

# Group 15 Elements

Group 15 includes nitrogen, phosphorus, arsenic, antimony and bismuth. As we go down the group, there is a shift from non-metallic to metallic through metalloid character. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a typical metal.

**Occurrence:** Molecular nitrogen comprises 78% by volume of the atmosphere. In the earth's crust, it occurs as sodium nitrate, NaNO<sub>3</sub> (called Chile saltpetre) and potassium nitrate (Indian saltpetre). It is found in the form of proteins in plants and animals. Phosphorus occurs in minerals of the apatite family, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>6</sub>. CaX<sub>2</sub> (X = F, Cl or OH) (e.g., fluorapatite Ca<sub>5</sub>(PO<sub>4</sub>)<sub>6</sub>. CaF<sub>2</sub>>) which are the main components of phosphate rocks. Phosphorus is an essential constituent of animal and plant matter. It is present in bones as well as in living cells. Phosphoproteins are present in milk and eggs. Arsenic, antimony and bismuth are found mainly as sulphide minerals.Trends of some of the atomic, physical and chemical properties of the group are discussed below.

**Electronic Configuration:** The valence shell electronic configuration of these elements is ns<sup>2</sup>np<sup>3</sup>. The s orbital in these elements is completely filled and p orbitals are half-filled, making their electronic configuration extra stable.

**Atomic and Ionic Radii:** Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d and/or f orbitals in heavier members.

**Ionisation Enthalpy:** Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled p orbitals electronic configuration and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is ΔH<sub>1</sub> < ΔH<sub>2</sub> < ΔH<sub>3</sub>

**Electronegativity:** The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced.

**Physical Properties:** All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids. Metallic character increases down the group. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a metal. This is due to decrease in ionisation enthalpy and increase in atomic size. The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth. Except nitrogen, all the elements show allotropy.

**Chemical Properties: Oxidation states and trends in chemical reactivity:**  
The common oxidation states of these elements are -3, +3 and +5. The tendency to exhibit -3 oxidation state decreases down the group due to increase in size and metallic character. In fact last member of the group, bismuth hardly forms any compound in -3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterised Bi (V) compound is BiF<sub>5</sub>. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group. Nitrogen exhibits + 1, + 2, + 4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxoacids.  
In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,  
3HNO<sub>2</sub> → HNO<sub>3</sub> + H<sub>2</sub>O + 2NO  
Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid. However +3 oxidation state in case of arsenic, antimony and bismuth becomes increasingly stable with respect to disproportionation.  
Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding. The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalence as in PF<sub>6</sub><sup>-</sup>.  
*Anomalous properties of nitrogen:*  
Nitrogen differs from the rest of the members of this group due to its small size, high electronegativity, high ionisation enthalpy and non-availability of d orbitals. Nitrogen has unique ability to form pπ - pπ multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Heavier elements of this group do not form pπ - pπ bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, nitrogen exists as a diatomic molecule with a triple bond (one s and two p) between the two atoms. Consequently, its bond enthalpy (941.4 kJ mol<sup>-1</sup>) is very high. On the contrary, phosphorus, arsenic and antimony form single bonds as P-P, As-As and Sb-Sb while bismuth forms metallic bonds in elemental state. However, the single N-N bond is weaker than the single P-P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form dπ - pπ bond as the heavier elements can e.g.,  
R<sub>3</sub>P = O or R<sub>3</sub>P = CH<sub>2</sub> (R = alkyl group). Phosphorus and arsenic can form dπ - dπ bond also with transition metals when their compounds like P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> act as ligands.

