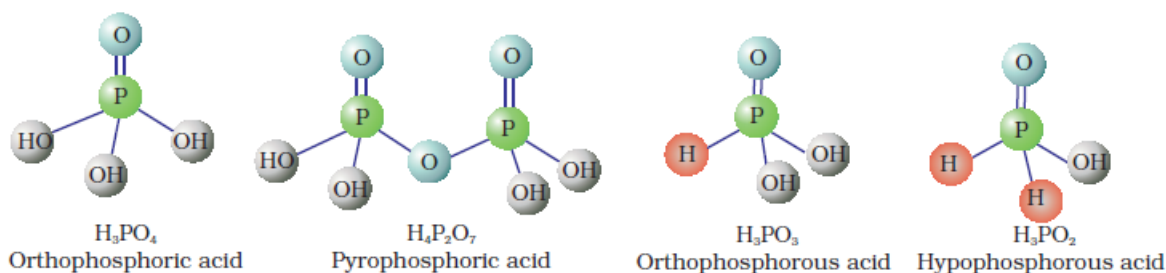
The P-H bonds do not contain acidic hydrogen and hence do not release hydrogen as H^+ ion. Reducing property is observed for these acids by loss of hydrogen as [H] atom. Only those H atoms which are attached with oxygen in P-OH group are ionisable and makes the compound

acidic. Thus, H_3PO_3 and H_3PO_4 are dibasic and tribasic, respectively as the structure of H_3PO_3 has two P–OH bonds and H_3PO_4 three P–OH bonds. Structure of oxoacids are shown in Fig.2.4. and their oxidation states are given in table 2.3.

Phosphorus as phosphate esters play an important role in life processes. These phosphate containing biomolecules are DNA, RNA, and cyclic AMP. The energy giving reactions in bioprocesses involve a transfer of phosphate groups between ADP and ATP.

Table 2.3: Oxoacids of phosphorus with their oxidation state

Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous (Phosphinic)	H_3PO_2	+1	One P – OH Two P – H One P = O	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+3	Two P – OH One P – H One P = O	$\text{P}_2\text{O}_3 + \text{H}_2\text{O}$
Pyrophosphorous	$\text{H}_4\text{P}_2\text{O}_5$	+3	Two P – OH Two P – H Two P = O	$\text{PCl}_3 + \text{H}_3\text{PO}_3$
Hypophosphoric	$\text{H}_4\text{P}_2\text{O}_6$	+4	Four P – OH Two P = O One P – P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three P – OH One P = O	$\text{P}_4\text{O}_{10} + \text{H}_2\text{O}$
Pyrophosphoric	$\text{H}_4\text{P}_2\text{O}_7$	+5	Four P – OH Two P = O One P – O – P	heat phosphoric acid
Metaphosphoric*	$(\text{HPO}_3)_n$	+5	Three P – OH Three P = O Three P – O – P	phosphorus acid + Br_2 , heat in a sealed tube



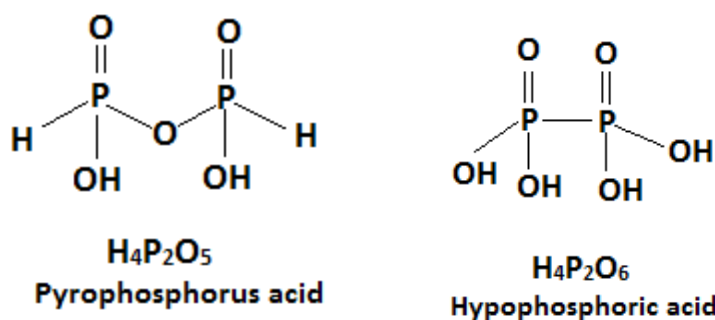


Fig 2.4. Solution state structures of oxoacids of phosphorus

Pure aqueous orthophosphoric acid and its salts -phosphates, find applications in food, detergent and toothpaste industries. When highly diluted, the aqueous acid does not have any specific odour and is non toxic. It is extensively used to impart sour or tart taste to carbonated soft drinks.

5. Summary

Phosphorus plays crucial role in the biochemistry of all living beings. It is a constituent element of the bones and energy giving molecules in the body. As phosphate fertilisers it has its importance in plant life as well. Phosphorus exists in many allotropic modifications, the common ones being white phosphorus, red phosphorus and black phosphorus. White phosphorus is the most reactive allotrope and gives rise to faint greenish glow on oxidation in air. Phosphorus forms stable binary compounds with metals, hydrogen, oxygen and halogens. These are phosphides, phosphine, halides and oxoacids. The compounds formed contain phosphorus in -3, +3 and +5 oxidation states. It forms trihalides and pentahalides out of which mainly chlorides are important. Phosphorus forms large number of oxoacids in which oxidation states of phosphorus range +1 to +5, with variable types of bonds like P=O, P-OH, P-H and P-P bonds. The number of these bonds, differ from one type of oxoacid to the other. The oxoacids containing P-H bonds are reducing in nature. The presence of ionisable O-H groups, make these compounds acidic in nature.