

## Nitrogen Family.

Nitrogen is the first member of group 15 or VA of the periodic table. It consists of five elements nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). The elements of this group are collectively called **pnictogens** and their compounds as pniconides. The name is derived from Greek word "Pniomigs" meaning suffocation. Pniconide contain  $M^{3-}$  species.

### Electronic configuration

Elements	Electronic configuration ( $ns^2 np^3$ )
${}_7N$	$1s^2, 2s^2 2p^3$ or $[He]2s^2 2p^3$
${}_{15}P$	$1s^2, 2s^2 2p^6, 3s^2 3p^3$ or $[Ne]3s^2 3p^3$
${}_{33}As$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^3$ or $[Ar]3d^{10} 4s^2 4p^3$
${}_{51}Sb$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^3$ or $[Kr]4d^{10} 5s^2 5p^3$
${}_{83}Bi$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^3$ or $[Xe]4f^{14} 5d^{10} 6s^2 6p^3$

### Physical properties

(1) **Physical state:** Nitrogen– (gas), phosphorus – (solid) (vaporizes easily), As, Sb, Bi–solids.

Note: Nitrogen is the most abundant gas in the atmosphere. It constitutes about 78% by volume of the atmosphere. Phosphorus is the most reactive element in this group and its yellow form is always kept under water.

(2) **Atomic radii:** Atomic radii increases with atomic number down the group i.e., from N to Bi due to addition of extra principal shell in each succeeding elements.

(3) **Ionisation energy:** The ionisation values of the elements of this group decreases down the group due to gradual increases in atomic size.

(4) **Electronegativity:** Generally the elements of nitrogen family have high value of electronegativity. This value shows a decreasing trend in moving down the group from nitrogen to bismuth.

(5) **Non-metallic and metallic character:** Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids (semi-metal) and bismuth a typical metal.

(6) **Molecular state:** Nitrogen readily forms triple bond (two  $p\pi-p\pi$  bonds) and exists as discrete diatomic gaseous molecule ( $N \equiv N$ ) at room temperature. Phosphorus, arsenic and antimony exist in the form of discrete tetra atomic molecules such as  $P_4, As_4, Sb_4$  in which the atoms are linked to each other by single bonds.

(7) **Melting and boiling points:** The melting points and boiling points of group 15 elements do not show a regular trend.

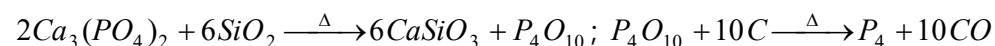
Note: M.pt. first increases from N to As and then decreases from As to Bi. Boiling point first increases from N to Sb. Boiling point of Bi is less than Sb.

(8) **Allotropy:** All the members of group 15 except Bi exhibit the phenomenon of allotropy.

(i) Nitrogen exists in two solid and one gaseous allotropic forms.

(ii) Phosphorus exists in several allotropic forms such as white, red, scarlet, violet and black form.

(a) White or yellow phosphorus: White phosphorus is prepared from rock phosphate  $Ca_3(PO_4)_2, SiO_2$  and coke which are electrically heated in a furnace.



When exposed to light, it acquires a yellow colour.

(b) Red phosphorus: It is obtained by heating yellow phosphorus, between 240–250°C in the presence of an inert gas. Yellow phosphorus can be separated from red phosphorus by reaction with NaOH (aq) or KOH (aq) when the former reacts and the latter remains unreacted.

(iii) Arsenic exists in three allotropic forms namely grey, yellow and black. Antimony also exists in three forms, viz., metallic, yellow and explosive.

(9) **Oxidation state:** The members of the group 15 exhibit a number of positive and negative oxidation states.

(i) **Positive oxidation states:** The electronic configuration ( $ns^2np^3$ ) for the valence shell of these elements shows that these elements can have +3 and +5 oxidation states. In moving down this group,

the stability of +3 oxidation state increases. It may be pointed out here that nitrogen does not exhibit an oxidation state of +5, because it fails to expand its octet due to nonavailability of vacant d-orbitals.

(ii) **Negative oxidation states:** For example oxidation state of nitrogen is -3. The tendency of the elements to show -3 oxidation state decreases on moving down the group from N to Bi.

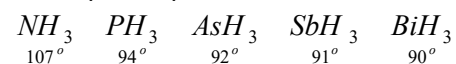
(10) **Catenation** (self linkage): Elements of group 15 also show some tendency to exhibit catenation. This tendency goes on decreasing in moving down the group due to gradual decrease in their bond (M-M) energies.

