P-BLOCK ELEMENTS

BORON FAMILY

1. EXTRACTION OF BORON

Amorphous boron of low purity (called moissan boron) is obtained by reducing B_2O_3 with Mg or Na at a high temperature. It is 95–98% pure (being contaminated with metal borides), and is black in colour.

$$\mathrm{Na_2[B_4O_5(OH)_4].8H_2O} \ \xrightarrow{\ \ \mathrm{acid} \ \ } \mathrm{H_3BO_3} \ \xrightarrow{\ \ \mathrm{heat} \ \ } \mathrm{B_2O_3} \ \xrightarrow{\ \ \mathrm{Mg\ or\ Na} \ \ } 2\mathrm{B} \ + \ 3 \ \mathrm{Mg\ O}$$

It is difficult to obtain pure crystalline boron, as it has a very high melting point $(2180^{\circ}C)$ and the liquid is corrosive. Small amounts of crystalline boron may be obtained:

- (a) By reducing BCl_3 with H_2 . This is done on the kilogram scale.
- (b) Pyrolysis of Bl₃ (Van Arkel method).
- (c) Thermal decomposition of diborane or other boron hydrides.

$$2BCl_{3} + 3H_{2} \xrightarrow{\text{red hot W or Ta filament}} 2B + 6HCl$$

$$2BI_{3} \xrightarrow{\text{red hot W or Ta filament} \atop \text{Van Arkel}} 2B + 3I_{2}$$

$$B_{2}H_{6} \xrightarrow{\text{heat}} 2B + 3H_{2}$$

Property of Boron

(a) Burning in air

$$4B + 3O_2 \longrightarrow 2B_2O_3$$

(b) Reaction with water

$$B + H_2O \xrightarrow{Cold \& hot} No reaction$$

$$2B + 3H_2O \xrightarrow{\text{Red hot}} B_2O_3 + H_2$$

(c) B + HCl \longrightarrow No reaction

$$B + H_2SO_4 \xrightarrow{\text{dil.}} No reaction$$

$$2B + 3H_2SO_4 \xrightarrow{\text{conc.}} 2H_3BO_3 + 3SO_2$$

$$\mathsf{B} + \mathsf{3HNO}_3 \longrightarrow \mathsf{H}_3 \mathsf{BO}_3 + \mathsf{3NO}_2$$

(d)
$$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$$

(e)
$$2B + N_2 \longrightarrow 2NB$$

$$4B + C \longrightarrow B_4C$$

(f)
$$3Mg + 2B \longrightarrow Mg_3B_2$$

2. BORANES

Boranes are boron hydrogen compounds with general molecular formula $B_n H_{n+4}$ or $B_n H_{n+6}$. They are electron deficient compounds. The lighter boranes (upto B_5) spontaneously react with air whereas remaining compound are air stable. The physical properties of boranes are given as under:

Formula	Name	Melting point	Boiling point
		()	()
B_2H_6	Diborane	- 165.6	- 92.5
$B_{4}H_{10}$	Tetraborane	- 120	18
B_5H_9	Pentaborane -9	- 46.6	48
B_5H_{11}	Pentaborane -11	- 123	63
$B_{6}H_{10}$	Hexaborane -10	- 62.5	110
$B_{6}H_{12}$	Hexaborane -12	- 82.3	80-90
$B_{8}H_{12}$	Octaborane -12	- 20	_
$B_{8}H_{14}$	Octaborane -14	- 20	_
$B_{9}H_{15}$	Enneborane	2.6	_
$B_{10}H_{14}$	Decaborane	99.7	213
B ₂₀ H ₁₆	Isosaborane-16	196.2	_

Preparation of Diborane

(a)
$$\mathrm{Mg_3B_2} + \mathrm{HCl} \longrightarrow \mathrm{B_2H_6} + \mathrm{B_4H_{10}} + \mathrm{B_5H_9} \mathrm{\ etc.}$$
 (10%)

(b)
$$B_4 H_{10} \xrightarrow{\Delta \atop 100 {}^{\circ} C} B_2 H_6 + H_2 + \text{higher borane}$$

(c) 2 BCI₃ (or B Br₃) + 6 H₂
$$\xrightarrow{\text{Electric}}$$
 B₂H₆ + 6HCl

(d) 3Li AlH₄ /LiBH₄ + 4BF₃
$$\longrightarrow$$
 3LiF/3BF₃ + 3 AlF₃ + 2 B₂H₆

Chemical properties

(a)
$$B_2 H_6 + O_2 \xrightarrow{\text{burns in}} B_2 O_3 + H_2 O_3$$

(b)
$$B_2H_6 + H_2O \xrightarrow{Cold \text{ is enough}} H_3BO_3 + 6H_2$$

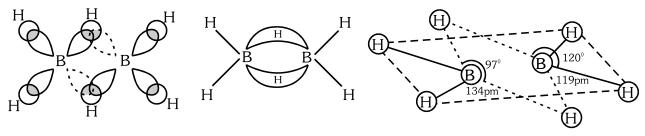
(b)
$$B_2H_6 + H_2O \xrightarrow{Cold \text{ is enough}} H_3BO_3 + 6H_2$$

(c) $B_2H_6 + 2KOH \longrightarrow 2KOBH_2 + 2H_2$

(d)
$$B_2H_6 + HC1 \xrightarrow{\text{anh.}} B_2H_5C1 + H_2$$

dry

Structure of diborane



The structure of diborane B2H6

The structure of diborane is shown in fig. The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three centre - two e⁻ bonds.

Bonding in diborane:— Each B atom uses sp³ hybrids for bonding. Out of the four sp³ hybrids on each B atom, one is without an electron shown in broken lines. The terminal B-H bonds are normal 2c-2e bonds but the two bridge bonds are 3c-2e bonds. The 3c-2e bridge bonds are also referred to as **banana bonds or tau bonds**.

3. BORIC ACID

Preparation

It is prepared by borax reacting with sulphuric acid.

$$Na_2 B_4 O_7 + H_2 SO_4 + 5H_2 O \longrightarrow Na_2 SO_4 + 4H_3 BO_3$$

Physical properties

- (a) Its crystals are soft, white, needle like having a soapy touch.
- (b) It is steam volatile.

Chemical properties

(a) Ortho boric acid does not donate proton, like most of the acids but rather it accepts OH⁻, therefore it is a lewis acid and is represented by B(OH)₂.

$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + [B(OH)_4]^- \qquad (P_{k_a} = 9.25)$$

(b) $B(OH)_3$ partially reacts with water to form H_3O^+ and $[B(OH)_4^-]$ and behaves as a weak acid. Thus $B(OH)_3$ can not be titrated satisfactorily with NaOH because a sharp end point is not obtained. If polyhydroxy compound like glycerol, mannitol or sugar are added to titration mixture than it can be titrated with NaOH.

$$B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4]$$

(c) Effect of temperature at $100~{\rm C}~{\rm H_3BO_3}$ losses water and convert into metaboric acid.

$$H_3BO_3 \xrightarrow{100^{\circ}C} HBO_2 + H_2O$$

metaboric acid form tetraboric acid on heating at 160 C.

