CHAPTER / 07

Group 15 Elements: Nitrogen Family

Topics Covered

- Occurrence
- Physical Properties
- Chemical Properties
- Dinitrogen (N_2)
- Ammonia (NH_3)
- Nitric Acid
- Oxides of Nitrogen
- Phosphorus
- Phosphine
- Phosphorus Halides
- Oxoacids of Phosphorus

Group VA consists of 5 elements, namely, **nitrogen** (N), **phosphorus** (P), **arsenic** (As), **antimony** (Sb) and **bismuth** (Bi). These elements are collectively called **pnicogens** (taken from Greek word *'pniomigs'* meaning suffocating) and their compounds are called **pniconides.**

Occurrence

Nitrogen constitutes about 78% (by volume) of atmosphere and is therefore, the most common gas. Phosphorus is the only element that does not occur in free state. It is usually found as phosphate. Nitrogen in combined state, is found as nitrates or in proteins and amino acids. The rest of the elements occur as sulphides or oxides. P is the eleventh most abundant element in the earth's crust.

Physical Properties

Different physical properties of group 15 elements and their trends are given below:

1. Electronic Configuration

The valence shell electronic configuration of these elements is $ns^2\ np^3$ (n = number of shells), i.e. *s*-orbital is fully filled, while *p*-orbital is half-filled in order to make it extra stable.

Electronic configuration of group 15 elements

Elements	Atomic number	Atomic mass	Electronic configuration
Nitrogen (N)	7	14	$[\mathrm{He}]2s^2, 2p^3$
Phosphorus (P)	15	31	$[\mathrm{Ne}]3s^2, 3p^3$
Arsenic (As)	33	75	$[\mathrm{Ar}]3d^{10}4s^2, 4p^3$
Antimony (Sb)	51	122	$[\mathrm{Kr}]4d^{10}5s^2, 5p^3$
Bismuth (Bi)	83	209	$[\mathrm{Xe}]4f^{14}5d^{10}6s^2, 6p^3$

2. Atomic and Ionic Radii

On moving down the group, as the atomic number increases the atomic radii increases due to increase in number of shells.

However, from Sb to Bi only small increase in covalent radius is observed. It is due to the presence of completely filled *d*-and/or *f*-orbitals in heavier members.

3. Ionisation Enthalpy

Ionisation enthalpy of group 15 elements is much more than that of group 14 elements in the respective period due to smaller atomic radii and extra stable electronic configuration of half-filled orbital.

On moving down the group, ionisation enthalpy decreases from N to Bi due to gradual increase in atomic radii and shielding effect.

4. Electronegativity

It decreases down the group from N to Bi indicating a gradual change from non-metallic to metallic character. These elements are more electronegative as compared to the elements of 14th group.

5. Atomicity

All the elements of this group are polyatomic. Nitrogen (dinitrogen) is a diatomic gas, while other members are solids of different atomicity .

6. Metallic Character

Metallic character increases down the group due to increase in the atomic size and decrease in ionisation enthalpy. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids and bismuth is a metal.

7. Melting Point

On moving down the group, the melting point first increases from N to As (because of the increase in atomic size) and then decreases upto Sb and Bi because of their tendency to form three covalent bonds instead of five covalent bonds due to inert pair effect.

This results in weakening of the attraction among their atoms thereby lowering their melting points.

8. Boiling Point

Boiling point in general increases from top to bottom due to increase in their atomic size. But NH_3, exceptionally, has more boiling point than PH_3 due to hydrogen bonding.

9. Allotropy

All elements tend to show allotropy except bismuth.

Chemical Properties

1. Oxidation States

The common oxidation states of group 15 elements are -3, $+3$ and $+5$. The tendency to show -3 oxidation state decreases down the group due to increase in atomic size and metallic character.

2. Disproportionation

Nitrogen shows $+1, +2, +4$ 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.

3. Reactivity towards Hydrogen

These elements form volatile hydrides with the formula EH_3 (where E = N, P, As, Sb, Bi). On moving down the group, thermal stability decreases from NH_3 to BiH_3 due to increase in the size and the bond length.

Reducing character increases down the group due to decrease in bond dissociation enthalpy.

The reducing character is as follows:

$$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$$

Basic character decreases down the group due to increase in atomic size. These hydrides are Lewis bases due to the presence of lone pair of electrons on the central atom. Order of basic character is :

$$NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$$

4. Reactivity towards Halogens (Formation of Halides)

These elements directly combine with halogen to form trihalides (EX_3) and pentahalides (EX_5). All trihalides are stable (except those of nitrogen, i.e. NBr_3 and NI_3) and have pyramidal shape.

In case of nitrogen, only NF_3 is known to be stable. Pentahalides involve sp^3d-hybridisation and have trigonal bipyramidal shape.

5. Reactivity towards Oxygen

All elements form oxides of type R_2O_3 and R_2O_5. Besides N, P, Sb and Bi also form dioxides of formula RO_2.

The stability of pentaoxides follows the order :

$$P_2O_5 > As_2O_5 > Sb_2O_5 > N_2O_5 > Bi_2O_5$$

6. Reaction with Sulphur

Except nitrogen, all other elements of group 15 react with sulphur to form sulphides. On going down the group, stability of sulphides increases due to increase in electropositive character.

7. Reactivity towards Metals

(Formation of Binary Compounds)

These elements react with metals to form their binary compounds exhibiting –3 oxidation state, e.g. Ca_3N_2, Ca_3P_2, Na_3As, Zn_3Sb_2 and Mg_3Bi_2, etc.

8. Formation of Oxyacids

All elements (except Bi) of this group form oxyacids. Nitrogen forms two important oxyacids, i.e. nitrous acid (HNO_2) and nitric acid (HNO_3). Phosphorus forms a large number of oxyacids like H_3PO_3 (phosphorus acid) (*ortho*-phosphoric acid) H_3PO_4, (pyrophosphoric acid) $H_4P_2O_7$, HPO_3 (metaphosphoric acid) etc. Arsenic forms H_3AsO_3 (arsenious acid) and H_3AsO_4 (arsenic acid). Antimony forms unstable H_3SbO_3 and bisumth forms stable $HBiO_3$ (metabismuthic acid).

Anomalous Behaviour of Nitrogen

Nitrogen, because of its small size, high electronegativity, high ionisation energy, non-availability of *d*-orbitals and capacity of $p\pi$- $p\pi$ multiple bond formation shows properties that are quite different from the other members of the group.

These properties are as follows :

(i) Nitrogen is a gas, while other members are found in solid state.

(ii) Nitrogen exists in diatomic form, while other elements like phosphorus, arsenic and antimony exist as tetra-atomic molecules (P_4, As_4, Sb_4).

(iii) Nitrogen forms trinegative ion, i.e. N^{3-} while other members do not.

(iv) Nitrogen is chemically inert under ordinary conditions due to high bond dissociation energy, while other members are quite reactive because of the presence of single bond in their molecules.

(v) Nitrogen does not show pentacovalency due to non-availability of *d*-orbitals, while it is shown by all other elements.

(vi) The hydride of nitrogen (NH_3) is highly basic in nature, while the hydrides of other elements are slightly basic. Moreover, only hydrides of nitrogen shows H-bonding, while those of other members do not.