Note: Out of the various allotropic forms of phosphorus, black phosphorus is a good conductor of electricity (similarity with graphite).

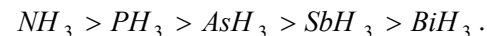
- ☐ Proteins, the building blocks of our body contain 16% of nitrogen in them.
- ☐ Radioactive phosphorus ( $P^{32}$ ) is used in the treatment of leukemia (blood cancer).
- ☐ The disease caused by the constant touch with white phosphorus is called Phossy Jaw.

## Chemical properties

(1) **Hydrides:** All the members form volatile hydrides of the type  $AH_3$ . All hydrides are pyramidal in shape. The bond angle decreases on moving down the group due to decrease in bond pair-bond pair repulsion.

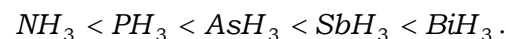


The decreasing order of basic strength of hydrides is as follows:



The increasing order of boiling points is as follows:  $PH_3 < AsH_3 < NH_3 < SbH_3$ .

$NH_3$  is thermally most stable and  $BiH_3$  is least stable. This is because in  $NH_3$ , N-H covalent bond is the strongest due to small size of N atom. Hence, the decomposition temperature of  $NH_3$  will be the highest. The increasing order of reducing character is as follows,



Note: Diphosphine ( $P_2H_4$ ) and hydrazine ( $N_2H_4$ ) are other two important hydrides. Hydrazine a strong reducing agent, is used in organic synthesis and rocket fuels and is prepared as follows,



- ❑ Phosphine is poisonous and does not form any complexes.
- ❑ Phosphine forms vortex rings of  $P_2O_5$  in the form of white smoke when it comes in contact with air due to combustion. This is due to impurities of diphosphine ( $P_2H_4$ ).
- ❑ Phosphine is used to prepare smoke screens in warfare. Calcium phosphide reacts with water to form phosphine which burns to give clouds of  $P_2O_5$  which acts as smoke screens.
- ❑ Liquor ammonia is a concentrated solution of  $NH_3$  in water.
- ❑ Ammonia will not burn in air, but burns in pure  $O_2$  with a yellowish flame to produce  $N_2$  and  $H_2O$ .

(2) **Halides:** The members of the family form trihalides ( $MX_3$ ) and pentahalides ( $MX_5$ ). The trihalides are  $sp^3$ -hybridized with distorted tetrahedral geometry and pyramidal shape while pentahalides are  $sp^3d$ -hybridized and are trigonal bipyramidal in shape. The trihalides are hydrolyzed by water and ease of hydrolysis decreases when we move down the group. Hence,  $NCl_3$  is easily hydrolyzed but  $SbCl_3$  and  $BiCl_3$  are partly and reversibly hydrolyzed.  $NF_3$  is not hydrolyzed due to lack of vacant d-orbital with nitrogen.  $PF_3$  and  $PF_5$  are also not hydrolyzed because the P – F bond is stronger than P – O covalent bond. The hydrolysis products of the other halides are as follows :  $NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$  ;  $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$   
 $2AsCl_3 + 3H_2O \rightarrow As_2O_3 + 6HCl$  ;  $SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$  ;  
 $BiCl_3 + H_2O \rightarrow BiOCl + 2HCl$

Their basic character follows this decreasing order as  $NI_3 > NBr_3 > NCl_3 > NF_3$ . Except  $NF_3$ , the trihalides of nitrogen are unstable and decompose with explosive violence.  $NF_3$  is stable and inert.  $NCl_3$  is highly explosive. Trifluorides and trichlorides of phosphorus and antimony act as Lewis acid. The acid strength decreases down the group. For example, acid strength of trichlorides is in the order ;  $PCl_3 > AsCl_3 > SbCl_3$ .

Nitrogen does not form pentahalides due to non-availability of vacant d-orbitals. The pentachloride of phosphorus is not very stable because axial bonds are longer (and hence weaker) than equatorial bond. Hence,  $PCl_5$  decomposes to give  $PCl_3$  and  $Cl_2$ ;  $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ .

The instability of  $PCl_5$  makes it a very good chlorinating agent. All pentahalides act as Lewis acids since they can accept a lone pair of electron from halide ion.