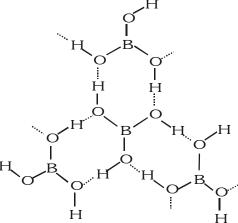
$$4HBO_2 \xrightarrow{160\,^{\circ}C} H_2B_4O_7 + H_2O$$

On strong heating B_2O_3 is produced

$$H_2B_4O_7 \longrightarrow 2B_2O_3 + H_2O$$

(d) Boric acid react with ethyl alcohol to form ethyl borate which

$$H_3BO_3 + 3C_9H_5OH \longrightarrow B(OC_9H_5)_3 + 3H_9O$$



Structure of boric acid, the dotted lines represent hydrogen bonds

burns with green edged flame.

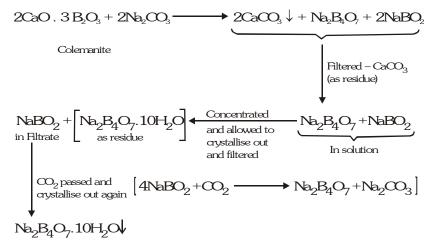
Structure of orthoboric acid

At lower concentration, its structure is a plane triangle.

4. BORAX

Preparation

- (a) In making glass, enamel and glaze of pottery.
- (b) As antiseptic in medicinal soaps preparation.



(c) Orthoboric acid on neutralization with Na_2CO_3 gives borax.

$$Na_2CO_3 + 4H_3BO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

(d) Colemanite is converted into borax by boiling it with concentrated solution of Na₂CO₃.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow Na_2B_4O_7 + 2CaCO_3 + 2NaBO_2.$$

Chemical properties

The solution of borax is alkaline in nature due to hydrolysis.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + 4H_3BO_3$$

5. **BORON TRIHALIDES**

Boron combines with halogens and forms the halides of type BX3, (X = F, Cl, Br, I)

Preparation

Except BF_3 , other trihalides can be prepared by the treatment of halogens on a mixture of B_2O_3 and carbon at high temperature.

$$B_2O_3 + 3C + 3X_2 \longrightarrow 2BX_3 + 3CO \quad (X = Cl_2, Br_2, I_2)$$

Properties

- (a) Due to small size and high charge density of B^{3+} ion, halides are covalent in nature.
- (b) These are non-electrolytes, as in liquid state they do not conduct electricity.
- (c) The boiling point are very low. The boiling point increases as the atomic number of halogen increases.
- (d) BF₃ is gas, BCl₃ (B.P. 13 C), BBr₃ (B.P. 90 C) are furning liquids while BI₃ (M.P. 310 C) is a fusible solid.
- (e) The trihalides are electron deficient compounds. Boron atom acquires six electrons on account of three B-X bonds, i.e., 2 electrons, short to complete an octet. Thus the boron atom in BX_3 molecule can accept two more electron. i.e, an electron pair from the donor atoms like N, P, O, S, F, etc., in NH_3 , PH_3 , PH_2 O, PH_2 S, PH_3 C, PH_3 C, P

$$\mathsf{H_3N}: \quad + \qquad \mathsf{BF_3} {\longrightarrow} \quad [\mathsf{H_3N} {\longrightarrow} \; \mathsf{BF_3}]$$

Donor Acceptor

(Lewis base) (Lewis acid)

(f) The relative lewis acid character of boron trihalides is found to follow the following order.

$$BI_3 > BBr_3 > BCl_3 > BF_3$$

but the expected order on the basis of electronegativity of the halogens (electronegativity of halogens decreases from F to I) should be -

$$BF_3 > BCl_3 > BBr_3 > BI_3$$

This anamoly is explained on the basis of the relative tendency of the halogen atom to back donate its unutilised electrons to vacant p-orbital of boron atom forming $p\pi - p\pi$ bond.

Extent of back bonding decrease from BF_3 to BI_3 with increase in size p-orbital of halogen.

 $p\pi$ - $p\pi$ back bonding is maximum in BF_3 due same energy and same size of 2p orbital of boran and filled 2p-orbital of F.

(g) All boron trihalides, except boron trifluoride, are hydrolysed to boric acid.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

The degree of hydrolysis increases from BCl_3 to BI_3 because covalent character increases. Due to resistance of BF_3 to hydrolysis and its tendency to act as lewis acid BF_3 is used as a catalyst in organic reactions.

 BF_3 form addition product with water as B-F bond is very strong

$$BF_3 + H_2O \longrightarrow H^+[BF_3HO]^-$$

6. ALUMINIUM

Properties

(a) Burning in air

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

(b) Reaction with water

Al +
$$3H_2O \longrightarrow Al (OH)_3 + \frac{3}{2}H_2$$

(c) $2Al + 6H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$

 ${\rm Al} + {\rm HNO_3} {-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-} {\rm Al_2O_3}$ (passive layer) and does not react further.

(d)
$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$$

(e) $2Al + N_2 \longrightarrow 2AlN$

$$4Al + 3C \longrightarrow Al_aC_3$$

7. <u>ALUMINIUM CHLORIDE</u> (AICl₃)

- (a) Hydrated AlCl₃ \rightarrow AlCl₃.6H₂O
- (i) AlCl₃ is prepared by dissolving aluminium oxide or its hydroxide in dilute HCl.

$$\begin{aligned} & \text{Al}_2\text{O}_3 & + \text{6HCl} & \longrightarrow & 2\text{AlCl}_3 & + 3\text{H}_2\text{O} \\ & \text{Al(OH)}_3 & + \text{3HCl} & \longrightarrow & \text{AlCl}_3 & + 3\text{H}_2\text{O} \end{aligned}$$

- (b) Anhydrous AlCl₃
- Anhydrous aluminium chloride can be obtained by passing dry chlorine gas and dry HCl gas over heated aluminium in vaccum.

$$2Al + 3Cl_2(dry) \longrightarrow 2AlCl_3$$

(ii) Macaffe's process - The anhydrous salt is prepared by heating alumina with coke and chlorine.

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO^{\uparrow}$$
(dry)

Properties

(a) Aluminium chloride is a white crystalline substance which fumes in moist air. It fumes in moist air due to its hydrolysis.

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl\uparrow$$

- (b) On heating it sublimates at 180°C.
- (c) At sublimation point its vapour density corresponds to formula Al_2Cl_6 i.e, it exists as a dimer. At higher temperatures i.e, above $750^{\circ}C$ it exists as a monomer $AlCl_2$.
- (d) It is largely covalent hence it does not conduct current in fused state.

Uses of AlCl₃

Anhydrous AlCl₃ is employed as a catalyst in organic reactions i.e, Friedal crafts reaction.

8. ALUM

- (a) Alums are double sulphates with their general formula $R_2SO_4.M_2(SO_4)_3.24H_2O$ where R = monovalent radical like Na^+ , K^+ , NH_4^+ and M = Trivalent radical like Al^{+3} , Cr^{+3} . Fe⁺³.
- (b) The different alums are -
- (i) Potash alum $K_2SO_4.Al_2$ (SO_4) $_3.24H_2O$
- (ii) Chrome alum $\rm K_2SO_4$ $\rm Cr_2(SO_4)_3$. 24 $\rm H_2O$
- (iii) Iron alum $(NH_4)_2SO_4$. $Fe_2(SO_4)_3$. $24H_2O$
- (iv) Ammonium alum $(NH_4)_2SO_4$. $Al_2(SO_4)_3$. $24H_2O$
- (c) In alums each metal ion is surrounded by six water molecules.
- (d) Lithium does not form alum because Li ion is too small to have a coordination number of six.