(vii) Nitrogen forms oxides of five types (i.e. N_2O, NO, N_2O_3, N_2O_4 and N_2O_5) while other members of the family form oxides of only two types (i.e. tri and pentaoxides).

(viii) Except NF_3, other halides of nitrogen i.e. NCl_3, NBr_3 and NI_3 are unstable, while the halides of other elements are fairly stable.

(ix) Nitrogen does not form complexes due to the non-availability of *d*-orbitals, while other members have a tendency of complex formation, e.g. $[PCl_6]^-$, $[AsCl_6]^-$ etc.

Dinitrogen (N_2)

It is the molecular form of elemental nitrogen and is chemically inert.

Preparation

It is prepared in laboratory by heating an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4Cl\,(aq) + NaNO_2(aq) \xrightarrow{\text{Heat}} N_2(g) + NaCl(aq) + 2H_2O(l)$$

NO and HNO_3 are also formed in this reaction as impurities in very small amounts which can be removed by passing the gas in *aq*. H_2SO_4 containing potassium dichromate ($K_2Cr_2O_7$).

- It can also be prepared by heating ammonium dichromate.

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

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

$$Ba(N_3)_2 \longrightarrow Ba + 3N_2$$

- Commercially, N_2 is produced by liquefaction and fractional distillation of air.

Physical Properties

(i) Nitrogen is a colourless, tasteless, odourless gas and non-toxic gas.

(ii) It is sparingly soluble in water.

(iii) Liquid nitrogen is colourless and boils at $-195.8°$ C.

(iv) It has a low freezing point of 77.2 K.

(v) Naturally occurring nitrogen consists of two isotopes N^{14} and N^{15}.

Chemical Properties

(i) Due to high bond enthalpy of $N \equiv N$ bond (946 kcal/mol), dinitrogen is inert at room temperature. However, reactivity increases rapidly with rise in temperature.

(ii) At higher temperatures, it combines with some metals (like lithium, calcium, magnesium, etc.) and forms ionic nitrides and with non-metals, it forms covalent nitrides.

$$3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$$

$$6Li + N_2 \xrightarrow{\Delta} 2Li_3N$$

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

$$N_2 + 3H_2 \overset{773K}{\rightleftharpoons} 2NH_3(g)\ ;\quad \Delta_f H^\circ = -46.1\ \text{kJ mol}^{-1}$$

(iv) It also combines with dioxygen at about 2000 K to form nitric oxide (NO).

$$N_2 + O_2(g) \xrightarrow{\text{Heat}} 2NO(g)$$

(v) When N_2 combines with CaC_2, the product is calcium cynamide, $CaCN_2(CaNCN)$ as :

$$CaC_2 + N_2 \longrightarrow CaNCN + C$$

(The reaction takes place at 1000°C in the current of N_2.)

Uses of Dinitrogen

(i) It is used in the manufacture of ammonia and other nitrogen containing chemicals, e.g. calcium cyanamide.

(ii) Liquid dinitrogen is used as a refrigerant to preserve biological materials and food items.

(iii) It is used to produce inert atmosphere in industries.

(iv) It is used in cryosurgery.

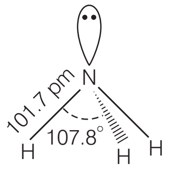
Ammonia (NH_3)

It is present in very small amounts in air and soil, where it is formed by the decay of nitrogenous organic matter such as urea.

$$NH_2CONH_2 + 2\,H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + CO_2 + H_2O$$

Structure

In ammonia, nitrogen atom is sp^3-hybridised. 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 figure below :



Structure of ammonia

Methods of Preparation

(i) NH_3 is prepared on industrial scale by **Haber's process** which involves the direct combination of N_2 and H_2 according to the equation :

$$N_2 + 3H_2 \text{ ”} \ 2NH_3;\ \Delta_f H^\circ = -46.1\ \text{kJ/mol}$$

The reaction is reversible, exothermic and proceeds with a tremendous decrease in volume.

Thus, it requires **low temperature** and **high pressure** for a better yield of ammonia (according to Le-Chatelier's principle) alongwith highly porous finely divided iron containing small amount of promotors (Mo or oxides of K and Al).

(ii) It can also be prepared by decomposing ammonium salts with caustic alkalies or lime. In laboratory, it is prepared by heating with slaked lime.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + H_2O + 2NH_3$$

Ammonia obtained, cannot be dried over concentrated sulphuric acid, calcium chloride or phosphorus pentoxide as the gas reacts with these substances. However, quicklime can be used.

(iii) It is also prepared by the hydrolysis of calcium cyanamide with superheated steam at 450 K.

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3 \uparrow$$

Physical Properties

(i) It is a colourless gas with a pungent odour. Freezing and boiling points of ammonia are 198.4 and 239.7 K, respectively.

(ii) Due to hydrogen bonding, NH_3 has higher melting and boiling points than expected for a compound of similar molecular mass.

Chemical Properties

(i) Ammonia burns in oxygen with a greenish-yellow flame as,

$$4NH_3 + 3O_2 \xrightarrow{\Delta} 2N_2 + 6H_2O$$

(ii) When electric spark is passed over a mixture of NH_3 and O_2, it gets exploded and if the temperature is 500°C and Pt gauze is present as catalyst, the following reaction occurs.

$$4NH_3 + 5O_2 \xrightarrow[\text{Electric spark, Pt gauze}]{500^\circ C} 4NO + 6H_2O$$

(iii) It acts as a reducing agent and reduces metallic oxides, like CuO and PbO to metals and itself gets oxidised to N_2,

e.g. $3CuO + 2NH_3 \longrightarrow 3Cu + 3H_2O + N_2$

(iv) With calcium, it forms calcium hydride and nitrogen.

$$2NH_3 + 3Ca \longrightarrow 3CaH_2 + N_2 \uparrow$$

(v) It reacts with conc. HCl and produces white fumes of ammonium chloride.

$$NH_3 + HCl \longrightarrow NH_4Cl$$

(vi) When heated with alkali metals and barium, amides are obtained.

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2$$

(vii) With chlorine, it forms NH_4Cl and nitrogen gas.

$$\underset{\text{Excess}}{8NH_3} + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

However, if chlorine is in excess, the following reaction occurs

$$NH_3 + \underset{\text{Excess}}{3Cl_2} \longrightarrow \underset{\text{(Explosive)}}{NCl_3} + 3HCl$$

(viii) Aqueous ammonia contains uncombined ammonia (46.2%), hydrated ammonia ($H_3N...HOH$, 52.4%) and relatively few (1.4%) NH_4^+ and OH^- ions. It precipitates many metallic hydroxides from their salt solutions. In some cases, the precipitated hydroxides dissolve in excess ammonia and form complex amines.

$$CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2\downarrow + (NH_4)_2SO_4$$

$$Cu(OH)_2 + 4NH_3 \longrightarrow [Cu(NH_3)_4](OH)_2$$

(ix) It gives yellow-brown colour or precipitate with Nessler's reagent (i.e. alkaline K_2HgI_4)

$$\underbrace{2K_2HgI_4 + 3KOH}_{\text{Nessler's reagent}} + NH_3 \longrightarrow \underset{\substack{\text{Iodide of Millon's base}\\ \text{(yellow-brown)}}}{H_2NHgOHgI} + 7KI + 2H_2O$$

(x) It gives yellow precipitate of ammonium chloroplatinate with chloroplatinic acid.

$$2NH_4Cl + H_2PtCl_6 \text{ ”} (NH_4)_2PtCl_6 + 2HCl$$

Liquid ammonia is an excellent ionising solvent. It ionises as shown below.

$$2NH_3 \text{ ”} NH_4^+ + NH_2^-$$

Alkali metals and to a lesser extent Ca, Sr and Ba dissolve in it and deep blue solutions are obtained. These deep blue solutions are excellent reducing agents and are electrical conductors due to the presence of solvated electrons.

