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 metalloidic 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, NaNO₃ (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, $Ca_9(PO_4)_6$. CaX_2 (X = F, Cl or OH) (e.g., fluorapatite $Ca_9(PO_4)_6$. CaF_2) 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 ns²np³. 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 $\Delta H_1 < \Delta H_2 < \Delta H_3$ **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 BiF₅. 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, 3HNO₂ → HNO₃ + H₂O + 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

Anomalous properties of nitrogen:

vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalence as in PF₆⁻. Nitrogen differs from the rest of the members of this group due to its small size, high electronegativity, high ionisation enthalpy and nonavailability of d orbitals. Nitrogen has unique ability to form $p\pi$ - $p\pi$ 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 $p\pi$ - $p\pi$ bonds as their atomic orbitals are so large and diffuse that they

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 $R_3P = O$ or $R_3P = CH_2$ (R = alkyl group). Phosphorus and arsenic can form $d\pi - d\pi$ bond also with transition metals when their compounds like

(i) Reactivity towards hydrogen: All the elements of Group 15 form hydrides of the type EH_3 where E = N, P, As, Sb or Bi. The hydrides show regular gradation in their properties. The stability of hydrides decreases from NH₃ to BiH₃ 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 BiH₃ is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. (ii) Reactivity towards oxygen: All these elements form two types of oxides: E_2O_3 and E_2O_5 . 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 E₂O₃ of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.

(calcium nitride) Ca₃P₂ (calcium phosphide), Na₃As₂ (sodium arsenide), Zn₃Sb₂ (zinc antimonide) and Mg₃Bi₂ (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.

acid containing potassium dichromate. It can also be obtained by the thermal decomposition of ammonium dichromate. $(NH_4)_2Cr_2O_7 \xrightarrow{Heat} N_2 + 4H_2O + Cr_2O_3$

Properties

 $6\text{Li} + \text{N}_2 \xrightarrow{\text{Heat}} 2\text{Li}_3\text{N}$ $3Mg + N_2 \xrightarrow{Heat} Mg_3N_2$ It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \Delta_f H^0 = -46.1 \text{ kJmol}^{-1}$

used as a refrigerant to preserve biological materials, food items and in cryosurgery.

Preparation:

On a large scale, ammonia is manufactured by Haber's process. $N_2(g) + 3H_2(g) = 2NH_3(g);$ $\Delta_f H^{\circ} = -46.1 \text{ kJ mol}^{-}$ 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 200×10^5 Pa (about 200 atm), a temperature of ~ 700 K and the use of a catalyst such as iron oxide with small amounts of K₂O and Al₂O₃ to increase the rate of attainment of equilibrium. Earlier, iron was used as a catalyst with molybdenum as a promoter. **Properties**

Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the formation of OH⁻ ions.

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 Cu²⁺, Ag⁺: Cu^{2+} (aq) + 4 NH₃(aq) \Rightarrow [Cu(NH₃)₄]²⁺(aq) (deep blue) (blue)

It forms ammonium salts with acids, e.g., NH₄Cl, (NH₄)₂SO₄, etc. As a weak base, it precipitates the hydroxides (hydrated oxides in case of some

 $AgCl(s) + 2NH_3(aq) \rightarrow Ag(NH_3)_2 Cl(aq)$ (colourless) (white ppt) Uses: Ammonia is used to produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate) and in

electrons as shown in the structure.

metals) of many metals from their salt solutions. For example,

 $ZnSO_4(aq) + 2NH_4OH(aq) \rightarrow Zn(OH)_2(s) + (NH_4)_2SO_4(aq)$

(white ppt)

Formula

 N_2O

NO

Oxidation

nitrogen

+ 1

+ 2

 $NH_3(g) + H_2O(l) = NH_4^+ (aq) + OH^- (aq)$

 $Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$

(colourless)

Name

Dinitrogen oxide

[Nitrogen(I) oxide]

Nitrogen monoxide

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:

[Nitrogen(III) oxide] acidic $673\,\mathrm{K}$ $2Pb(NO_3)_2$ Nitrogen dioxide NO_2 brown gas, + 4 $4NO_2 + 2PbO$ [Nitrogen(IV) oxide] acidic $2NO_2 \xrightarrow{Cool} N_2O_4$ Dinitrogen tetroxide + 4 colourless solid/ N_2O_4 liquid, acidic [Nitrogen(IV) oxide] $4\text{HNO}_3 + P_4O_{10}$ Dinitrogen pentoxide +5 colourless solid, N_2O_5 → 4HPO. + 2N.O.