Properties

- (a) It is a white crystalline solid highly soluble in water.
- (b) On heating it undergoes dehydration and swells up.
- (c) It is highly acidic in aqueous solution due to the hydrolysis of aluminium sulphate to sulphuric acid
- (d) It is a double salt and its aqueous solution gives reaction of all the constituents ions K^+ , Al^{+3} , SO_4^{-2} .

Uses

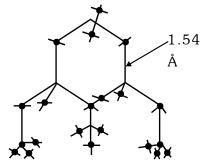
- (a) Alum is used to stop bleeding.
- (b) It is used for purification of water.
- (c) It is used as a mordant in dyeing industry.
- (d) Alum is used for tanning of leather.

CARBON FAMILY

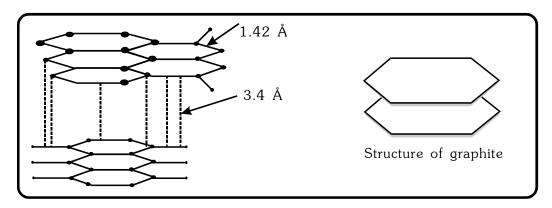
1. ALLOTROPIC FORM OF CARBON

(A) CRYSTALLINE

- (a) Diamond
- (i) Three dimensional polymeric structure.
- (ii) In diamond each carbon is in sp³ hybridized state and is linked to four other neighbouring carbon atoms held at the corners of a regular tetrahedron by covalent bonds.



- (iii) In this structure C-C distance is $1.54\ \mbox{\normalfont\AA}$ with a bond angle of $109.5\ .$
- (iv) Due to these strong covalent bonds, diamond is the hardest substance Crystal structure of diahaving abnormally high melting point (3600 $\,$ C) and is extremely inert, $\,$ mond chemically.
- (v) It has very high refractive index (2.5), i.e. light rays are slowed down by the tightly bound electron.
- (vi) Due to unavailability of mobile electrons it is non-conductor of electricity.
- (b) Graphite
- (i) Unlike diamond, it has a two dimensional laminar structure.
- (ii) The adjacent layers of sheet are held together by weak vander Waal forces.
- (iii) Here each carbon atom is in sp^2 hybridised state and is thus attached to three other carbon atoms by three σ bonds forming a hexagonal planar structure.
- (iv) The fourth electron present in an unhybridised p-orbital of each carbon atom of a hexagonal unit then overlap with each other to form a pi bond.
- (v) The C-C bond length in graphite is shorter (1.42 Å) than that of diamond (1.54Å).



- (vi) Since π -electrons (π e^-) are free to move throughout the entire layers, graphite is a good conductor of electricity. Its conductivity increases with temperature.
- (vii) It is a soft greasy, dark greyish coloured crystalline solid having density $2.5~\mathrm{g~mL^{-1}}$
- (viii) Since it leaves a black mark on paper it is called black lead or plumbago
- (ix) It is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ less than diamond.

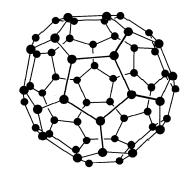
Graphite $\frac{1600^{\circ}C}{50,000-60,000atm}$ diamond

Amorphous:

- (c) Fullerenes
- (i) Discovered by smily & robert curl (Noble prize 1996)
- (ii) Fullerene normally contain C_{60} with smaller quantity of C_{70}

Structure of C₆₀

- (i) C_{60} is also called buckminster fullerene in honour of robert buckminster fuller.
- (ii) Shape of C_{60} is Soccer ball & C_{70} is Rugby ball.
- (iii) $C_{70} \& C_{60}$ having hexagonal & pentagonal unit.



(B) AMORPHOUS

Coal

- (a) Naturally form & artificially.
- (b) It is found in different form.

Ex. Peat, Lignite, Bituminous, Anthracite

- (c) Max percent of C = Anthracite Min percent of C = Peat
- (d) Calorific value Max in = Anthracite

2. <u>CARBIDES</u>

Carbides are of three types according to the type of bonding

- (a) Salt like carbides (ionic bonding)
- (i) These are formed by strong electropositive elements of groups 1, 2 and 13
- (ii) These are transparent crystalline substances and do not conduct electric current in the solid state.
- (iii) These are easily hydrolysed by water or dilute acids to give aliphatic hydrocarbons,

Methanides (Methides): Methanides are the carbides which give methane on hydrolysis. They contain C^{4-} ions.

$$Be_{2}C + 4H_{2}O \longrightarrow 2Be (OH)_{2} + CH_{4}$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al (OH)_3 + 3CH_4$$

Acetylides : These are the carbides which yield acetylene on hydrolysis. They contain the ion C_2^{2-}

Ex. CaC₂, BaC₂ and MgC₂

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$
 or $C_2^{2-} + 2H^+ \longrightarrow C_2H_2$

Note: Most of these carbides have ionic NaCl - type of structure.

Allylides: These carbides give methylacetylene or allylene (CH $_3$ - C \equiv CH). On hydrolysis they contain C_3^{4-} ions.

The only example of this class is Mg₂C₂

$$Mg_{2}C_{3} + 4H_{2}O \longrightarrow 2Mg(OH)_{2} + CH_{3} - C \equiv CH$$

- (b) Covalent carbides (giant molecular structure)
- (i) Covalent carbides are the compounds of carbon with elements having similar electronegativity.
- (ii) These are covalent, polymeric, thermally stable, extremely hard, high melting and technically inert solid.
- (iii) B_4C and SiC are two main covalent carbides.
- (c) Alloy type or interstitial type carbide

Transition metals like Ti, Zr, Hf, V, Nb, Ta and Mo form these carbides. The metals retains their **close packed lattice** and carbons are incorporated in their interstitial spaces. These carbides are extremly hard and have very high melting points. The carbides of V and Ta are very hard hence they are used for manufacture of high speed cutting tools.

3. CARBON MONOXIDE (CO)

Preparation

(a) It is invaribely present in automobile exhaust gas.

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$$

(b) Pure CO

$$\text{HCOOH} \xrightarrow{\text{H}_2\text{SO}_4} \text{CO} + \text{H}_2\text{O}$$

(c) Industrially it is obtained in the form of water gas and producer gas when air (moist) is passed over a bed of white hot coke.