Note: Solid  $PCl_5$  is an ionic compound consisting of  $[PCl_4]^+$   $[PCl_6]^-$ ,  $[PCl_4]^+$  has a tetrahedral structure, while  $[PCl_6]^-$  has an octahedral structure.

Since,  $PCl_5$  reacts readily with moisture it is kept in well stoppered bottles.

$PI_5$  Does not exist due to large size of I atoms and lesser electronegativity difference between phosphorus and iodine.

Down the group, the tendency to form pentahalides decreases due to inert pair effect. e.g.,  $BiF_5$  does not exist.

(3) **Oxides:** These elements form oxides of the type  $X_2O_3$ ,  $X_2O_4$  and  $X_2O_5$ .

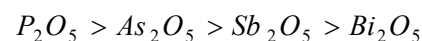
(i) **Oxides of Nitrogen:** Nitrogen forms two more oxides i.e.,  $N_2O$  and NO and both are neutral. Nitrous oxide ( $N_2O$ ) has a sweet taste and its main use is as anaesthetic. When inhaled in mild quantities it causes hysterical laughter so it is also called Laughing gas. Nitric oxide (NO) can be obtained by treating a mixture of sodium nitrite and ferrous sulphate with dil.  $H_2SO_4$ .

Other oxides of nitrogen are:  $NO_2$ ,  $N_2O_3$ ,  $N_2O_5$ .

The acidic strength of oxides:  $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$ .

(ii) **Oxides of phosphorus:**  $P_4O_6$  (Phosphorus trioxide),  $P_4O_{10}$  (Phosphorus pentoxide).

(iii) **Oxides of other elements:** The decreasing order of stability of oxides of group 15 follows as,



Except  $P_2O_5$ , all pentoxides show oxidising properties. Also  $P_2O_5$  is acidic in nature.  $N_2O_5$  is the strongest oxidising agent. The nature of oxides of group 15 elements is as follows,

$N_2O_3$  and  $P_2O_3$  (acidic);  $As_2O_3$  and  $Sb_2O_3$  (amphoteric);  $Bi_2O_3$  (basic)

(4) **Oxyacids:** Oxyacids of nitrogen are  $HNO_2$ ,  $HNO_3$ ,  $H_4N_2O_4$  and  $HNO_4$ , which are explosive.

(Nitroxylic acid)

(Pernitric acid)

Note:  $HNO_3$  is called aqua fortis and prepared from air (Birkel and Eyde process) and  $NH_3$  (Ostwald process). It acts as a strong oxidising agent.

Oxyacids of phosphorus are,

(i)  $H_3PO_2$  (Hypophosphorus acid): Reducing agent and monobasic.

(ii)  $H_3PO_3$  (Orthophosphorus acid): Reducing agent and dibasic.

(iii)  $H_3PO_4$  (Orthophosphoric acid): Weak tribasic acid.

(iv)  $H_4P_2O_7$  (Pyrophosphoric acid): It is obtained by heating  $H_3PO_4$  to  $220^\circ\text{C}$ . It is tetrabasic.

(v)  $HPO_3$  (Metaphosphoric acid): It is formed by the dehydration of  $H_3PO_4$  at  $316^\circ\text{C}$ . Also exists as a trimer and is monobasic.

(vi)  $H_4P_2O_6$  (Hypophosphoric acid): Tetrabasic

(vii)  $H_4P_2O_5$  (Pyrophosphoric acid): Dibasic acid

### **Anomalous behaviour of Nitrogen**

Nitrogen is known to differ from other members of the family because of the following facts,

- (i) Its small size
- (ii) Its high electronegativity
- (iii) Its high ionization energy
- (iv) Non-availability of d-orbital in the valence shell.
- (v) Its capacity to form  $p\pi-p\pi$  multiple bonds.

The main points of difference are,

(1) Nitrogen is a gas ( $N_2$ ) while other members are solids.

(2) Nitrogen is diatomic while other elements like phosphorus and arsenic form tetra-atomic molecules ( $P_4, As_4$ ).

(3) Nitrogen form five oxides ( $N_2O, NO, N_2O_3, N_2O_4$  and  $N_2O_5$ ) while other members of the family form two oxides (tri and pentaoxides).