Uses

(i) It is used for the manufacture of other reagents like HNO_3 (Ostwald's process), $NaHCO_3$ (Solvay process), $(NH_4)_2SO_4$, etc.

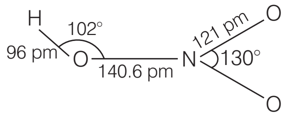
(ii) It is used as a cleansing agent for removing greese.

(iii) It is used as a refrigerant.

(iv) It is also used for the synthesis of urea, an excellent fertilizer.

Nitric Acid (HNO_3)

In gaseous state, HNO_3 exists as a planar molecule with the structure as shown below:



Structure of nitric acid

Methods of Preparation

1. In the **laboratory,** it is prepared by heating $NaNO_3$ or KNO_3 with conc. H_2SO_4. Reddish brown vapours of HNO_3 so produced, are condensed in a water-cooled receiver.

$$NaNO_3 + H_2SO_4(\text{conc.}) \longrightarrow NaHSO_4 + HNO_3$$

2. **On a large scale,** the acid is generally prepared by **Ostwald's process** which consists of the following steps :

***Step* 1** NH_3 (N = –3) obtained by Haber's process is oxidised to NO (N = +2) by atmospheric O_2 (free from dust) in the presence of platinum-gauze catalyst electrically heated at 750 – 900° C

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O\ (\Delta H = -90.0 \text{ kJ})$$

Since, the reaction is exothermic, heat generated in the reaction maintains the temperature for the catalyst.

***Step* 2** NO produced as above is oxidised by atmospheric O_2 to NO_2 which is cooled to about 50°C and then absorbed in water (in the presence of air) to give HNO_3.

$$2NO + O_2 \longrightarrow 2NO_2$$

$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

(The usual concentrated nitric acid contains 98% HNO_3 and its specific gravity = 1.5).

Physical Properties

(i) It is a colourless liquid (f.p. 231.4K and b.p 355.6 K) in its pure form and becomes yellow due to the presence of NO_2 as an impurity.

(ii) Laboratory grade nitric acid contains ~ 68 % of HNO_3 by mass and has a specific gravity of 1.504.

(iii) It is soluble in water in all proportions.

Chemical Properties

(i) **Acidic Properties** Nitric acid behaves as a strong acid producing nitrate and hydronium ions in an aqueous solution.

$$HNO_3(aq) + H_2O\ (l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

(ii) Nitric acid is a very strong oxidising agent which attacks on many metals except noble metals such as gold and platinum.

The products of oxidation depend upon the concentration of acid, temperature and nature of material undergoing oxidation.

Oxidation of some compounds are as follows :

(a) Iodide (I^-) to iodine (I_2)

$$2KI + 4HNO_3 \longrightarrow I_2 + 2NO_2 + 2H_2O + 2KNO_3$$

(b) Lead sulphide (PbS) to lead sulphate ($PbSO_4$)

$$8HNO_3 + 3PbS \longrightarrow 3PbSO_4 + 4H_2O + 8NO$$

(c) Hydrogen sulphide (H_2S) to sulphur (S)

$$2HNO_3 + H_2S \longrightarrow 2NO_2 + 2H_2O + S$$

(iii) **Reaction with Copper and Zinc** Cu reacts with dilute HNO_3 to give NO and with conc. HNO_3 to give NO_2.

$$3Cu + 8HNO_3(dil.) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3(conc.) \longrightarrow Cu\,(NO_3)_2 + 2NO_2 + 2H_2O$$

Zinc reacts with dil. HNO_3 to give N_2O and with conc. HNO_3 to give NO_2.

$$4Zn + 10\,HNO_3(dil.) \longrightarrow 4Zn\,(NO_3)_2 + 5H_2O + N_2O$$

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

(iv) **Reaction with Carbon, Sulphur, Phosphorus** Concentrated nitric acid also oxidises non-metals and their compounds, e.g. iodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to sulphuric acid (H_2SO_4) and phosphorus to phosphoric acid (H_3PO_4).

$$I_2 + 10\,HNO_3 \longrightarrow 2HIO_3 + 10\,NO_2 + 4H_2O$$

$$C + 4\,HNO_3 \longrightarrow CO_2 + 2H_2O + 4\,NO_2$$

$$S_8 + 48\,HNO_3 \longrightarrow 8H_2SO_4 + 48\,NO_2 + 16H_2O$$

$$P_4 + 20\,HNO_3 \longrightarrow 4H_3PO_4 + 20\,NO_2 + 4H_2O$$

(v) **Reaction with Noble Metals** Noble metals like gold and platinum do not react with nitric acid. However, they dissolve in *aqua-regia* forming respective chlorides.

$$Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$$

$$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$

(vi) **Reaction with Iron** Iron reacts with cold and dilute nitric acid to produce ferric nitrate and nitrogen dioxide.

$$Fe + 6HNO_3 \longrightarrow Fe(NO_3)_3 + 3NO_2\uparrow + 3H_2O$$

(vii) **Brown Ring Test for Nitrates** This test depends on the ability of Fe^{2+} to reduce nitrates to nitric oxide which reacts with Fe^{2+} to form a brown coloured complex. This test is usually carried out by adding freshly prepared dilute ferrous sulphate to an aqueous solution containing nitrate ions, followed by careful addition of conc. H_2SO_4 along the sides of the test tube so that separate layer of brown ring at the interface between the solution and sulphuric acid is formed. Brown ring, thus formed indicates the presence of nitrate ions in solution.

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe\,(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{(Brown ring)}}{[Fe\,(H_2O)_5(NO)]^{2+}} + H_2O$$

Uses

Nitric acid is used:

(i) as a laboratory reagent and for preparing *aqua-regia.*
(ii) as strong oxidising agent.
(iii) to clean noble metals such as Au, Ag, Pt.
(iv) to make explosive materials such as TNT, picric acid, gun-cotton, etc.
(v) in making of colour, perfume, artificial fibre, etc.
(vi) for the manufacture of fertilizers.