2 C +
$$O_2$$
+ $4N_2$ \longrightarrow 2CO + $4N_2$
C + H_2 O \longrightarrow CO + H_2 (water gas)

Properties

- (a) It is highly poisonous as it combines with haemoglobin to form carboxy haemoglobin which is not capable to absorb oxygen.
- (b) It burns with blue flame to form CO₂. This is an exothermic process

2 CO +
$$O_2 \longrightarrow 2CO_2$$
 + Heat

(c) Chemical reactions

Fe₂O₃

$$600^{\circ} - 900^{\circ} \text{ C} \longrightarrow 2\text{Fe} + 3\text{O}_{2}$$
CO
$$Cl_{2} \text{ Sun light} \longrightarrow \text{COCl}_{2} \text{ (Phosgene)}$$

$$Ni, 80^{\circ}\text{C} \longrightarrow \text{Ni}(\text{CO})l_{4} \text{ (mond's process)}$$

How to detect

Burns with blue flame CO is passed through PdCl₂ solution giving rise to black ppt.

$$\label{eq:co_def} \text{CO} + \text{PdCl}_2 + \text{H}_2\text{O} \longrightarrow \text{CO}_2 \uparrow + \text{Pd} \downarrow + 2\text{HCl}$$
 Black metallic deposition

How to estimate

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

 $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

What are its absorbers

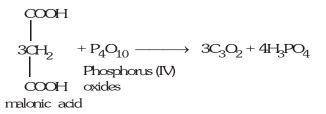
$$Cu_2Cl_2: CuCl + CO + 2H_2O \longrightarrow [CuCl(CO) (H_2O)_2]$$

4. CARBON SUB OXIDE

$$O = C = C = C = O$$

Preparation

By heating malonic acid with phosphorus penta oxide



Properties

- (a) Colourless gas, Boiling point 6°C
- (b) Very readily polymerises to give coloured salts.
- (c) It decomposes at 200°C $C_3O_2 \xrightarrow{200^{\circ}C} CO_2 + 2C$

5. SILICON (Si)

Silicon is the second most abundant (27.2%) element after oxygen (45.5%) in the earth's crust. It does not occur free in nature but in the combined state, it occurs widely in form of silica and silicates. All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or iron. Aluminium silicate is however the most common constituent of rocks and clays.

Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

- (a) Feldspar $K_2O.Al_2O_3.6SiO_2$
- (b) Kaolinite Al_2O_3 . 2 SiO_2 . $2H_2O$
- (c) Asbestos CaO. 3MgO.4SiO₂

Preparation

(a) From silica (sand): Elemental silicon is obtained by the reduction of silica (SiO₂) with high purity coke in an electric furnace.

$$SiO_2$$
 (s) + 2C (s) \longrightarrow Si (s) + 2CO (g)

(b) From silicon tetrachloride (SiCl₄) or silicon chloroform (SiHCl₃): Is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen.

$$SiCl_4(\ell) + 2H_2(g) \longrightarrow Si(s) + 4HCl(g)$$

 $SiHCl_3(s) + H_2(g) \longrightarrow Si(s) + 3HCl(g)$

Physical Properties

- (a) Elemental silicon is very hard having diamond like Structure.
- (b) It has shining luster with a melting point of 1793 K and boiling point of about 3550 K.
- (c) Silicon exists in three isotopes, i.e. $\frac{28}{14}$ Si, $\frac{29}{14}$ Si and $\frac{30}{14}$ Si but $\frac{28}{14}$ Si is the most common isotope.

Chemical properties

Silicon is particularly unreactive at room temperature towards most of the elements except fluorine. Some important chemical reactions of silicon are discussed below

(a) Action of air: Silicon reacts with oxygen of air at 1173 K to form silicon dioxide and with nitrogen of air at 1673 K to form silicon nitride.

$$Si(s) + O_2 (g) \xrightarrow{1173K} SiO_2$$

(Silicon dioxide)

3Si (s) +
$$2N_2$$
(g) $\xrightarrow{1673K}$ Si₃N₄(s)

Silicon nitride

(b) Action of steam: It is slowly attacked by steam when heated to redness liberating dihydrogen gas.

$$Si (s) + 2H_2O (g) \xrightarrow{redness} Si_3O_2 + 2H_2 (g)$$

(c) **Reaction with halogens**: It burns spontaneously in fluorine gas at room temperature to form silicon tetrafluoride (SiF_{a}).

Si (s) +
$$2F_2$$
 (g) $\xrightarrow{\text{RoomTemperature}}$ Si $F_4(\ell)$

However, with other halogens, it combines at high temperatures forming tetrahalides.

(d) **Reaction with carbon :** Silicon combines with carbon at 2500 K forming silicon carbide (SiC) known as carborundum.

Si (s) + C (s)
$$\xrightarrow{2500\text{K}}$$
 SiC (s)

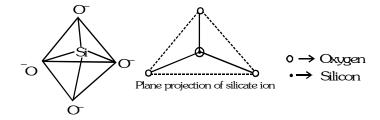
carborundum is an extremely hard substance next only to diamond. It is mainly used as an abrasive and as a refractory material.

Uses

- (a) Silicon is added to steel as such or more usually in form of ferrosilicon (an alloy of Fe and Si) to make it acid-resistant.
- (b) High purity silicon is used as semiconductors in electronic devices such as transistors.
- (c) It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

6. <u>SILICATES</u>

Silicates have basic unit of SiO_4^{4-} , each silicon atom is bonded with four oxide ions tetrahedrally.

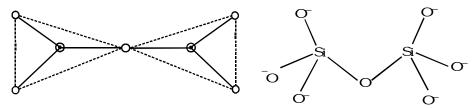


There are following types of silicates

(a) Orthosilicates: These silicates contain single discrete unit of SiO₄⁴⁻ tetrahedral.

Ex. Willemite $[Zn_2SiO_4]$

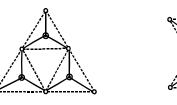
(b) Pyrosilicates

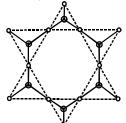


These silicates contain two units of ${\rm SiO_4^{\,4^-}}$ joined along a corner containing oxygen atom. These are also called as island silicate.

Ex. Hemimorphite $Zn_3(Si_2O_7)Zn(OH)_2$ H_2O , Pyrosilicates ion $Si_2O_7^{6-}$

(c) **Cyclic structure :** Cyclic or ring silicate having general formula $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ Structure and example of cyclic silicates containing $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ ions are given below

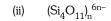


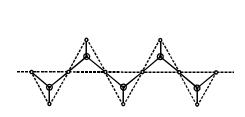


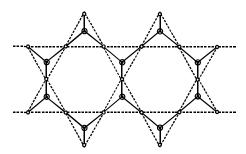
 $\textbf{Ex.} \quad \text{Beryl} \quad \text{Be}_{3}\text{Al}_{2}\text{Si}_{6}\text{O}_{18}$

(d) Chain silicates: Chain silicates are formed by sharing two oxygen atoms by each tetrahedral. Anions of chain silicate have two general formula.

(i)
$$(SiO_3)_n^{2n-}$$



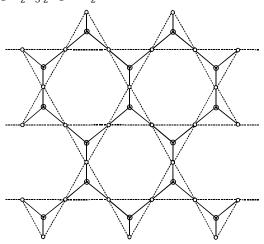




Ex. Spodumene $\text{Li}_2\text{Al}(\text{SiO}_3)_2$

Tremolite $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$

(e) Two dimensional sheet silicates: In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedral, such sharing forms two dimensional sheet structure with general formula $(Si_2O_5)_n^{2n-}$ Ex. Talc $Mg(Si_2O_5)_2Mg(OH)_2$



- (f) Three dimensional sheet silicates: These silicates involve all four oxygen atoms in sharing with adjacent SiO_4^{4-} tetrahedral.
 - Ex. Quartz, Zeolites and Ultramarines

7. <u>SILANE</u>

- (a) Only these two are found. ${\rm SiH_4~\&~Si_2H_6}$ (Formula ${\rm Si_nH_{2n~+~2}}$).
- (b) Higher molecules are not formed. So, Si can't show catenation property.