- (4) Hydrides of nitrogen show H-bonding while those of other elements do not.
- (5) Nitrogen does not show pentacovalency because of absence of d-orbitals while all other elements show pentacovalency.
- (6) Nitrogen does not form complexes because of absence of d-orbitals while other elements show complex formation e.g.,  $[PCl_6]^-$ ,  $[AsCl_6]^-$  etc.
- (7) The hydride of nitrogen ( $NH_3$ ) is highly basic in nature while the hydrides of other elements are slightly basic.
- (8) Except for  $NF_3$ , other halides of nitrogen e.g.,  $NCl_3$ ,  $NBr_3$  and  $NI_3$  are unstable while the halides of other elements are fairly stable.

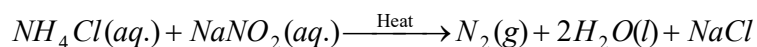
### Nitrogen and its compounds

$N_2$  was discovered by **Daniel Rutherford**. It is the first member of group 15 in the periodic table.

(1) **Occurrence:**  $N_2$ , occurs both in the free state as well as in the combined state.  $N_2$  occurs in atmosphere to the extent of 78% by volume in free state.  $N_2$  is present in many compounds such as potassium nitrate (nitre). Sodium nitrate (Chile salt peter) and many ammonium compounds.  $N_2$  is an important constituent of proteins in plants and animals in combined state.

(2) **Preparation:** It is prepared by the following methods,

(i) **Laboratory method:** In the laboratory  $N_2$  is prepared by heating an aqueous solution containing an equivalent amounts of  $NH_4Cl$  and  $NaNO_2$ .



(ii) **Commercial preparation:** Commercially  $N_2$  is prepared by the fractional distillation of liquid air.

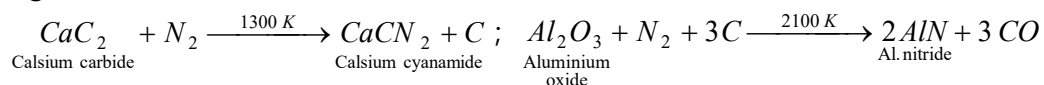
(3) **Physical properties:**  $N_2$  is a colorless, odorless and tasteless gas. It is a non-toxic gas. Its vapour density is 14. It has very low solubility in water.

#### (4) Chemical properties

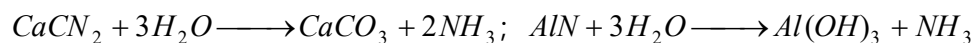
(i)  $N_2$  is neutral towards litmus. It is chemically unreactive at ordinary temp. It is neither combustible nor it supports combustion.

(ii) The N – N bond in  $N_2$  molecule is a triple bond ( $N \equiv N$ ) with a bond distance of 109.8 pm and bond dissociation energy of  $946 \text{ kJ mol}^{-1}$

(iii) **Combination with compounds:**  $N_2$  combines with certain compounds on strong heating .eg



Both these compounds are hydrolyzed on boiling with water to give ammonia.



Therefore, calcium cyanamide is used as a fertilizer under the name nitrolim ( $CaCN_2 + C$ )

(5) **Uses of nitrogen:**  $N_2$  is mainly used in the manufacture of compounds like  $NH_3, HNO_3, CaCN_2$  etc.

#### (6) Compounds of nitrogen

##### (i) Hydrides of nitrogen

##### Ammonia

Ammonia is the most important compound of nitrogen. It can be manufactured by Haber's process. In this process, a mixture of  $N_2$  and  $H_2$  in the ratio of 1 : 3 is passed over heated Fe at 650 – 800K as catalyst and Mo as promotor,  $N_2 + 3H_2 \rightleftharpoons 2NH_3, \Delta H = -93.6 \text{ kJ mol}^{-1}$  This is a reversible exothermic reaction.

Ammonia is prepared in the laboratory by heating ammonium salt ( $NH_4Cl$ ) with a strong alkali like NaOH



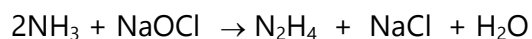
$NH_4Cl + NaOH \longrightarrow NH_3 + H_2O + NaCl$  Ammonia can be dried by passing over quick lime (CaO). However, it cannot be dried with dehydrating agents such as conc.  $H_2SO_4$ ,  $P_2O_5$  and anhydrous  $CaCl_2$  because ammonia reacts with these compounds.