Oxides of Nitrogen

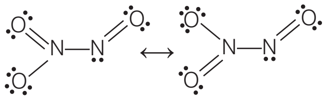
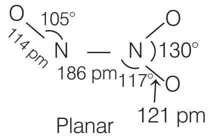
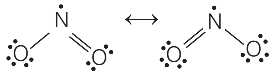
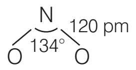
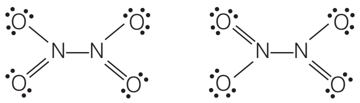
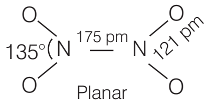
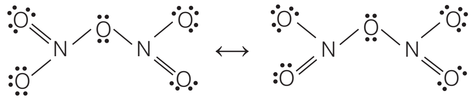
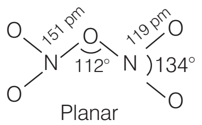
Nitrogen forms a number of oxides in different oxidation states. The preparation and properties of these oxides can be summarised as :

Preparation and Properties of Various Oxides of Nitrogen

Formula	Name	Preparation	Properties
N_2O	Nitrous oxide or laughing gas	$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$	Colourless gas, rather unreactive.
NO	Nitrogen monoxide (Nitric oxide)	$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$	Colourless gas, reactive, paramagnetic.
NO_2	Nitrogen dioxide	$Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$	Brown gas, reactive, paramagnetic.
N_2O_3	Dinitrogen trioxide or nitrous anhydride	$2NO + N_2O_4 \longrightarrow 2N_2O_3$	Dark blue in the liquid or solid state, unstable in the gas phase.
N_2O_4	Dinitrogen tetroxide (mixed anhydride of N_2O and NO)	$2NO_2 \underset{\text{heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4$	Colourless, exists in equilibrium with NO_2 in both the gaseous and liquid state.
N_2O_5	Dinitrogen pentoxide	$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$	Unstable as gas; in the solid state exists as $[NO_2]^+[NO_3]^-$.

Lewis dot resonance structures and bond parameters of some oxides of nitrogen are given in following table :

Resonance Structures and Bond Parameter of Oxides of Nitrogen

Formula	Resonance Structure	Bond Parameters
N_2O		N—N—O 113 pm 119 pm Linear
NO		N—O 115 pm
N_2O_3		 Planar
NO_2		 Angular
N_2O_4		 Planar
N_2O_5		 Planar

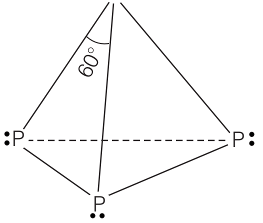
Phosphorus

It is the second member of the nitrogen family. Its atomic number is 15 and electronic configuration is $1s^2, 2s^2\ 2p^6,\ 3s^2\ 3p^3$. It is widely distributed in nature and does not occur in free state.

Allotropes of Phosphorus

1. White Phosphorus

White P is a waxy translucent solid, readily soluble in CS_2. Below 800° C, its vapour density corresponds to formula P_4, while above 800° C, it dissociates to P_2. It melts at 44.1° C and boils at 280° C. Its ignition temperature is very low. When exposed to air, it undergoes oxidation which gradually raises its temperature and ultimately, it catches fire when temperature exceeds 30° C. That's why, it is always kept in water. Being extremely poisonous, it proves fatal if taken internally. P glows in dark on account of its slow oxidation (phosphorescence). It is readily soluble in turpentine oil and ether. Its structure in P_4 form can be seen as :

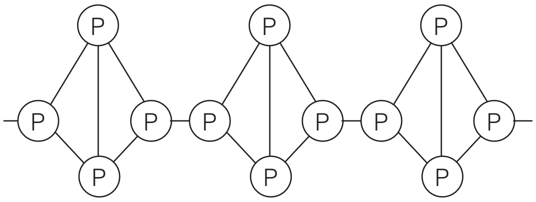


Tetrahedral phosphorus molecule

2. Red Phosphorus

Red phosphorus is obtained by heating white phosphorus at 573 K 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, non-poisonous and insoluble in water as well as in carbon disulphide.

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_4 tetrahedral linked together in the manner as shown in figure :



Red phosphorus

3. Black Phosphorus

It is the most stable allotrope of phosphorus. It has two forms namely, α-black phosphorus and β -black phosphorus. α-black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K.

It can be sublimed in air and has opaque monoclinic or rhombohedral crystals. It has layered structure in which each P atom is covalently bonded to 3 neighboursing P atoms. It does not oxidise in air.

$$\text{Red phosphorus} \xrightarrow{803\text{ K}} \alpha\text{-black phosphorus}$$

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

$$\text{White phosphorus} \xrightarrow[12000\text{ atm}]{473\text{ K}} \beta\text{-black phosphorus}$$

Phosphine (PH_3)

Phosphine is a flammable and toxic gas which has significant industrial application.

Preparation

(i) In the laboratory, it is prepared by heating white phosphorus with concentrated sodium hydroxide solution in an inert atmosphere of CO_2.

$$P_4 + 3NaOH + 3H_2O \xrightarrow{\text{D, }CO_2} PH_3\uparrow + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2}$$

(ii) It is also prepared by the reaction of calcium phosphide with water or dil. HCl.

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$
$$Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$$

Physical Properties

(i) It is colourless, highly reactive and extremely toxic gas with a slight smell of garlic or rotten fish.

(ii) It liquefies at – 89°C and solidifies at –134°C.

(iii) It is highly poisonous in nature.

Chemical Properties

(i) Its solution in water decomposes in the presence of light giving red phosphorus and H_2.

$$4PH_3(aq) \xrightarrow{h\nu} \underset{\text{Red phosphorus}}{P_4} + 6H_2(g)$$

(ii) It is absorbed in copper sulphate solution or mercuric chloride solution to form corresponding phosphides.

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$
$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$$

(iii) It is weakly basic like ammonia and gives phosphonium compounds with acids.

$$PH_3 + HBr \longrightarrow PH_4Br$$

(iv) Phosphine reacts with chlorine to produce phosphonium chloride.

$$PH_3 + 4Cl_2 \xrightarrow{30°C} PCl_5 + 3HCl$$

(v) PH_3 is a better reducing agent than NH_3 and reduces

(a) Ag^+ to Ag metal as

$$8Ag^+ + PH_3 + 4H_2O \longrightarrow H_3PO_3 + 8Ag\downarrow + 8H^+$$

(b) Cu^{2+} to Cu metal as

$$4Cu^{2+} + PH_3 + 4H_2O \longrightarrow H_3PO_4 + 4Cu\downarrow + 8H^+$$

(vi) A pure sample of phosphine is not spontaneously inflammmable. It burns in air or oxygen when heated at 150°C.

$$2PH_3 + 4O_2 \xrightarrow{\Delta} P_2O_5 + 3H_2O$$

However, white smoke (vortex rings) is formed, if PH_3 comes in contact with air. This is because of the formation of vortex ring of P_2O_5 due to impurity of P_2H_4 (diphosphine).

Uses of Phoshine

(i) It is used in *Holme's signals.*

(ii) It is used in *smoke screens.*

(iii) For making metallic phosphides.

Phosphorus Halides

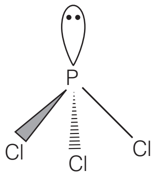
Phosphorus forms two types of halides PX_3 (X = F, Cl, Br and I) and PX_5 (X = F, Cl and Br).