Hot Mg + Si-vap
$$\longrightarrow$$
 Mg₂Si $\xrightarrow{\text{dil.H}_2SO_4}$ MgSO₄ + SiH₄ + Si₂H₆ + ...

- (c) \mbox{SiH}_{4} is more reactive than $\mbox{CH}_{4}.$ due to following reason
- (i) $Si^{\delta+} H^{\delta-}$ and $C^{\delta-} H^{\delta+}$

C-electronegative than H

Si less electronegative than H

So bond polarity is reversed when Nu- attacks, so it faces repulsion in C but not in Si

- (ii) Silicon is having vacant d orbital which is not in case of carbon
- (iii) Silicon is larger in size compared to C. By which the incoming Nu^- doesn't face any steric hindrance to attack at Si whereas CH_4 is tightly held from all sides.

8. SILICONES

These are organosilicon polymers containing R₂SiO repeating units and empirical formula analogous to ketone (R₂CO)

Alkyl substituted: These are formed by hydrolysis of alkyl chlorosilanes and their polymerisation. The alkyl or aryl substituted chlorosilanes are prepared by the reaction of Grignard reagent and silicon tetrachlorides.

Organic polymers containing silicon in them are called as silicones.

(a) Straight chain silicone

$$2RCl \xrightarrow{Si} R_2SiCl_2$$

Dialkyldichloro Silane

The terminal 'OH' groups which are active, allow the polymerisation reaction to continue and the length of the chain continues to increase

(c) A complex cross-linked polymer is obtained on the hydrolysis of alkyl trichloro silane.

$$\begin{array}{c} \text{CI} & \text{OH} \\ \text{R-Si-CI} & \xrightarrow{\text{3H}_2\text{O}} & \text{R-Si-OH} \\ \text{I} & \text{-3HCI} & \text{I} \\ \text{CI} & \text{OH} \end{array}$$

(d) Cyclic (ring) silicones are formed when water is eliminated from the terminal -OH groups of linear silicones.

R₃SiCl on hydrolysis forms only a dimer

$$R_3SiO \ \ \ \ \ \ \ H + OH \ \ SiR_3 - \longrightarrow R_3Si - O - SiR_3$$

Uses

- (a) They are used as greases, varnishes and resins.
- (b) As they are water repellants, they are used for water-proofing.
- (c) They are good electric insulators.

9. SILICA (SiO₂)

Silica or silicon dioxide occurs in nature in the free state as sand, quartz and flint and in the combined state as silicates like Feldspar $K_2O.Al_2O_3.6SiO_2$, Kaolinite Al_2O_3 . $2SiO_2$. $2H_2O$ etc.

Properties

- (a) Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.
- (b) Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.

$$SiO_2(s) + 4HF(\ell) \longrightarrow SiF_4(\ell) + 2H_2O(\ell)$$

(c) It also combines with metallic oxides at high temperature giving silicates.

$$SiO_{2}(s) + CaO(s) \xrightarrow{\Delta} CaSiO_{2}(s)$$

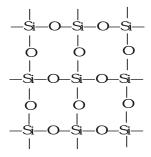
(d) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.

$$\begin{split} &\text{SiO}_2(\textbf{s}) \,+\, \text{Na}_2 \text{CO}_3(\textbf{s}) \,\longrightarrow\, \text{Na}_2 \text{SiO}_3(\textbf{s}) \,+\, \text{CO}_2(\textbf{g}) \\ &\text{SiO}_2(\textbf{s}) \,+\, \text{Na}_2 \text{SO}_4(\textbf{s}) \,\longrightarrow\, \text{Na}_2 \text{SiO}_3(\textbf{s}) \,+\, \text{SO}_3(\textbf{g}) \\ &3 \text{SiO}_2(\textbf{s}) \,+\, \text{Ca}_3(\text{PO}_4)_2 \,\, (\textbf{s}) \,\longrightarrow\, 3 \,\, \text{CaSiO}_3 \,\, (\textbf{s}) \,+\, \text{P}_2 \text{O}_5(\textbf{g}) \end{split}$$

The first two examples quoted here are important in glass making.

Structures of Silica

Silica has a three-dimensional network structure. In silica, silicon is sp^3 -hybridized and is thus linked to four oxygen atoms and each oxygen atom is linked to two silicon atoms forming a three-dimensional giant molecule as shown in figure. This three-dimensional network structure Imparts stability to SiO_2 crystal and hence a large amount of energy is required to break the crystal resulting in high melting point.



Uses

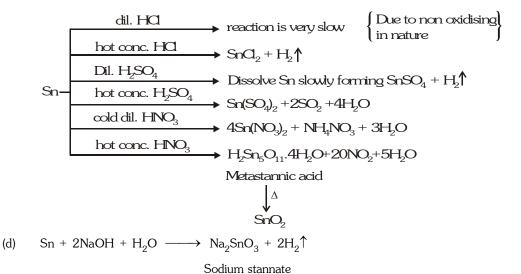
- (a) Sand is used in large quantities to make the cement.
- (b) Being transparent to ultraviolet light, large crystal of quartz are used for making lenses for optical instruments and for controlling the frequency of radio-transmitters.
- (c) Powdered quartz is used for making silica bricks.
- (d) Silica gel (SiO₂.xH₂O) is used as a desiccate (for absorbing moisture) and as an adsorbent in chromatography.

10. COMPOUNDS OF Sn (TIN)/ LEAD

(a)
$$\begin{array}{c} 15^{\circ}\text{C} \\ +\text{O}_{2} \\ \text{Cl}_{2}, \Delta \\ \end{array} \\ \text{Sn} \begin{array}{c} \text{SnO}_{2} \text{ [Burns with a bright flame]} \\ \text{Sn} \begin{array}{c} \text{SnO}_{4} \\ \text{SnS}_{2} \\ \end{array}$$

(b) Sn +
$$2H_2O$$
 $\xrightarrow{\text{room temp.}}$ No reaction $\xrightarrow{\text{At high temp.}}$ Sn O_2 + $2H_2$

(c) Reaction with acid



 $\textbf{Note:} \ KOH \ [In absence of air] \ Na_2SnO_2 \ forms \ and \ in \ contact \ with \ air \ it \ readily \ converts \ into \ Na_2SnO_3 \ determined \ and \ and$

11. SnO (grey) and SnO₂ (white)

Preparation

$$\begin{array}{c} +\frac{1}{2}O_{2} \\ & +\frac{1}$$

Properties

Both are amphoteric in nature

$$SnO_{2} + H_{2}O$$

$$2HO \qquad SnO_{2} + H_{2}O$$

$$2NaOH/KOH \qquad Na_{2}SnO_{2}/K_{2}SnO_{2} + H_{2}O$$

$$2NaOH/KOH \qquad Na_{2}SnO_{3}/K_{2}SnO_{3} + Sn + H_{2}O$$

$$Bi(OH)_{3} + [Sn(OH)_{4}]^{2-} \longrightarrow Bi \downarrow + [Sn(OH)_{6}]^{2-}$$

$$black$$

$$SnO_{2} + 2H_{2}SO_{4} \longrightarrow Sn(SO_{4})_{2} + 2H_{2}O$$
(Soluble only in hot conc. $H_{2}SO_{4}$)
$$SnO_{2} + 2NaOH \longrightarrow Na_{2}SnO_{3} + H_{2}O$$

$$SnO_{2} + 4S + 2Na_{2}CO_{3} \longrightarrow Na_{2}SnS_{3} + Na_{2}SO_{4} + 2CO_{2}$$

Note: insoluble in all acids even if in aqua ragia.