[Nitrogen(V) oxide]		\rightarrow 4HPO ₃ + 2N ₂ O ₅ acidic		
ewis dot main reson	ance structures and bond	parameter	rs of oxides are g	given in Table belo
Formula	Resonance Structures		Bond Parameter	S .
(1) Nitrous oxide (N ₂ O) N ₂ O	$\vec{N} = \vec{N} = $		N = N − O	-
(2) Nitric oxide (NO)				
NO	$: \stackrel{\frown}{N} = \stackrel{\frown}{\Omega}: \longleftrightarrow \stackrel{\frown}{N} = \stackrel{\frown}{\Omega}^{r}$:N = O: N 238 pm () ,
(3) Dinitrogen trioxide			0 1	N ,
	i i i i i i i i i i i i i i i i i i i). /0:	O 105*	_{\$} 0
N_2O_3	Nn-N" →	и́— и́	150° CN N 1	14 pm
	io ö	-	121 pm	
(4) Nitrogen dioxide (NO ₂)				
NO_2	10 * Ot .	, N , Ö	O O Angular	
(5) Nitrogen dioxide		-	0	
	īġ / ġī īö)	ő:	175 pm	
N_2O_4	N-N-N	Ň- Ň	135*(N — N	
	:0: :0;	` <u>ö</u> :	Planar	
(6) Dinitrogen penta oxide	. 6			
N.O	N T IS	5 \ \sqrt{3.}	% 3 % 3 %	,0

In the laboratory, nitric acid is prepared by heating KNO₃ or NaNO₃ and concentrated H₂SO₄ in a glass retort. NaNO₃ + H₂SO₄ → NaHSO₄ + HNO₃ On a large scale it is prepared mainly by Ostwald's process. This method is based upon catalytic oxidation of NH₃ by atmospheric oxygen.

In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions. $HNO_3(aq) + H_2O(l) \rightarrow H_3O^{\dagger}(aq) + NO_3^{-}(aq)$

NO thus formed is recycled and the aqueous HNO₃ can be concentrated by distillation upto $\sim 68\%$ by mass. Further concentration to 98% can be

It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K). Laboratory grade nitric acid contains ~ 68% of the HNO₃ by mass

H₂SO₄, and phosphorus to phosphoric acid. $I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$ $C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$ $S_8 + 48HNO_3 \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$ $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

 $4Zn + 10HNO_3(dilute) \rightarrow 4 Zn (NO_3)_2 + 5H_2O + N_2O$

 $Zn + 4HNO_3(conc.) \rightarrow Zn (NO_3)_2 + 2H_2O + 2NO_2$

achieved by dehydration with concentrated H₂SO₄.

Properties

Phosphorus

Phosphine

Properties:

 $3\text{CuSO}_4 + 2\text{PH}_3 \rightarrow \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4$

 $3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCl$

Phosphorus Pentachloride

 $P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$

 $PCl_5 \xrightarrow{Heat} PCl_3 + Cl_2$

Preparation:

 $P_4 + 10Cl_2 \rightarrow 4PCl_5$

 $PH_3 + HBr \rightarrow PH_4Br$

 $[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$ (brown)

pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds. Other major uses are in the

glows in dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving PH₃.

White phosphorus is a translucent white waxy solid. It is poisonous, insoluble in water but soluble in carbon disulphide and

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

Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the

dark. It is polymeric, consisting of chains of P₄ tetrahedra linked together

Uses: The major use of nitric acid is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and

water as well as in carbon disulphide.

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

Red Phosphorous

 $P_4 + 5O_2 \rightarrow P_4O_{10}$

Properties: It is a colourless oily liquid and hydrolyses in the presence of moisture. $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

It reacts with organic compounds containing –OH group such as CH₃COOH, C₂H₅OH.