Phosphorus Trichloride (PCl_3)

It is an important industrial chemical used for preparation of other chemicals and as pesticides, plasticiser, flame retardant, etc.

Structure of Phosphorus Trichloride

It has pyramidal shape due to the presence of one lone pair of electron and bond angle of 100°. Phosphorus is sp^3-hybridised.



Preparation

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

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

(ii) It is also obtained by the reaction of P_4 with $SOCl_2$.

$$\underset{\text{White phosphorus}}{P_4} + \underset{\text{Thionyl chloride}}{8SOCl_2} \longrightarrow 4PCl_3 + 4SO_2 + \underset{\text{Sulphur monochloride}}{2S_2Cl_2}$$

Properties

(i) It is a colourless oily liquid and gets hydrolysed in the presence of moisture forming phosphorus acid and fumes of HCl.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

(ii) It reacts with organic compounds having —OH group, e.g. CH_3COOH, C_2H_5OH and forms their chloride compounds.

$$3\ CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$

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

Phosphorus Pentachloride

Its formula is PCl_5.

Method of Preparation

It is prepared either by passing dry Cl_2 gas (in excess) over PCl_3 or by the action of SO_2Cl_2 on P_4 or PCl_3.

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

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

Physical Properties

It is yellowish white crystalline compound with a sharp odour, m.p. – 45°C (under pressure) and sublimation temperature 160°C.

Chemical Properties

(i) It gets hydrolysed to $POCl_3$ in moist air which finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \longrightarrow \underset{\text{Phosphoric acid}}{H_3PO_4} + 3HCl$$

(ii) When heated, it sublimes but decomposes on strong heating.

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$$

(iii) It converts organic compounds like alcohols, acids, aldehydes to halides.

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

$$CH_3CHO + PCl_5 \longrightarrow CH_3CHCl_2 + POCl_3$$

(iv) Finely divided metals also react with PCl_5 to form corresponding chlorides.

$$2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$$

$$Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3$$

Uses

(i) It is used in the synthesis of some organic compounds, e.g. C_2H_5Cl, CH_3COCl, etc.

(ii) It is used as a chlorinating agent in organic chemistry.

Oxoacids of Phosphorus

Phosphorus forms a number of oxoacids. There are two types of oxoacids, one having P in +1 or +3 oxidation state, i.e. phosphorus acids; other having P in +4 or +5 oxidation state, i.e phosphoric acids.

Characteristics of Oxoacids of Phosphorus

(i) In all oxoacids, phosphorus is tetrahedrally surrounded by other atoms.

(ii) All these acids contain atleast one $P{=}O$ bond and one P—OH bond.

(iii) The oxoacids in which P has lower oxidation state (less than + 5) contain either P—P, (e.g. $H_4P_2O_6$) or P—H bonds. (e.g. H_3PO_2) (but not both) in addition to these bonds ($P{=}O$ and P — OH).

(iv) In these oxoacids, H-atom of OH group is ionisable and cause basicity, whereas H-atom directly bonded to P-atom is non-ionisable. Thus, H_3PO_3 and H_3PO_4 are dibasic and tribasic respectively.

(v) The acids which contain P—H bond, have strong reducing properties. Thus, hypophosphorous acid acts as a good reducing agent because it contains two P—H bonds.

e.g. $$4AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow 4\,Ag + 4HNO_3 + H_3PO_4$$

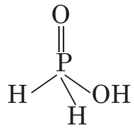
(vi) The oxoacids in + 3 oxidation state of phosphorus tend to disproportionate to higher and lower oxidation states.

e.g. $$4H_3\overset{+3}{P}O_3 \longrightarrow 3H_3\overset{+5}{P}O_4 + \overset{-3}{P}H_3$$

Preparation of Oxoacids of Phosphorus

Some important oxoacids are discussed below:

(i) **Hypophosphorous Acid** (H_3PO_2) It is a monobasic acid due to the presence of one replaceable hydrogen. It has 'P' in + 1 oxidation state.

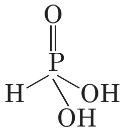


Structure of H_3PO_2

(ii) **Orthophosphorous Acid** (H_3PO_3)

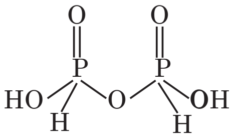
It is formed by the dissolution of P_2O_3 in water.

$$P_2O_3 + 3H_2O \longrightarrow 2H_3PO_3$$



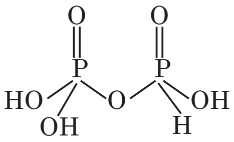
Structure of H_3PO_3

(iii) **Pyrophosphorous Acid** ($H_4P_2O_5$) It is dibasic due to the presence of two replaceable hydrogen atoms. It has P in + 3 oxidation state.



Structure of $H_4P_2O_5$

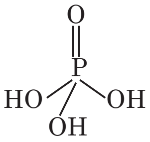
(iv) **Hypophosphoric Acid** ($H_4P_2O_6$) It is tetrabasic and P is in + 4 oxidation state.



Structure of $H_4P_2O_6$

(v) **Orthophosphoric Acid** (H_3PO_4)

It is a tribasic acid and P is in + 5 oxidation state.

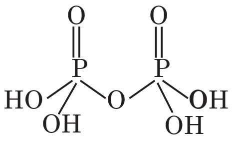


Structure of H_3PO_4

(vi) **Pyrophosphoric Acid** ($H_4P_2O_7$)

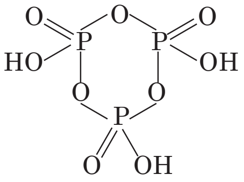
It is prepared by heating H_3PO_4.

$$2H_3PO_4 \xrightarrow{\Delta} H_4P_2O_7 + H_2O$$

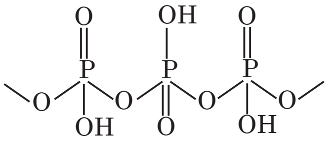


Structure of $H_4P_2O_7$

(vii) **Metaphosphoric Acid** $(HPO_3)_n$ It forms trimer as well as polymer. It is a monobasic acid having P in +5 oxidation state.



Structure of cyclotrimetaphosphoric acid, $(HPO_3)_3$



Structure of polymetaphosphoric acid, $(HPO_3)_n$

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Important Questions

Q.1 Elements of group-15 belong to **[Textbook]**

(a) *s*-block (b) *p*-block (c) *d*-block (d) *f*-block

Sol *(b)* Group-15 elements are also called *p*-block as in these elements the last electron enters the *p*-subshell. These are placed on the right side of the main periodic table.

Q.2 The outer electronic configuration of group 15 elements is

(a) ns^2np^1 (b) ns^2np^2 (c) ns^2np^3 (d) ns^2np^4

Sol (*c*) The valence shell electronic configuration of group 15 elements is $ns^2\ np^3$ (where n = number of shells).

Q.3 In the reduction of HNO_3 to N_2O, the number of moles of electrons involved per mole of HNO_3 is **[Textbook]**

(a) 8 (b) 4 (c) 2 (d) 3

Sol (*b*) Reduction of HNO_3 to N_2O takes place as follows:

$$2\,H\overset{+5}{N}O_3 + 8e^- \longrightarrow \overset{+1}{N_2}O$$

Thus, 4 electrons are required per mol.