12. STANNOUS CHLORIDE (SnCl₂)

Preparation

(a) Sn + 2HCl
$$\xrightarrow{\text{hot.conc.}}$$
 SnCl₂ + H₂ \uparrow

(b) Anhydrous salt cannot be obtained by heating the hydrated salt as it undergoes hydrolysis and a white solid of tin hydroxy chloride is formed.

$$\rm SnCl_2$$
 . 2H2O — $\rm Sn(OH)Cl+HCl\uparrow+H_2O\uparrow \Rightarrow Hence~anh.~SnCl_2~cannot~be~obtained. $\rm \downarrow$ $\rm SnO+HCl\uparrow$$

$$SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCl \uparrow$$
 fumes comes out

(c) A piece of Sn is always added to preserve a solution fo SnCl₂.

6
$$\operatorname{SnCl_2}$$
 + $2\operatorname{H_2O}$ + $\operatorname{O_2}$ \longrightarrow 2 $\operatorname{SnCl_4}$ + 4Sn (OH) $\operatorname{Cl}\downarrow$ (white ppt) $\operatorname{SnCl_4}$ + Sn \longrightarrow 2SnCl₂

Properties

(a)
$$\operatorname{SnCl}_2 + \operatorname{HCl} \longrightarrow \operatorname{HSnCl}_3 \xrightarrow{\operatorname{HCl}} \operatorname{H}_2\operatorname{SnCl}_4$$

Chlorostannous acid

(b) Reducing Properties

$$\begin{array}{l} \operatorname{Sn^{+2}} + 2\operatorname{Fe^{+3}} \longrightarrow 2\operatorname{Fe^{+2}} + \operatorname{Sn^{+4}} \\ 2\operatorname{Cu^{+2}} + \operatorname{Sn^{+2}} \longrightarrow 2\operatorname{Cu^{+}} + \operatorname{Sn^{+4}} \\ \operatorname{Hg^{+2}} + \operatorname{Sn^{+2}} \longrightarrow \operatorname{Hg} \downarrow + \operatorname{Sn^{+4}} \\ \operatorname{C_6H_5NO_2} + 3\operatorname{SnCl_2} + 6\operatorname{Hcl} \longrightarrow \operatorname{C_6H_5NH_2} + 3\operatorname{SnCl_4} + 2\operatorname{H_2O} \\ \operatorname{K_2Cr_2O_7} + \operatorname{SnCl_2} + \operatorname{Hcl} \longrightarrow \operatorname{Cr^{+3}} + \operatorname{Sn^{+4}} + \operatorname{KCl} + \operatorname{H_2O} \end{array}$$

(c) Readily combines with $I_2 \Rightarrow SnCl_2I_2 \Rightarrow$ This reaction is used to estimate tin.

13. STANNIC CHLORIDE (SnCl_d)

Preparation

(a) Sn
$$+ 2Cl_2 \xrightarrow{\text{Excess}} \text{SnCl}_4$$

(Molten) (dry)

(b)
$$2\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow 2\text{Hg} \downarrow + \text{SnCl}_4$$

(c) Sn + Aqua ragia
$$\longrightarrow$$
 SnCl₄ + NO + H₂O

Properties

(a)
$$SnCl_4 + 2HCl \longrightarrow H_2SnCl_6$$
 (Hexachloro stannic(IV) acid)

(b)
$$\operatorname{SnCl}_4 + 2\operatorname{NH}_4\operatorname{Cl} \longrightarrow (\operatorname{NH}_4)_2\operatorname{SnCl}_6$$

Note: $SnCl_4.5H_2O$ is known as butter of tin \Rightarrow used as mordant.

 $(NH_4)_2SnCl_6$ is known as 'Pink salt' \Rightarrow used as calico printing.

Mosaic gold : SnS₂ yellow crystalline substance

$$\begin{array}{lll} & \text{Sn + 4NH}_4\text{Cl} & \longrightarrow & (\text{NH}_4)_2 \text{ SnCl}_4 + 2\text{NH}_3 + \text{H}_2 \\ & 2(\text{NH}_4)_2 \text{ SnCl}_4 + 2\text{S} & \longrightarrow & \text{SnS}_2 + 2\text{NH}_4\text{Cl} + (\text{NH}_4)_2 \text{ SnCl}_6 \end{array}$$

Distinction of Sn⁺²/Sn⁺⁴

(b)
$$Hg^{+2}$$
 (c) $Fe^{+3} + [K_3Fe(CN)_6] \xrightarrow{Sn^{+2}} Blue ppt.$

14. OXIDES OF LEAD

Lead monoxide (pbo)

Preparation: It exists in two forms.

Laboratory preparetion

Properties: It is an amphoteric oxide insoluble in water.

PbO +
$$2\text{HNO}_3 \longrightarrow \text{Pb (NO}_3)_2 + \text{H}_2\text{O}$$
PbO + $2\text{NaOH} \longrightarrow \text{Na}_2\text{PbO}_2 + \text{H}_2\text{O}$

Sesquioxide (Pb₂O₃) (b)

Preparation

$$\begin{array}{lll} \mbox{2Pb} & + & \mbox{NaOCl} & \longrightarrow \mbox{Pb}_2\mbox{O}_3 & + \mbox{NaCl} \\ \mbox{hot sol}^n. & \mbox{Limited} \\ \mbox{of NaOH} & \mbox{amount} \\ \end{array}$$

Properties

$$Pb_2O_3 + 2HNO_3 \longrightarrow PbO_2 + Pb(NO_3)_2 + H_2O$$

Note: This reaction suggests that Pb₂O₃ contains PbO₂.

Red lead (Minium or sindhur) (Pb₃O₄)

Preparation

6 PbO + O₂
$$\xrightarrow{340^{\circ}\text{C}}$$
 Pb₃O₄

Properties

(d) Lead Dioxide (PbO₂)

Preparetion

(i)
$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

(ii)
$$(CH_3COO)_2Pb + Ca(OH)_2 \longrightarrow Pb(OH)_2 + (CH_3COO)_2Ca$$

(iii)
$$2Pb(OH)_2 + 2Ca(OCl)_2 \longrightarrow 2PbO_2 + CaCl_2 + 2H_2O + O_2$$

Calcium hypochlorite

(iv)
$$\begin{array}{cccc} {\rm Pb(OH)}_2 + {\rm CaOCl}_2 & \longrightarrow & {\rm PbO}_2 + {\rm CaCl}_2 + {\rm H}_2{\rm O} \\ & & {\rm Bleaching\ powder} \end{array}$$