$NH_3$  is a colorless gas with a characteristic pungent smell called ammoniacal smell. It is highly soluble in water and its solution is basic in nature,  $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$NH_3$  is expected to have a tetrahedral geometry, but the lone pair distorts its geometry and the molecule has pyramidal geometry with N – H bond length of 101.7 pm and a bond angle of  $107.5^\circ$ . Liquid ammonia is widely used as a refrigerant due to its high heat of vaporization.

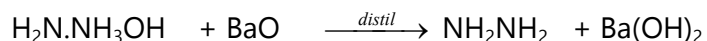
### Hydrazine, (NH<sub>2</sub> – NH<sub>2</sub>)

Hydrazine is prepared commercially by boiling aqueous ammonia or urea with sodium hypochloride in the presence of glue or gelatin.



The resulting solution is concentrated and anhydrous hydrazine may be obtained by further distillation over barium oxide. Alternatively, the hydrazine present in the resulting solution is precipitated as sparingly soluble crystalline hydrazine sulphate on treatment with sulphuric acid,  $NH_2NH_2 + H_2SO_4 \rightarrow N_2H_4.H_2SO_4$ .

The precipitate is removed and treated with an alkali when hydrazine hydroxide  $H_2N.NH_3OH$  is obtained. This is distilled under reduced pressure, over barium oxide to liberate free hydrazine.



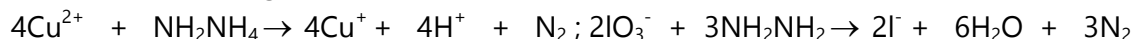
**Physical properties:** Anhydrous hydrazine is a colorless fuming liquid (m.p.  $2^\circ\text{C}$  and b.p.  $114^\circ\text{C}$ ) soluble in water in all proportions. It is also soluble in alcohol. It is strongly hygroscopic.

**Chemical properties:** It behaves as a diacid base, Thus with hydrochlorides it forms hydrazine monochloride  $H_2N.NH_3Cl$  and hydrazine dichloride  $ClH_3N.NH_3Cl$ .

(i) Hydrazine burns in air with the evolution of heat.  $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$   $\Delta H = -622 \text{ kJ}$

The alkyl derivative of hydrazine are used as rocket fuels.

(ii) It reduces Fehling's solution to red cuprous oxide and iodates to iodides.



**Uses:** Hydrazine is used as a rocket fuel. It is also used as a reagent in organic chemistry.

(ii) **Oxides of nitrogen:** Nitrogen combines with  $O_2$  under different conditions to form a number of binary oxides which differ with respect to the oxidation state of the nitrogen atom. The important oxides are  $N_2O$ ,  $NO$ ,  $N_2O_3$ ,  $NO_2$ ,  $N_2O_4$  and  $N_2O_5$ .

### Oxides of Nitrogen

Oxide	Oxidation State of N	Physical appearance	Structure
Nitrous oxide ( $N_2O$ )	+1	Colourless gas	$N \equiv N \rightarrow O$
Nitric oxide (NO)	+2	Colourless	$N = O$
Dinitrogen trioxide ( $N_2O_3$ )	+3	Blue solid	
Dinitrogen tetroxide ( $N_2O_4$ )	+4	Colourless liquid	
Nitrogen dioxide ( $NO_2$ )	+4	Brown gas	
Dinitrogen pentoxide ( $N_2O_5$ )	+5	Colourless gas	

Oxide of Nitrogen	Preparation
Nitrous Oxide ( $N_2O$ )	By heating ammonium nitrate upto $240^\circ C$
	$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$
	Collected over hot water.
Nitrous oxide (NO)	(a) By the action of cold dil. $HNO_3$ on copper turnings (Laboratory method)
	$3Cu + 8 \text{ dil. } HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$
	(b) By the action of $H_2SO_4$ on a mixture of $FeSO_4$ and $KNO_3$ (4:1)
	$2KNO_3 + 5H_2SO_4 + 6FeSO_4 \rightarrow 2KHSO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2NO$
	(c) By catalytic oxidation of ammonia.
	$4NH_3 + 5O_2 \xrightarrow[850^\circ C]{Pt} 4NO + 6H_2O$