Q.4 Which of the following oxides combines with Fe(II) ions to form a brown complex? **[Textbook]**

(a) N_2O (b) NO (c) N_2O_5 (d) N_2O_3

Sol (*b*) In the ring test of NO_3^- ion, Fe^{2+} ion reduces nitrate ion to nitric oxide, which combines with Fe^{2+} (*aq*) ion to form a brown complex.

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{Brown complex}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$$

Q.5 Which of the following is neutral? **[Textbook]**

(a) N_2O_3 (b) N_2O_4 (c) N_2O_5 (d) N_2O

Sol (*d*) Nitrous oxide (N_2O) is a neutral oxide, which shows neither basic non acidic properties when, it react with water.

Q.6 Conc. HNO_3 oxidises phosphorus to **[Textbook]**

(a) H_3PO_4 (b) P_2O_5
(c) H_2PO_3 (d) $H_4P_2O_7$

Sol (*a*) The reaction of phosphorus with conc. HNO_3 leads to the formation of H_3PO_4. In this reaction, the oxidation state of phosphorus is +5.

$$P_4 + 20HNO_3 \longrightarrow 20NO_2 + 4H_3PO_4 + 4H_2O$$

Q.7 Which of the following liberates H_2 with nitric acid? **[Textbook]**

(a) Zn (b) Cu (c) Mg (d) Hg

Sol (*c*) Magnesium reacts with very dilute nitric acid to liberate hydrogen gas. The oxidising action of the acid is much reduced due to its over dilution.

$$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2(g)\uparrow$$

Q.8 Which of the following is least basic? **[Textbook]**

(a) NF_3 (b) NCl_3 (c) NI_3 (d) NBr_3

Sol (*a*) As the size of halide ion increases, the electronegativity of halide ion decreases and the basic character of NX_3 increases. Hence, NF_3 is least basic because F is most electronegative and it will attract the lone pair of N-atom and thus the electrons will be less available.

Q.9 Which of the following is most explosive? **[Textbook]**

(a) NCl_3 (b) PCl_3
(c) $AsCl_3$ (d) All of these

Sol (*a*) The electronegativity difference between nitrogen and chlorine is comparatively less, thus N-Cl bond is relatively weaker. Due to the less stability of NCl_3, it is most explosive.

Q.10 In the manufacture of safety match sticks we use **[Textbook]**

(a) white P (b) black P (c) violet P (d) red P

Sol (*d*) In the manufacture of safety match sticks, we use red phosphorus because it is much more stable.

Q.11 Which is oxidised in air? **[Textbook]**

(a) white P (b) CH_4 (c) H_2O (d) SO_2

Sol (*a*) White phosphorus is highly reactive and spontaneously ignites at about 30°C in moist air.

Q.12 When conc. H_2SO_4 is added to dry KNO_3, brown fumes are evolved. These fumes are **[Textbook]**

(a) SO_2 (b) SO_3 (c) N_2O (d) NO_2

Sol (*d*) When conc. H_2SO_4 is added to dry KNO_3, brown fumes are evolved. These fumes are of NO_2.

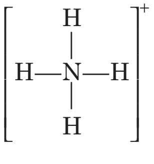
$$KNO_3 + \text{Conc. } H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$

$$4HNO_3 + \underset{\substack{\text{Paper}\\\text{pallet}}}{C} \longrightarrow \underset{\substack{\text{Brown}\\\text{fumes}}}{4NO_2}\uparrow + CO_2 + 2H_2O$$

Q.13 Which of the following has tetrahedral structure? **[Textbook]**

(a) NH_3 (b) NH_4^+
(c) $K_4[Fe(CN)_6]$ (d) $[Ni(CN)_4]^{2-}$

Sol *(b)* NH_4^+ ion has tetrahedral structure.



Q.14 Phosphine is prepared by the reaction of **[Textbook]**

(a) P and H_2SO_4 (b) P and NaOH
(c) P and H_2S (d) P and HNO_3

Sol *(b)* White phosphorus is heated with concentrated sodium hydroxide solution in an inert atmosphere of CO_2 to form phosphine (PH_3).

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 \uparrow + 3NaH_2PO_2$$

Q.15 *Aqua-regia* is a mixture of **[Textbook]**

(a) $3HCl + HNO_3$ (b) $3HNO_3 + HCl$
(c) $H_3PO_4 + H_2SO_4$ (d) $HCl + CH_3COOH$

Sol *(a) Aqua-regia* is a mixtrue of nitric acid (HNO_3) and hydrochloric acid (HCl), optimally in a molar ratio of 1 : 3.

Q.16 With excess of Cl_2, ammonia gives **[Textbook]**

(a) NCl_3 (b) HCl (c) NH_4Cl (d) N_2O

Sol *(a)* Excess of chlorine (Cl_2) is treated with ammonia to give nitrogen trichloride (NCl_3) and hydrogen chloride (HCl).

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

Q.17 NH_3 is a Lewis base. It forms complexes with cations. Which one of the following cations does not form complex with NH_3? **[Textbook]**

(a) Ag^+ (b) Cu^{2+} (c) Cd^{2+} (d) Pb^{2+}

Sol *(d)* Pb^{2+} is a *p*-block element, thus it does not form complex ion.

Q.18 Which of the following forms of phosphorus is most stable? **[Textbook]**

(a) Red P (b) White P
(c) Black P (d) All of these

Sol *(c)* Black phosphorus has a layered structure and it is a highly polymerised form of phosphorus. Therefore, black phosphorus is the most stable allotrope of phosphorus.

Q.19 $FeSO_4$ forms brown ring with **[Textbook]**

(a) NO_3 (b) NO_2
(c) NO (d) N_2O_3

Sol *(c)* $FeSO_4$ forms brown ring by common nitrate test the reactions are as follows :

$$6FeSO_4 + 2H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$[Fe(H_2O)_6]SO_4 + NO \longrightarrow [Fe(H_2O)_5(NO)]SO_4 + H_2O$$

Q.20 In Birkland and Eyde process, the temperature of electric arc is about? **[Textbook]**

(a) 1500°C (b) 4000°C
(c) 3000°C (d) 2000°C

Sol *(c)* The temperature of electric arc is about 3000°C in Birkland and Eyde process.

Q.21 The anhydride of HNO_2 is **[Textbook]**

(a) NO (b) N_2O_3 (c) N_2O (d) N_2O_5

Sol *(b)* The anhydride of HNO_2 is N_2O_3. The anhydride of an acid is the acidic oxide which on hydration forms the acid.

Q.22 Which of the following does not exist? **[Textbook]**

(a) NCl_5 (b) AsF_5 (c) PF_5 (d) $SbCl_5$

Sol *(a)* NCl_5 does not exist because nitrogen atom does not have *d*-orbitals in the second energy level to accomodate electrons from chorine atoms. Nitrogen cannot accomodate more than 8 electrons in its valence shell.