**(i) Reactivity towards hydrogen:** All the elements of Group 15 form hydrides of the type EH<sub>3</sub> where E = N, P, As, Sb or Bi. The hydrides show regular gradation in their properties. The stability of hydrides decreases from NH<sub>3</sub> to BiH<sub>3</sub> which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH<sub>3</sub> is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order NH<sub>3</sub> > PH<sub>3</sub> > AsH<sub>3</sub> > SbH<sub>3</sub> > BiH<sub>3</sub>.  
**(ii) Reactivity towards oxygen:** All these elements form two types of oxides: E<sub>2</sub>O<sub>3</sub> and E<sub>2</sub>O<sub>5</sub>. The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type E<sub>2</sub>O<sub>3</sub> of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.  
**(iii) Reactivity towards halogens:** These elements react to form two series of halides: EX<sub>3</sub> and EX<sub>5</sub>. Nitrogen does not form pentahalide due to non-availability of the d orbitals in its valence shell. Pentahalides are more covalent than trihalides. All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only NF<sub>3</sub> is known to be stable. Trihalides except BiF<sub>3</sub> are predominantly covalent in nature.  
**(iv) Reactivity towards metals:** All these elements react with metals to form their binary compounds exhibiting -3 oxidation state, such as, Ca<sub>3</sub>N<sub>2</sub> (calcium nitride) Ca<sub>3</sub>P<sub>2</sub> (calcium phosphide), Na<sub>3</sub>As<sub>2</sub> (sodium arsenide), Zn<sub>3</sub>Sb<sub>2</sub> (zinc antimonide) and Mg<sub>3</sub>Bi<sub>2</sub> (magnesium bismuthide).

## Dinitrogen

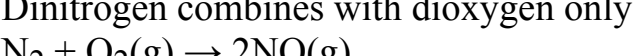
### Preparation:

Dinitrogen is produced commercially by the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.p. 90 K).

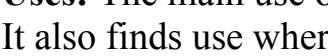
In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.



Small amounts of NO and HNO<sub>3</sub> are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate. It can also be obtained by the thermal decomposition of ammonium dichromate.

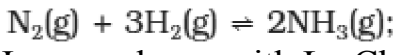


Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

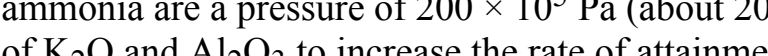


### Properties

Dinitrogen is a colourless, odourless, tasteless and non-toxic gas. Nitrogen atom has two stable isotopes: <sup>14</sup>N and <sup>15</sup>N. It has a very low solubility in water (23.2 cm<sup>3</sup> per litre of water at 273 K and 1 bar pressure) and low freezing and boiling points. Dinitrogen is rather inert at room temperature because of the high bond enthalpy of N≡N bond. Reactivity, however, increases rapidly with rise in temperature. At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:



It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia:



Dinitrogen combines with dioxygen only at very high temperature (at about 2000 K) to form nitric oxide, NO.

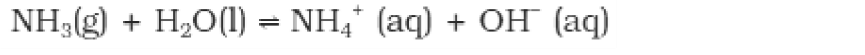


**Uses:** The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen, (e.g., calcium cyanamide). It also finds use where an inert atmosphere is required (e.g., in iron and steel industry, inert diluent for reactive chemicals). Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

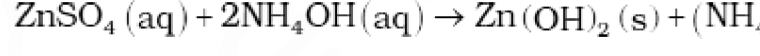
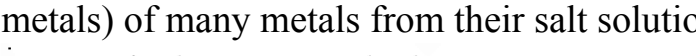
## Ammonia

### Preparation:

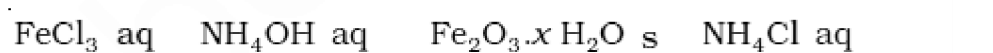
Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.



On a small scale ammonia is obtained from ammonium salts which decompose when treated with caustic soda or calcium hydroxide.



On a large scale, ammonia is manufactured by Haber's process.



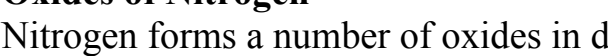
In accordance with Le Chatelier's principle, high pressure would favour the formation of ammonia. The optimum conditions for the production of ammonia are a pressure of 200 × 10<sup>5</sup> Pa (about 200 atm), a temperature of ~ 700 K and the use of a catalyst such as iron oxide with small amounts of K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> to increase the rate of attainment of equilibrium. Earlier, iron was used as a catalyst with molybdenum as a promoter.