It has a pyramidal shape as shown, in which phosphorus is sp³ hybridised.

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

Finely divided metals on heating with PCl5 give corresponding chlorides. $2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$ $Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$ It is used in the synthesis of some organic compounds, e.g., C₂H₅Cl, CH₃COCl.

Polymetaphosphoric acid, (HPO₃),

 $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$ $Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$ In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO₂. $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$ (sodium hypophosphite) absorbed in HI to form phosphonium iodide (PH₄I) which on treating with KOH gives off phosphine. $PH_3+HI \longrightarrow PH_4I (+KOH) \longrightarrow KI+H_2O+PH_3$

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

It is slightly soluble in water. The solution of PH₃ in water decomposes in presence of light giving red phosphorus and H₂. When absorbed in

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_3 (X = F, Cl, Br, I) and PX_5 (X = F, Cl, Br). **Phosphorus Trichloride Preparation:** It is obtained by passing dry chlorine over heated white phosphorus. $P_4 + 6Cl_2 \rightarrow 4PCl_3$ It is also obtained by the action of thionyl chloride with white phosphorus.

Properties: PCl₅ is a yellowish white powder and in moist air, it hydrolyses to POCl₃ and finally gets converted to phosphoric acid. $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$ $POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$

When heated, it sublimes but decomposes on stronger heating.

It can also be prepared by the action of SO₂Cl₂ on phosphorus.

In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown. The three equatorial P–Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.

In the solid state it exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral and the anion, [PCl₆] octahedral. C1**Oxoacids of Phosphorus:** Phosphorus forms a number of oxoacids. The important oxoacids of phosphorus with their formulas, methods of preparation and the presence of some characteristic bonds in their structures are given in Table. Name Formula Oxidation Characteristic Preparation state of bonds and their number phosphorus H₂PO₂ Hypophosphorous +1 One P - OH white P₄ + alkali (Phosphinic) Two P - H One P = O $P_{2}O_{3} + H_{2}O$ Orthophosphorous H_2PO_3 +3 Two P - OH One P - H (Phosphonic) One P = O

One P - O - P Metaphosphoric* Three P - OH (HPO₂)_n +5 phosphorus acid Three P = OThree P - O - P sealed tube Exists in polymeric forms only. Characteristic bonds of (HPOs)3 have been given in the Table. The structures of some important oxoacids are given below:

 $H_4P_2O_6$ Four P - OH red P₄ + alkali Hypophosphoric +4 Two P = O One P - P H_3PO_4 +5 Three P - OH $P_4O_{10}+H_2O$ Orthophosphoric One P = OPyrophosphoric $H_4P_2O_7$ +5 Four P - OH heat phosphoric Two P = O

Cyclotrimetaphosphoric acid, (HPO₃)₃

 $H_4P_2O_5$ +3 Two P - OH PCl₂ + H₂PO₂ Pyrophosphorous Two P - H Two P = OThe compositions of the oxoacids are interrelated in terms of loss or gain of H₂O molecule or O-atom.

H,P,O, H₃PO₄ Orthophosphoric acid H,PO, H,PO, Pyrophosphoric acid Orthophosphorous acid Hypophosphorous acid

and phosphine. $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

In oxoacids phosphorus is tetrahedrally surrounded by other atoms. All these acids contain at least one P=O bond and one P-OH bond. The oxoacids in which phosphorus has lower oxidation state (less than +5) contain, in addition to P=O and P-OH bonds, either P-P (e.g., in $H_4P_2O_6$) or P-H (e.g., in H₃PO₂) bonds but not both. These acids in +3 oxidation state of phosphorus tend to disproportionate to higher and lower oxidation states. For example, orthophophorous acid (or phosphorous acid) on heating disproportionates to give orthophosphoric acid (or phosphoric acid)

four, nitrogen cannot form $d\pi - p\pi$ bond as the heavier elements can e.g., $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

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⁻¹) is very high. On the contrary, phosphorus, arsenic and antimony form single bonds as P–P, As–As

(iii) Reactivity towards halogens: These elements react to form two series of halides: EX₃ and EX₅. 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 NF₃ is known to be stable. Trihalides except BiF₃ 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, Ca₃N₂