Dinitrogen trioxide(N <sub>2</sub> O <sub>3</sub> )	(a) By the action of 50% HNO <sub>3</sub> on arsenious oxide. 2HNO <sub>3</sub> + As <sub>2</sub> O <sub>3</sub> + 2H <sub>2</sub> O → NO + NO <sub>2</sub> + 2H <sub>3</sub> AsO <sub>4</sub>
	↓ 250 K
Nitrogen dioxide (NO <sub>2</sub> )	N <sub>2</sub> O <sub>3</sub> (a) By heating nitrates of heavy metals, e.g., lead nitrate.
	2Pb(NO <sub>3</sub> ) <sub>2</sub> $\xrightarrow{673\text{ K}}$ 4NO <sub>2</sub> + 2PbO + 2O
	(b) By heating copper turnings with conc. HNO <sub>3</sub> .
	Cu + 4 conc. HNO <sub>3</sub> → Cu(NO <sub>3</sub> ) <sub>2</sub> + 2H <sub>2</sub> O + 2NO <sub>2</sub>
Dinitrogen pentoxide(N <sub>2</sub> O <sub>5</sub> )	(a) By dehydrating HNO <sub>3</sub> with phosphorus pentoxide
	4HNO <sub>3</sub> + P <sub>4</sub> O <sub>10</sub> → 2N <sub>2</sub> O <sub>5</sub> + 4 HPO <sub>3</sub>

### (iii) Oxyacids of nitrogen

#### Oxyacids of nitrogen

Name of oxoacid	M. F.	Structure	Oxidation State of N	Basicity	pK <sub>a</sub>	Nature
Hyponitrous acid	H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>		+1	2(dibasic)	Very weak	Highly explosive
Nitrous acid	HNO <sub>2</sub>	$\begin{array}{c} \text{H} - \text{N} = \text{O} \\ \downarrow \\ \text{O} \end{array}$	+3	1 (monobasic)	3.3	Unstable Weak acid
Nitric acid	HNO <sub>3</sub>	$\begin{array}{c} \text{H} - \text{O} - \text{N} = \text{O} \\ \downarrow \\ \text{O} \end{array}$	+5	1 (monobasic)	-3.0	Stable, Strong acid

Pernitric acid	HNO <sub>4</sub>	$\begin{array}{c} \text{O} = \text{N} - \text{O} - \text{O} - \text{H} \\ \downarrow \\ \text{O} \end{array}$	+5	1 (monobasic )	Unstable and explosive
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### Phosphorus and its compounds

It is the second member of group 15 (VA) of the Periodic table. Due to larger size of P, it cannot form stable P  $\pi$  - P  $\pi$  bonds with other phosphorous atoms whereas nitrogen can form P  $\pi$  - P  $\pi$  bonds .

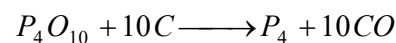
(1) **Occurrence:** Phosphorous occurs mainly in the form of phosphate minerals in the crust of earth. Some of these are:

- (i) Phosphorite  $Ca_3(PO_4)_2$ ,
- (ii) Fluorapatite  $Ca_5(PO_4)_3F$ ,
- (iii) Chlorapatite  $3Ca_3(PO_4)_2 \cdot CaCl_2$ ,
- (iv) Hydroxyapatite;  $Ca_5(PO_4)_3OH$  .

Phosphates are essential constituents of plants and animals. It is mainly present in bones, which contains about 58% calcium phosphate.

(2) **Isolation:**Elemental phosphorus is isolated by heating the phosphorite rock with coke and sand in an electric furnace at about 1770K,  $2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}$  ;

Calcium silicate



(3) **Allotropic forms of phosphorus:** Phosphorus exists in three main allotropic forms,

- (i) White phosphorus
- (ii) Red phosphorus
- (iii) Black phosphorus

### Some physical properties of three forms of phosphorus

Properties	White phosphorus	Red phosphorus	Black phosphorus
Colour	White but turns yellow on exposure	Dark red	Black
State	Waxy solid	Brittle powder	Crystalline

Density	1.84g cm <sup>-3</sup>	2.1 g cm <sup>-3</sup>	2.69 g cm <sup>-3</sup>
Ignition temperature	307 K	533 K	673 K
Stability	Less stable at ordinary temperature	More stable at ordinary temperature	Most stable
Chemical reactivity	Very reactive	Less reactive	Least reactive

## Compounds of phosphorus

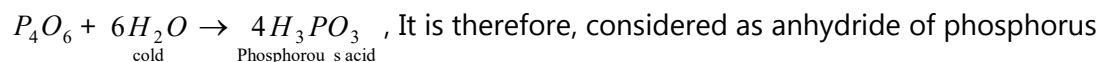
(1) **Oxides and oxyacid's of phosphorus:** Phosphorus is quite reactive and forms number of compounds in oxidation states of -3, +3 and +5.