### Properties

Ammonia is a colourless gas with a pungent odour. Its freezing and boiling points are 198.4 and 239.7 K respectively. In the solid and liquid states, it is associated through hydrogen bonds as in the case of water and that accounts for its higher melting and boiling points than expected on the basis of its molecular mass.

The ammonia molecule is trigonal pyramidal with the nitrogen atom at the apex. It has three bond pairs and one lone pair of electrons as shown in the structure.

Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the formation of OH<sup>-</sup> ions.



It forms ammonium salts with acids, e.g., NH<sub>4</sub>Cl, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, etc. As a weak base, it precipitates the hydroxides (hydrated oxides in case of some metals) of many metals from their salt solutions. For example,



(white ppt)

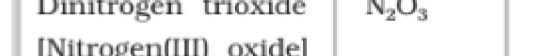


brown ppt

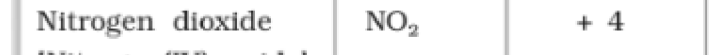
The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule makes it a Lewis base. It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of metal ions such as Cu<sup>2+</sup>, Ag<sup>+</sup>:



(blue) (deep blue)



(colourless) (white ppt)



(white ppt) (colourless)

**Uses:** Ammonia is used to produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate) and in the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid. Liquid ammonia is also used as a refrigerant.

## Oxides of Nitrogen

Nitrogen forms a number of oxides in different oxidation states. The names, formulas, preparation and physical appearance of these oxides are given in Table below:

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N <sub>2</sub> O	+ 1	<chem>NH4NO3 -&gt;[heat] N2O + 2H2O</chem>	colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	<chem>2NaNO2 + 2FeSO4 + 3H2SO4 -&gt; Fe2(SO4)3 + 2NaHSO4 + 2H2O + 2NO</chem>	colourless gas, neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N <sub>2</sub> O <sub>3</sub>	+ 3	<chem>2NO + N2O5 -&gt;[298K] 2N2O3</chem>	blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO <sub>2</sub>	+ 4	<chem>2Pb(NO3)2 -&gt;[673K] 4NO2 + 2PbO</chem>	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N <sub>2</sub> O <sub>4</sub>	+ 4	<chem>2NO2 -&gt;[cool] N2O4</chem>	colourless solid/liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N <sub>2</sub> O <sub>5</sub>	+5	<chem>4HNO3 + P4O10 -&gt; 4HPO3 + 2N2O5</chem>	colourless solid, acidic

Lewis dot main resonance structures and bond parameters of oxides are given in Table below:

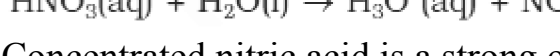
Formula	Resonance Structures	Bond Parameters
(1) Nitrous oxide (N <sub>2</sub> O)	$\text{N}\equiv\text{N}-\ddot{\text{O}} \longleftrightarrow \text{N} \equiv \text{N}^+ - \ddot{\text{O}}^-$	N $\overset{112\text{ pm}}{\text{---}} \text{N} \overset{119\text{ pm}}{\text{---}} \text{O}$
(2) Nitric oxide (NO)	$\text{N} \equiv \ddot{\text{O}} \cdot \longleftrightarrow \cdot \ddot{\text{O}} = \text{N}$	N $\equiv \text{O}$ N $\overset{106\text{ pm}}{\text{---}} \text{O}$ $\overset{119\text{ pm}}{\text{---}}$ N
(3) Dinitrogen trioxide	$\text{N} \equiv \text{N}^+ - \ddot{\text{O}}^- \longleftrightarrow \cdot \ddot{\text{O}} = \text{N} - \text{N} \equiv \text{O}$	N $\equiv \text{O}$ N $\overset{106\text{ pm}}{\text{---}} \text{O}$ $\overset{119\text{ pm}}{\text{---}}$ N
(4) Nitrogen dioxide (NO <sub>2</sub> )	$\text{N} \equiv \text{N}^+ - \ddot{\text{O}}^- \longleftrightarrow \cdot \ddot{\text{O}} = \text{N} - \text{N} \equiv \text{O}$	N $\equiv \text{O}$ N $\overset{106\text{ pm}}{\text{---}} \text{O}$ $\overset{119\text{ pm}}{\text{---}}$ N
(5) Nitrogen dioxide	$\text{N} \equiv \text{N}^+ - \ddot{\text{O}}^- \longleftrightarrow \cdot \ddot{\text{O}} = \text{N} - \text{N} \equiv \text{O}$	N $\equiv \text{O}$ N $\overset{106\text{ pm}}{\text{---}} \text{O}$ $\overset{119\text{ pm}}{\text{---}}$ N
(6) Dinitrogen pentoxide	$\text{N} \equiv \text{N}^+ - \ddot{\text{O}}^- \longleftrightarrow \cdot \ddot{\text{O}} = \text{N} - \text{N} \equiv \text{O}$	N $\equiv \text{O}$ N $\overset{106\text{ pm}}{\text{---}} \text{O}$ $\overset{119\text{ pm}}{\text{---}}$ N