 $\textbf{Properties}: In soluble in water and HNO_3, \ But \ reacts \ with \ (hot \ conc.) \ HCl/H_2SO_4 \ and \ in \ hot \ NaOH/KOH.$

$$\begin{array}{c} \text{PbO}_2 + 4\text{HCl} \xrightarrow{\hspace{0.5cm} \text{Cold conc.}} \text{PbCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O} \\ \\ 2\text{PbO}_2 + 2\text{H}_2\text{SO}_4 \xrightarrow{\hspace{0.5cm} \text{conc.}} \\ 2\text{PbO}_2 + 2\text{NaOH} \xrightarrow{\hspace{0.5cm} \text{heat} \\ \hspace{0.5cm} \text{conc.sol.}} \text{Na}_2\text{PbO}_3 + 4\text{H}_2\text{O} \\ \\ \text{Sodium plumbate} \end{array}$$

$$\begin{array}{l} \text{PbO}_2 + \text{SO}_2 & \longrightarrow \text{PbSO}_4 [\text{spontaneously}] \end{array} \begin{cases} \begin{array}{l} \text{PbS} + 4\text{O}_3 & \longrightarrow \text{PbSO}_4 + 4\text{O}_2 \\ \text{PbS} + 4\text{H}_2\text{O}_2 & \longrightarrow \text{PbSO}_4 + 4\text{H}_2\text{O} \end{array} \end{cases} \\ \text{PbO}_2 + 2\text{HNO}_3 + (\text{COOH})_2 & \longrightarrow \text{Pb(NO}_3)_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} \\ \\ 2\text{MnSO}_4 + 5\text{PbO}_2 + 6 \text{ HNO}_3 & \longrightarrow 3\text{Pb(NO}_3)_2 + 2\text{PbSO}_4 \\ \downarrow + 2\text{HMnO}_4 + 2 \text{ H}_2\text{O} \end{array}$$

 $\textbf{Note:} \mathsf{PbO}_2$ is a powerful oxidising agent.

15. LEAD CHLORIDE/PLUMBUS CHLORIDE (PbCl₂)

$$PbCl_2$$
 Exists as $H_2[PbCl_6]$
 $PbO_2 + 4HCl \longrightarrow PbCl_4 + 2H_2O$
{ice cold conc. saturated with Cl_2 }
 $PbCl_4 + 2HCl \longrightarrow H_2[PbCl_6]$

16. LEAD TETRAACETATE

Preparation

$$Pb_3O_4 + 8AcOH$$
 (hot glacial) \longrightarrow $Pb(OAc)_4 + 2Pb(OAc)_2 + 4H_2O$
 $Pb(OAc)_2$ is also converted into $Pb(OAc)_4$ by passing into Cl_2
 $2Pb(OAc)_2 + Cl_2 \longrightarrow Pb(OAc)_4 + PbCl_2 \downarrow$

Properties: It is used as oxidising agent in organic chemistry to oxidise 1, 2-diol to aldehydes and Ketones.

$$\begin{array}{c} \text{RCH(OH)} \\ | \\ \hline \\ \text{RCH(OH)} \end{array} \longrightarrow 2 \text{RCHO} + \text{H}_2 \text{O}$$

17. TETRAETHYL LEAD

4 Na - Pb(alloy 10% - Na) +
$$4C_2H_5Cl$$
 (vap.) \longrightarrow 3Pb + Pb(Et)₄ + 4NaCl

- It is antiknocking agent.
- Pb is used as a lead storage cell.

$$Pb + PbO_2 + 2H_2SO_4 \stackrel{discharge}{\longleftarrow} 2PbSO_4 + 2H_2O_4$$

NITROGEN FAMILY

1. NITROGEN (N₂)

Preparation

(a)
$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

(b)
$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$$

(c)
$$Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$$
 Purest N_2 obtained $2NaN_3 \xrightarrow{\Delta} 2Na + 3N_2$ by this method

(d)
$$2 \text{ NH}_3 + 3 \text{NaOCl} \xrightarrow{\Delta} \text{N}_2 + 3 \text{NaCl} + 3 \text{H}_2 \text{O}$$

(e)
$$2NO + 2Cu$$
red over heated $\longrightarrow 2CuO + N_2$
Black

(f) Cl_2 passed into liquor NH_3

$$3Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl$$

$$6NH_3 + 6HCl \longrightarrow 6NH_4Cl$$

$$3Cl_2 + 8NH_3 \longrightarrow N_2 + 6NH_4Cl$$

In this method NH_3 conc. should not be lowered down beyond an particular limit.

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

(Trimendously explosive)

Properties

- (a) It is inert due to high bond energy.
- (b) It is absorbed by hot metal like Ca, Mg, Al etc.

$$3Ca + N_2 \longrightarrow Ca_3N_2$$

$$2Al + N_2 \longrightarrow 2AIN$$

$$Al_2O_3 + 3C + N_2 \xrightarrow{\Delta} 2AIN + 3CO$$

Inorganic graphite $(BN)_x$: White slippery solid having 2D-sheet structure.

$$(BN)_x \xrightarrow{3000^{\circ}C} (BN)_x$$

3-D network structure similar to diamond (Borazon) which is harder than diamond and used for dimond cutting.

$$Na_2B_4O_7 + 2NH_4Cl \xrightarrow{\Delta} 2NaCl + 2NH_3 + 2B_2O_3 + H_2O$$

 $B_2O_3 + 2NH_3 \xrightarrow{\Delta} 2BN + 3H_2O$

(c) $\rm N_2$ can be absorbed by calcium carbide at the temp around 1000°C

$$CaC_2 + N_2 \xrightarrow{1000^{\circ}C} \underbrace{CaNCN}_{nitrolim}$$
 (It is very good fertiliser)

Cyanamide ion

$$\begin{array}{ccc}
2\Theta & & & & \\
N - & & & & \\
\Theta & & & & & \\
N = & & & & \\
N = & & & & \\
\end{array}$$

2. AMMONIA (NH₃)

Preparation

- Nitrate or nitrite reduction: $NO_3^-/NO_2^- + Zn /Al + NaOH \longrightarrow NH_3 + [Zn(OH)_4]^2 / [Al(OH)_4]^3$ (a)
- (b)
- $\label{eq:Metal_nitride} \begin{array}{lll} \text{Metal nitride hydrolysis}: & \text{N}^{3-} + 3\text{H}_2\text{O} & \longrightarrow & \text{NH}_3 \\ \end{array} \\ + 3\text{OH}^- \\ \text{Haber's process}: & \text{N}_2 + 3\text{H}_2 & \xrightarrow{450\,^{\circ}\text{C}} & 2\text{NH}_3 \\ \end{array}$ (c)

Note: NH₃ can't be dried by H₂SO₄, P₂O₅ and anhydrous CaCl₂ because -

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$H_2O + NH_3 + P_2O_5 \longrightarrow (NH_4)_3PO_4$$

$$CaCl_2 + 8NH_3 \longrightarrow CaCl_2.8 \text{ NH}_3 \text{ (forms adduct)}$$

Quick lime is used for this purpose

Properties

(a) It dissolves several electropositive metals like Li, Na, K, Rb, Cs, Sr, Ba etc.