 $NH_4CI(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl (aq)$ Small amounts of NO and HNO3 are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide. $Ba(N_3)_2 \rightarrow Ba + 3N_2$

Dinitrogen is a colourless, odourless, tasteless and non-toxic gas. Nitrogen atom has two stable isotopes: 14N and 15N. It has a very low solubility in water (23.2 cm³ 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:

Dinitrogen combines with dioxygen only at very high temperature (at about 2000 K) to form nitric oxide, NO. $N_2 + O_2(g) \rightarrow 2NO(g)$ 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

Ammonia Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea. $NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$ On a small scale ammonia is obtained from ammonium salts which decompose when treated with caustic soda or calcium hydroxide. $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$ $(NH_4)_2 SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$

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

(white ppt) FeCl₃ aq NH₄OH aq $Fe_2O_3.x H_2O_S$ NH₄Cl aq

Common

preparation

 $N_2O + 2H_2O$

 $2NaNO_2 + 2FeSO_4 + 3H_2SO_4$

 $NH_4NO_9 \xrightarrow{Heat}$

the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid. Liquid ammonia is also used as a refrigerant. Table : Oxides of Nitrogen

Physical

colourless gas,

colourless gas,

neutral

[Nitrogen(II) oxide] neutral \rightarrow Fe₂(SO₄)₃ + 2NaHSO₄ $+2H_{2}O + 2NO$ $2NO + N_2O_4 \xrightarrow{250 \text{ K}} 2N_2O_3$ blue solid, Dinitrogen trioxide N_2O_3 + 3

$N_{2}O$ $(2) \text{ Nitric oxide (NO)}$ NO $: \hat{N} = O: \longrightarrow \hat{N} = O:$ $(3) \text{ Dinitrogen trioxide}$ $N_{2}O_{3}$ $(4) \text{ Nitrogen dioxide (NO}_{2})$ NO_{2} $(5) \text{ Nitrogen dioxide}$ $N_{2}O_{4}$ $(6) \text{ Dinitrogen penta oxide}$ $N_{2}O_{5}$ $N = O: N =$		
NO $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ (3) Dinitrogen trioxide $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0: \longrightarrow \hat{N} = 0F $ $: \hat{N} = 0: \longrightarrow \hat{N} = 0: \longrightarrow \hat{N} = 0.$ $: \hat{N} = 0: \longrightarrow \hat{N} = 0: \longrightarrow \hat{N} = 0.$ $: \hat{N} = 0: \longrightarrow \hat{N} = 0: \longrightarrow \hat{N} = 0.$ $: \hat{N} = 0: \longrightarrow \hat{N} = 0: \longrightarrow \hat{N} = 0.$ $: \hat{N} = 0: \longrightarrow \hat{N} = 0: \longrightarrow \hat{N} = 0.$ $: N$	(1) Nitrous oxide (N ₂ O) N_2 O $: N = N = 0$: $N = N = N = N = N = N = N = N = N = N $	N = N 119 pm O
(3) Dinitrogen trioxide $ \begin{array}{cccccccccccccccccccccccccccccccccc$	(2) Nitric oxide (NO)	
N_2O_3 N_2O_3 N_2O_3 N_1O_2 N_2O_4 N_2O_4 N_2O_4 N_2O_5 N_2O_5 N_2O_5 N_1O_2 N_2O_5 N_1O_2 N_2O_5 N_2O_5 N_1O_2 N_2O_5 N_2O_5 N_2O_5 N_1O_2 N_2O_5 N_2O_5 N_1O_2 N_2O_5 N_1O_2 N_2O_5 N_2O_5 N_1O_2 N_2O_5 N_1O_2 N_1O_2 N_1O_2 N_1O_3 N_1O_4 N_1O_4 N_1O_4 N_1O_5 N_1O_4 N_1O_5 N_1O_4 N_1O_5 N	NO $: \vec{N} = \vec{Q}: \longleftrightarrow \vec{N} = \vec{Q}.$:N = O: N 238 pm O
$N_{2}O_{3}$ $N_{2}O_{3}$ $N_{2}O_{3}$ $N_{3}O_{4}$ $N_{2}O_{4}$ $N_{2}O_{5}$ $N_{3}O_{4}$ $N_{2}O_{5}$ $N_{3}O_{4}$ $N_{2}O_{5}$ $N_{3}O_{4}$ $N_{3}O_{5}$ $N_{4}O_{5}$ $N_{5}O_{6}$ $N_{5}O_{7}$ $N_{7}O_{7}$ $N_{7}O_{7}$ $N_{7}O_{7}O_{7}$ $N_{7}O_{7}O_{7}$ $N_{7}O_{7}O_{7}$ $N_{7}O_{7}O_{7}O_{7}$ $N_{7}O_{7}O_{7}O_{7}O_{7}$ $N_{7}O_{7}O_{7}O_{7}O_{7}O_{7}O_{7}O_{7}O$	(3) Dinitrogen trioxide	0 ····· N
NO ₂ $ \begin{array}{ccccccccccccccccccccccccccccccccccc$	N_2O_3 \longrightarrow $N-N$	150° N 114 pm
$N_{2}O_{4}$ $N_{2}O_{4}$ $N_{2}O_{5}$ $N_{3}O_{5}$ $N_{4}O_{5}$ $N_{5}O_{5}$ $N_{$	$NO_2 \qquad \qquad NO_2$	0 134 0
$N_2O_5 \qquad \begin{array}{c c} \ddot{O} & \ddot{O} $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	136°(N — N
N_2O_5 N		
	N_2O_5	