## Nitric Acid

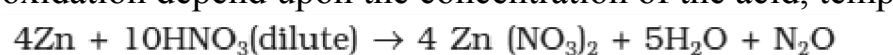
Nitrogen forms oxoacids such as H<sub>2</sub>N<sub>2</sub>O<sub>2</sub> (hyponitrous acid), HNO<sub>2</sub> (nitrous acid) and HNO<sub>3</sub> (nitric acid). Amongst them HNO<sub>3</sub> is the most important.

### Preparation:

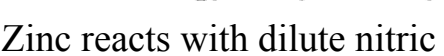
In the laboratory, nitric acid is prepared by heating KNO<sub>3</sub> or NaNO<sub>3</sub> and concentrated H<sub>2</sub>SO<sub>4</sub> in a glass retort.



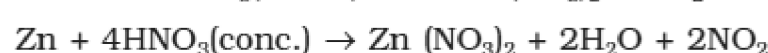
On a large scale it is prepared mainly by Ostwald's process. This method is based upon catalytic oxidation of NH<sub>3</sub> at atmospheric oxygen.



Nitric oxide thus formed combines with oxygen giving NO<sub>2</sub>.



Nitrogen dioxide so formed, dissolves in water to give HNO<sub>3</sub>.



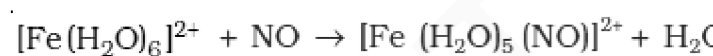
NO thus formed is recycled and the aqueous HNO<sub>3</sub> can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H<sub>2</sub>SO<sub>4</sub>.

### Properties

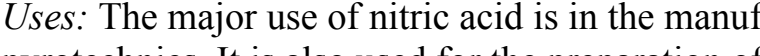
It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K). Laboratory grade nitric acid contains ~ 68% of the HNO<sub>3</sub> by mass and has a specific gravity of 1.504.

In the gaseous state, HNO<sub>3</sub> exists as a planar molecule with the structure as shown.

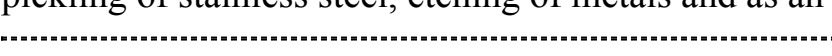
In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.



Concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

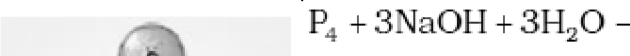


Zinc reacts with dilute nitric acid to give N<sub>2</sub>O and with concentrated acid to give NO<sub>2</sub>.



Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Concentrated nitric acid also oxidises non-metals and their compounds. Iodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to H<sub>2</sub>SO<sub>4</sub> and phosphorus to phosphoric acid.



Brown Ring Test: The familiar brown ring test for nitrates depends on the ability of Fe<sup>2+</sup> to reduce nitrates to nitric oxide, which reacts with Fe<sup>2+</sup> to form a brown coloured complex. The test is usually carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicates the presence of nitrate ion in solution.



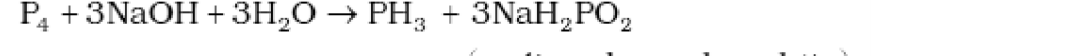
(brown)

**Uses:** The major use of nitric acid is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds. Other major uses are in the pickling of stainless steel, etching of metals and as an oxidiser in rocket fuels.