(i) **Oxides:** Phosphorus forms two common oxides namely, (a) phosphorus trioxide ( $P_4O_6$ ) and (b) phosphorus penta oxide ( $P_4O_{10}$ ).

(a) Phosphorus (III) oxide ( $P_4O_6$ ): It is formed when P is burnt in a limited supply of air,  $P_4 + 3O_2 \xrightarrow{\text{(limited)}}$

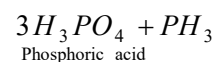


It is a crystalline solid with garlic odour. It dissolves in cold water to give phosphorous acid,



acid.

With hot water, it gives phosphoric acid and inflammable phosphine,  $P_4O_6 + 6H_2O \text{ (hot)} \rightarrow$



It reacts vigorously with  $Cl_2$  to form a mixture of phosphoryl chloride and meta phosphoryl chloride.

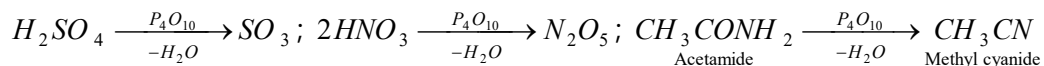


(b) Phosphorus (V) oxide ( $P_4O_{10}$ ): It is prepared by heating white phosphorus in excess of air,  $P_4 + 5O_2 \text{ (excess)} \rightarrow P_4O_{10}$ . It is snowy white solid. It readily dissolves in cold water forming metaphosphoric acid.

$P_4O_{10} + 2H_2O \xrightarrow{\text{(Cold)}} 4HPO_3$  . With hot water, it gives phosphoric acid,  
(Cold) Metaphosphoric acid

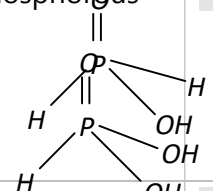
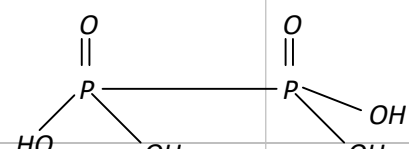

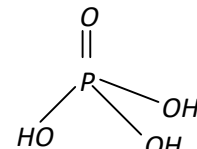
$P_4O_{10} + 6H_2O \xrightarrow{\text{Hot}} 4H_3PO_4$  .  
Hot Phosphoric acid

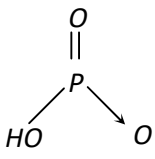
$P_4O_{10}$  is a very strong dehydrating agent. It extracts water from many compounds including  $H_2SO_4$  and  $HNO_3$ ,



(ii) **Oxyacids of phosphorus:** Phosphorus forms a number of oxyacid's which differs in their structure and oxidation state of phosphorus.

### Oxyacid's of phosphorus

Name	Formula	Oxidation state of P	Basicity	Structure
Hypophosphorous acid 	$H_3PO_2$	+1	Monobasic	
Phosphorous acid 	$H_3PO_3$	+3	Dibasic	
Hypophosphoric acid 	$H_4P_2O_6$	+4	Tetrabasic	
Orthophosphoric acid 	$H_3PO_4$	+5	Tribasic	

Metaphosphoric acid	$(HPO_3)_n$	+5	Monobasic	
Pyrophosphoric acid (Diphosphoric acid).	$H_4P_2O_7$	+5	Tetrabasic	

**Chemical Fertilizers:** The chemical substances which are added to the soil to keep up the fertility of soil are called fertilizers.

**Types of fertilizers:** Chemical fertilizers are mainly of four types,

(i) **Nitrogenous fertilizers:** e.g. Ammonium sulphate  $(NH_4)_2SO_4$ , Calcium cyanamide  $CaCN_2$ , Urea  $NH_2CONH_2$  etc.

(ii) **Phosphatic fertilizers:** e.g.  $Ca(H_2PO_4)_2 \cdot H_2O$  (Triple super phosphate), Phosphatic slag etc.

(iii) **Potash fertilizers:** e.g. Potassium nitrate  $(KNO_3)$ , Potassium sulphate  $(K_2SO_4)$  etc.

(iv) **Mixed fertilizers:** These are made by mixing two or more fertilizers in suitable proportion. e.g. NPK (contains nitrogen, phosphorus and potassium).

NPK is formed by mixing ammonium phosphate, super phosphate and some potassium salts.