Nitric Acid Nitrogen forms oxoacids such as H₂N₂O₂ (hyponitrous acid), HNO₂ (nitrous acid) and HNO₃ (nitric acid). Amongst them HNO₃ is the most important. **Preparation:** $4NH_{3}\left(g\right)+5O_{2}\left(g\right)\xrightarrow{Pt/Rhgauge catalyst} 4NO\left(g\right)+6H_{2}O\left(g\right)$ (from air) Nitric oxide thus formed combines with oxygen giving NO₂. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ Nitrogen dioxide so formed, dissolves in water to give HNO₃. $3NO_2(g) + H_2O(1) \rightarrow 2HNO_3(aq) + NO(g)$

and has a specific gravity of 1.504.

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. $4Zn + 10HNO_3(dilute) \rightarrow 4 Zn (NO_3)_2 + 5H_2O + N_2O$ $Zn + 4HNO_3(conc.) \rightarrow Zn (NO_3)_2 + 2H_2O + 2NO_2$ Zinc reacts with dilute nitric acid to give N_2O and with concentrated acid to give NO_2 .

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

 $)_{130^{\circ}}$ In the gaseous state, HNO₃ exists as a planar molecule with the structure as shown.

Brown Ring Test: The familiar brown ring test for nitrates depends on the ability of Fe2+ to reduce nitrates to nitric oxide, which reacts with Fe2+ 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. $NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$

 $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$ (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 P4 molecule where the angles are only 60° . It readily catches fire in air to give dense white fumes of P_4O_{10} .

It consists of discrete tetrahedral P₄ molecule as shown in figure.

prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

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

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.,

pickling of stainless steel, etching of metals and as an oxidiser in rocket fuels.

When pure, it is non inflammable but becomes inflammable owing to the presence of P2H4 or P4 vapours. To purify it from the impurities, it is

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

 $\mathrm{P_4} + 8\mathrm{SOCl}_2 \rightarrow 4\mathrm{PCl}_3 + 4\mathrm{SO}_2 + 2\mathrm{S}_2\mathrm{Cl}_2$

 $C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$ $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

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

 $3\text{CH}_3\text{COOH} + \text{PCl}_3 \rightarrow 3\text{CH}_3\text{COCl} + \text{H}_3\text{PO}_3$

 $3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$

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, AgNO₃ to metallic silver. 4 AgNO $_3$ + 2H $_2$ O + H $_3$ PO $_2$ \rightarrow 4Ag + 4HNO $_3$ + H $_3$ PO $_4$

These P-H bonds are not ionisable to give H+ 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_3PO_3 and H_3PO_4 are dibasic and tribasic, respectively as the structure of H_3PO_3 has two P-OH bonds and H₃PO₄ three.