## Phosphorus

**Allotropic Forms:** Phosphorus is found in many allotropic forms, the important ones being white, red and black.

*White phosphorus* is a translucent white waxy solid. It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving PH<sub>3</sub>.



(sodium hypophosphite)

White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions because of angular strain in the P<sub>4</sub> molecule where the angles are only 60°. It readily catches fire in air to give dense white fumes of P<sub>4</sub>O<sub>10</sub>.



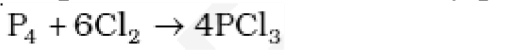
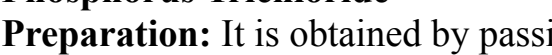
It consists of discrete tetrahedral P<sub>4</sub> molecule as shown in figure.

*Red phosphorus* is obtained by heating white phosphorus at 573K in an inert atmosphere for several days. When red phosphorus is heated under high pressure, a series of phases of black phosphorus is formed. Red phosphorus possesses iron grey lustre. It is odourless, nonpoisonous and insoluble in water as well as in carbon disulphide. It is chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark. It is polymeric, consisting of chains of P<sub>4</sub> tetrahedra linked together

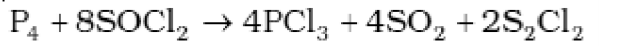
*Black phosphorus* has two forms α-black phosphorus and β-black phosphorus. α-Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals. It does not oxidise in air. β-Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

## Phosphine

**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 CO<sub>2</sub>.



(sodium hypophosphite)

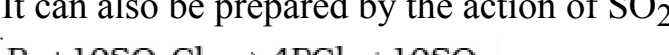
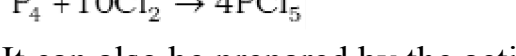
When pure, it is non inflammable but becomes inflammable owing to the presence of P<sub>2</sub>H<sub>4</sub> or P<sub>4</sub> vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH<sub>4</sub>I) which on treating with KOH gives off phosphine.



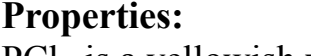
### Properties:

It is a colourless gas with rotten fish smell and is highly poisonous. It explodes in contact with traces of oxidising agents like HNO<sub>3</sub>, Cl<sub>2</sub> and Br<sub>2</sub> vapours.

It is slightly soluble in water. The solution of PH<sub>3</sub> in water decomposes in presence of light giving red phosphorus and H<sub>2</sub>. When absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.



Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g.,



**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.

## Phosphorus Halides

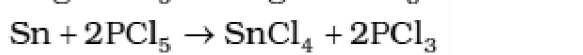
Phosphorus forms two types of halides, PX<sub>3</sub> (X = F, Cl, Br, I) and PX<sub>5</sub> (X = F, Cl, Br).

### Phosphorus Trichloride

**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.



### Properties:

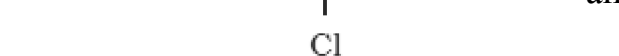
PCl<sub>5</sub> is a yellowish white powder and in moist air, it hydrolyses to POCl<sub>3</sub> and finally gets converted to phosphoric acid.



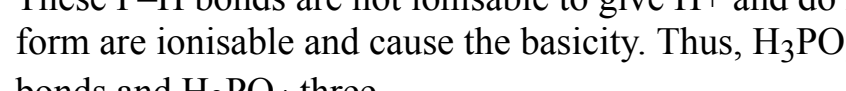
When heated, it sublimes but decomposes on stronger heating.



It reacts with organic compounds containing -OH group converting them to chloro derivatives.



The acids which contain P–H bond have strong reducing properties. Thus, hypophosphorous acid is a good reducing agent as it contains two P–H bonds and reduces, for example, AgNO<sub>3</sub> to metallic silver.



These P–H bonds are not ionisable to give H<sup>+</sup> and do not play any role in basicity. Only those H atoms which are attached with oxygen in P–OH form are ionisable and cause the basicity. Thus, H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> are dibasic and tribasic, respectively as the structure of H<sub>3</sub>PO<sub>3</sub> has two P–OH bonds and H<sub>3</sub>PO<sub>4</sub> three.

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