Q.23 The gas obtained on heating ammonium nitrite is **[Textbook]**

(a) N_2O (b) N_2 (c) N_2O_3 (d) N_2O_4

Sol *(b)* When ammonium nitrite (NH_4NO_2) is heated, it decomposes to give nitrogen gas.

$$NH_4NO_2(aq) \longrightarrow N_2(g)\uparrow + 2H_2O(l)$$

Q.24 Extra pure N_2 can obtained by heating **[Textbook]**

(a) NH_3 and CuO (b) NH_4NO_3
(c) $(NH_4)_2Cr_2O_7$ (d) $Ba(N_3)_2$

Sol *(d)* Barium azide can be used as a source for obtaining highly pure nitrogen gas by heating. This reaction liberates metallic barium also.

$$Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba(s) + 3N_2(g)$$

Q.25 Balance the reaction : **[Textbook]**

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O + NO$$

Sol $3Cu + \text{dil. } 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

Q.26 Phosphine catches fire because of the presence of ……… as impurities in it. **[Textbook]**

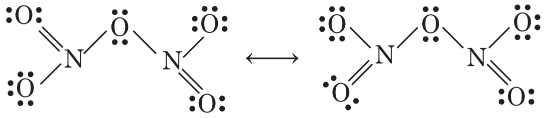
Sol HNO_3, Cl_2 and Br_2 vapours.

Q.27 What is producer gas? **[Textbook]**

Sol Producer gas is the mixture of CO and N_2 gases.

Q.28 What is the covalence of nitrogen in N_2O_5?

Sol. Since, nitrogen atom has 4 shared electron pairs, the covalence of nitrogen is 4.



Q.29 What happens a when white phosphorus is heated with conc. NaOH solution in an inert atmosphere of CO_2?

Sol. White phosphorus dissolves in boiling NaOH producing phosphine gas and sodium hypophosphite.

$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3 \uparrow$$

Q.30 What happens, when PCl_5 is heated?

Sol. When PCl_5 is heated, PCl_3 is formed because in PCl_5, 3 bonds are equatorial and two are axial. When it is heated, the axial bonds are broken and PCl_3 is formed.

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

2 MARK *Questions*

Important Questions

Q.31 Explain, why NH_3 is basic, while BiH_3 is only feebly basic? **[Textbook]**

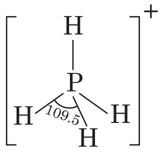
Sol Electronegativity decreases from N to Bi in the group, hence ability of such elements to accept H^+ ion also decreases down the group. Hence, BiH_3 is only feeblybasic. **(2)**

Q.32 The HNH bond angle is higher than HPH, HAsH and HSbH angles, why? **[Textbook]**

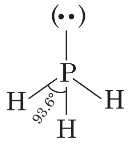
Sol The decrease in electronegativity down the group leads the bond pairs to lie close to each other as repulsion is less. **(2)**

Q.33 Bond angle in PH_4^+ is higher than that in PH_3. Why? **[Textbook]**

Sol. In both PH_3 and PH_4^+, P is sp^3-hybridised. In PH_3, there is a lone pair of electron whereas in PH_4^+, all the 4 orbitals are bonded. Due to lone pair-bond pair repulsion in PH_3, the bond angle is less than 109.5°. **(2)**



PH_4^+
Tetrahedral



PH_3
Pyramidal

(2)

Q.34 Why does $R_3P{=}O$ exist but $R_3N{=}O$ does not (R = alkyl group)?

Sol. Nitrogen cannot form dπ-pπ multiple bond with oxygen because *d*-orbitals do not exist in N-atom. Thus, covalency of N cannot go beyond 4.
In $R_3N{=}O$, covalency of N should be 5. So, these compounds do not exist. Whereas *d*-orbitals are present in phosphorus, so, P can form *d*π-*p*π multiple bond and expand it covalency beyond 4. Thus, P forms $R_3P{=}O$ in which the covalency of P is 5. **(2)**

Q.35 Explain, why nitrogen does not form NF_5, while phosphorus can form PF_5?

Sol. Nitrogen does not have vacant *d*-orbital to expand its covalency beyond 4. On the other hand, phosphorus has vacant *d*-orbitals to expand its covalency and forms PF_5. **(2)**

Q.36 (i) Nitric oxide becomes brown when released in air. Why?

(ii) $BiCl_3$ is more stable than $BiCl_5$.Why?

Sol. (i) Nitric oxide combines with oxygen when exposed to air to give nitrogen dioxide which is brown in colour.

$$2NO + O_2 \longrightarrow 2NO_2 \qquad \textbf{(1)}$$

(ii) Bi has little tendency to form pentahalides because + 5 oxidation state of Bi is much less stable than + 3 oxidation state due to inert pair effect. **(1)**

Q.37 Why are pentahalides more covalent than trihalides?

Or Account for the following. PCl_5 is more covalent than PCl_3.

Sol. Higher the positive oxidation state of central atom, more will be its polarising power, which in turn, increases the covalent character of the bond formed between the central atom and the halogen atom.
In pentahalides, the central atom is in + 5 oxidation state while in trihalides, it is in +3 oxidation state.Therefore, pentahalides are more covalent than trihalides. **(2)**

3 MARK *Questions*

Important Questions

Q.38 (i) Why is the reactivity of nitrogen different from that of phosphorus?

(ii) Can PCl_5 act as an oxidising as well as reducing agent?

Sol. (i) Nitrogen exists as a diatomic molecule with a triple bond between two N-atoms. The bond dissociation enthalpy of this triple bond ($N{\equiv}N$) is very high (941.94 kJ mol^{-1}) due to which nitrogen is inert and unreactive at room temperature.

It contrast, phosphorus exists as a tetra-atomic molecule (P_4). As P—P bond is much weaker than $N{\equiv}N$ bond, therefore P—P bond can be broken easily and hence, phosphorus is much more reactive than nitrogen. **(1½)**

(ii) The oxidation state of P in PCl_5 is +5. Since, P has five electrons in its valence shell, therefore it cannot increase its oxidation state beyond +5 by donating electrons. Thus, PCl_5 cannot act as a reducing agent. However, it can decrease its oxidation state from +5 to +3 or some lower value, therefore it can act as an oxidising agent. e.g. PCl_5 oxidises Ag to AgCl, Sn to $SnCl_4$, H_2 to HCl.

$$\overset{(0)}{2Ag} + \overset{(+5)}{PCl_5} \longrightarrow \overset{(+1)}{2Ag}\,Cl + \overset{(+3)}{PCl_3}$$

$$\overset{(0)}{Sn} + 2PCl_5 \longrightarrow \overset{(+4)}{Sn}Cl_4 \;+\; 2PCl_3$$

$$PCl_5 \;+\; \overset{(0)}{H_2} \longrightarrow PCl_3 + 2\overset{(+1)}{H}Cl$$

In the above reactions, oxidation number of P decreases from +5 to +3 and that of Ag increases from 0 to +1, Sn from 0 to +4 and H from 0 to +1. Hence, PCl_5 can act only as an oxidising agent. **(1½)**

Q.39 Illustrate how copper metal can give different products on reaction with HNO_3.

Sol. The products of the reaction of copper with HNO_3 depend on the concentration of HNO_3.

Copper metal reacts with dilute HNO_3 to form nitrogen (II) oxide (NO). **(1)**

$$3Cu + 8HNO_3\,(\text{dilute}) \xrightarrow{\Delta} 3Cu\,(NO_3)_2 + 2NO + 4H_2O \quad \textbf{(1)}$$

Copper metal reacts with conc. HNO_3 to form nitrogen (IV) oxide or nitrogen dioxide.

$$Cu + 4HNO_3\,(\text{conc.}) \longrightarrow Cu\,(NO_3)_2 + 2NO_2 + 2H_2O \quad \textbf{(1)}$$

Q.40 (i) Account for the following :

(a) PCl_4^- does not exist.

(b) Tendency to form pentahalides decreases down the group in group 15 of the periodic table.

(ii) Complete the following chemical equations:

(a) $P_4 + SO_2Cl_2 \longrightarrow$

(b) $P_4 + NaOH + H_2O \longrightarrow$

(c) $I_2 + HNO_3(\text{conc.}) \longrightarrow$

Sol. (i) (a) P in PCl_4^- exists in oxidation state of +3 which is less stable, hence, PCl_4^- is not likely to exist.

(b) This is due to inert pair effect. The stability of + 5 oxidation state decreases down the group in group 15. **(1½)**

(ii) (a) $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 \;+\; 10SO_2$ **(½)**

(b) $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$ **(½)**

(c) $I_2 + 10HNO_3\,(\text{conc.}) \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$ **(½)**

7 MARK *Questions*

Important Questions

Q.41 Describe the laboratory method of preparation of phosphine. State three of its properties with reactions.

Sol **Preparation of Phosphine** Refer to text on page 130. **(7)**

Q.42 On heating, a compound A gives a gas B which is a constituent of air. This gas when treated with 3 moles of hydrogen (H_2) in the presence of a catalyst gives another gas C which is basic in nature. Gas C on further, oxidation in moist condition gives a compound D which is a part of acid rain. Identify compounds A to D and also give necessary equations of all the steps involved.

Sol. The main constituents of air are nitrogen (78%) and oxygen (21%). Only N_2 reacts with three moles of H_2 in the presence of a catalyst to give NH_3 (ammonia) which is a gas having basic nature. Hence, compound C is NH_3 and B is N_2. On oxidation, NH_3 gives NO_2, which in moist conditions forms HNO_3, a part of acid rain. So, the compound D is HNO_3. Since, N_2, i.e. B is obtained by heating compound A, therefore A must be a nitrite. Thus, A is ammonium nitrite, NH_4NO_2. Hence, the compounds A to D are:

$A = NH_4NO_2$, $B = N_2$, $C = NH_3$, $D = HNO_3$ **(2)**

Reactions involved can be given as :

(i) $\underset{(A)}{NH_4NO_2} \xrightarrow{\Delta} \underset{(B)}{N_2} + 2H_2O$ **(1)**

(ii) $\underset{(B)}{N_2} + 3H_2 \underset{\text{Catalyst}}{\overset{\Delta}{\rightleftharpoons}} \underset{(C)}{2NH_3}$ **(1)**

(iii) $4\,\underset{(C)}{NH_3} + 5O_2 \xrightarrow{\text{Oxidation}} 4NO + 6H_2O$ **(1)**

(iv) $2NO + O_2 \longrightarrow 2NO_2$ **(1)**

(v) $3\,NO_2 + H_2O \longrightarrow \underset{(D)}{2HNO_3} + NO$ **(1)**

Chapter Test

1 MARK *Questions*

1 The brown ring test for nitrates depends upon **[Textbook]**
(a) the reduction of nitrate to nitric oxide
(b) oxidation of nitric oxide to nitrogen dioxide
(c) reduction of ferrous sulphate to iron
(d) oxidising action of sulphuric acid

2 An inorganic salt (*A*) is decomposed on heating to give two products (*B*) and (*C*). Compound (*C*) is a liquid at room temperature and is neutral to litmus, while compound (*B*) is a colourless neutral gas. Compounds (*A*), (*B*) and (*C*) are **[Textbook]**
(a) NH_4NO_3, N_2O and H_2O
(b) NH_4NO_2, NO and H_2O
(c) CaO, H_2O and $CaCl_2$
(d) $Ba(NO_3)_2$, H_2O and NO_2

3 Sequence of acidic character is **[Textbook]**
(a) $SO_2 > CO_2 > CO > N_2O_5$
(b) $SO_2 > N_2O_5 > CO > CO_2$
(c) $N_2O_5 > SO_2 > CO > CO_2$
(d) $N_2O_5 > SO_2 > CO_2 > CO$

4 Which statement is wrong for NO? **[Textbook]**
(a) It is anhydride of HNO_2
(b) Its dipole moment is 0.22D
(c) It forms dimer
(d) It is paramagnetic

[***Ans.*** **1.** (a), **2.** (a), **3.** (d), **4.** (a)]

5 The oxidation number of Fe in brown ring $[Fe\,(H_2O)_5NO]^{2+}$ is .... [***Ans.*** 2]

6 Why is nitrogen a gas, whereas phosphorus is a solid?

2 MARK *Questions*

7 What happens when ammonia gas is passed through copper sulphate solution? Give reactions? **[Textbook]**

8 How is ammonia prepared in the laboratory? **[Textbook]**

9 In what way can it be proved that PH_3 is basic in nature?

10 What happens when ammonia is passed over red hot copper oxide? **[Textbook]**

11 State the reaction of conc. HNO_3 with sulphur. Give equation. **[Textbook]**

12 MX_5 (M = P, As, Sb and Bi) are known but MH_5 are not known, why?

3 MARK *Questions*

13 Arrange the following in the order of increasing bond strength : NH_3, PH_3, AsH_3, SbH_3, BiH_3. Give suitable explanation for your answer. **[Textbook]**

14 How is nitrogen prepared in the laboratory? Write the reaction of thermal decomposition of sodium azide.

15 Give the disproportionation reaction of H_3PO_3. **[Textbook]**

16 Give reasons for the differences in the following:
(i) Reactivities of nitrogen and phosphorus
(ii) Stabilities of +3 oxidation state of P and B.

17 Describe the brown ring test for nitrates.

7 MARK *Questions*

18 Discuss briefly the principle involved in the Ostwald's process of manufacture of HNO_3. How does conc. HNO_3 reacts with iodine and copper? **[Textbook]**

19 Complete the following reactions :
(i) $PCl_5 + Ag \longrightarrow$ (ii) $PH_3(g) + O_2(g) \longrightarrow$
(iii) $PCl_3(l) \xrightarrow{\text{Moist air}}$ (iv) $PCl_5(s) \xrightarrow{\text{Moist air}}$
(v) $NaHPO_2 + HCl \longrightarrow$
(vi) $AgCl\,(s) + NH_3(aq) \longrightarrow$
(vii) $P_4 + 3NaOH + 3H_2O \xrightarrow[\Delta]{CO_2}$

20 How is ammonia prepared in the laboratory? **[Textbook]**

Write with equation what happens when it reacts with (i) cupric oxide (ii) insufficient quantity of chlorine (iii) $CuSO_4$ solution (iv) excess of chlorine.