Ex. K in liq $NH_3 \Rightarrow$ (i) Blue in colour

- (ii) Conducts electricity
- (iii) Having reducing property

$$K \longrightarrow K^+ + e^-$$

$$\downarrow \qquad \qquad \downarrow$$

$$K^+(NH_3)_n \qquad e(NH_3)_x$$

$$solvated e^-$$
It is the cause for above property

$$\begin{array}{c} K_2[\mathrm{Ni}(\mathrm{CN})_4] \xrightarrow{\mathrm{NH}_3\mathrm{NH}_3\mathrm{K}_4[\mathrm{Ni}(\mathrm{CN})_4] \\ \mathrm{Square\,planar} \end{array}$$

Square planar Tetrahedral

(b)
$$Ag(NO_3)$$
 (aq) + $BaCl_2$ (aq) \longrightarrow $AgCl \downarrow$ + $Ba(NO_3)_2$

Filtrate Residue $AgCl \downarrow$ + $AgCl \downarrow$ +

 ${\rm CH_3COOH}$ is strong acid in liquid ${\rm NH_3}$ while in water is weak acid. (c)

AcOH
$$\rightleftharpoons$$
 AcO⁻ + H⁺
NH₃ + H⁺ \rightleftharpoons NH₄⁺ and H₂O + H⁺ \Longrightarrow H₃O⁺
Basisity order NH₃ > H₂O

Hydrolysis and Ammonolysis occurs is a same way. (d)

$$SiCl_4 + 4H_2O \longrightarrow 4HCl + Si(OH)_4 \xrightarrow{\Delta} Si_3O_2 + 2H_2O$$

 $SiCl_4 + 8NH_3 \longrightarrow 4NH_4Cl + Si(NH_2)_4 \xrightarrow{\Delta} Si_3N_2 + NH_3\uparrow$

Rate of hydrolysis and Ammonolysis will be affected by the presence of HCl vapour & NH₄Cl vapour respectively.

(e)
$$NH_4^+$$
 - Salts Preparation
Gypsum suspension saturated \longrightarrow $CaCO_3 + (NH_4)_2SO_4 \xrightarrow{NaNO_3} NH_4NO_3$ with NH_3 and CO_2 passed \longrightarrow $NH_4(NO_2) \xleftarrow{NaNO_2} NH_4CI \xrightarrow{CaCO_3} (NH_4)_2CO_3$

3. OXIDES OF NITROGEN

Preparation and Properties of Oxides of Nitrogen

Formula	Name	Preparation & Structure	Properties
N ₂ O	Dinitrogen monoxide (Nitrous oxide) Laughing gas	$NH_4NO_3 \rightarrow N_2O + 2H_2O$ $N \equiv N \rightarrow O$ (sp, Linear polar molecule)	Colourless gas, rather unreactive, diamegnatic neutral to litmus
NO	Nitrogen monoxide (Nitric oxide)	(a) $3\text{Cu} + 8\text{HNO}_3 \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO}$ (b) $4\text{NH}_3 + 5\text{O}_2 \xrightarrow{\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O}$	Colourless gas, paramagnetic, Neutral to
NO ₂	Nitrogen dioxide Mixed anhydride	$Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$ 0 132°	Brown gas, reactive, paramagnetic, angular and polar $2NO_2 \xrightarrow{H_2O} HNO_2 + HNO_3$
N ₂ O ₃	Dinitrogen trioxide	NO + NO ₂ Low T N ₂ O ₃ $O = N - O - N = O \text{ or}$ $O = N - N - O - N = O \text{ or}$	Dark blue in liquid (-30°C) or solid state, unstable in the gas phase $N_2O_3 \xrightarrow{H_2O} 2HNO_2$
N ₂ O ₄	Dinitrogen tetroxide	$2NO_2 \xrightarrow{Low T} N_2O_4$ $2NO_2 \xrightarrow{N-N} O$	Colourless, exists in equilibrium with NO_2 both in the gaseous and liquid state, in solid state, $\mathrm{N}_2\mathrm{O}_4$ is unstable.
N ₂ O ₅	Dinitrogen pentoxide	$2HNO_3 + P_2O_5 \rightarrow H_2O + N_2O_5$ $H_2O + P_2O_5 \rightarrow 2HPO_3$	No existance in gas phase, in the solid state exists as nitronium nitrate $[\mathrm{NO_2}] \ ^+ [\mathrm{NO_3}]^-$

4. NITROUS ACID (HNO₂)

Preparation

(a) M-nitrite
$$\xrightarrow{\text{dil.acid}}$$
 HNO₂

(b)
$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$

Properties

(a) Oxidising property: Because of its easy oxidation to liberate nascent oxygen, it acts as a strong oxidant $2HNO_2 \longrightarrow H_2O + 2NO + (O)$

$$2KI + 2HNO_2 + 2HCI \longrightarrow 2KCI + 2H_2O + 2NO + I_2$$

$$SnCl_2 + 2HNO_2 + 2HCI \longrightarrow SnCl_4 + 2NO + 2H_2O$$

$$SO_2 + 2HNO_2 \longrightarrow H_2SO_4 + 2NO$$

$$H_2S + 2HNO_2 \longrightarrow 2H_2O + S \downarrow + 2NO$$

$$2FeSO_4 + 2HNO_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NO + 2H_2O$$

$$Na_3AsO_3 + 2HNO_2 \longrightarrow Na_3AsO_4 + 2NO + H_2O$$

(b) Reducing property: Nitrous acid also acts as a reducing agent as it can be oxidised into nitric acid.

$$\begin{split} & \text{HNO}_2 + (\text{O}) \longrightarrow \text{HNO}_3 \\ & 2 \text{KMnO}_4 + 5 \text{HNO}_2 + 3 \text{H}_2 \text{SO}_4 \longrightarrow \text{K}_2 \text{SO}_4 + 2 \text{MnSO}_4 + 5 \text{HNO}_3 + 3 \text{H}_2 \text{O} \\ & \text{K}_2 \text{Cr}_2 \text{O}_7 + 3 \text{HNO}_2 + 4 \text{H}_2 \text{SO}_4 \longrightarrow \text{K}_2 \text{SO}_4 + \text{Cr}_2 \ (\text{SO}_4)_3 + 3 \text{HNO}_3 + 4 \text{H}_2 \text{O} \\ & \text{H}_2 \text{O}_2 + \text{HNO}_2 \longrightarrow \text{H}_2 \text{O} + \text{HNO}_3 \\ & 2 \text{HNO}_2 + \text{NH}_2 \text{CONH}_2 \longrightarrow 2 \text{N}_2 + \text{CO}_2 + 3 \text{H}_2 \text{O} \\ & \text{Urea} \\ & \text{HNO}_2 + \text{NH}_3 \longrightarrow \text{NH}_4 \text{NO}_2 \longrightarrow \text{N}_2 + 2 \text{H}_2 \text{O} \\ & \text{HNO}_2 + \text{C}_2 \text{H}_5 \text{NH}_2 \longrightarrow \text{C}_2 \text{H}_5 \text{OH} + \text{N}_2 + \text{H}_2 \text{O} \\ & \text{HNO}_2 + \text{C}_6 \text{H}_5 - \text{NH}_2 & \text{HCI} \longrightarrow {}^{<5\,^{\circ}\text{C}} \longrightarrow \text{C}_6 \text{H}_5 \text{N} = \text{NCI} + 2 \text{H}_2 \text{O} \end{split}$$

Benzene diazonium chloride

5. NITRIC ACID (HNO₃)

It was named aqua fortis (means strong water) by alchemists.

Preparation

(a) Laboratory Method

$$KNO_3$$
 + conc. H_2SO_4 \longrightarrow $KHSO_4$ + HNO_3 (vap) vapours of nitric acid evolved are condensed in a glass receiver.

- (b) Industrial Preparation
- (i) Birkeland Eyde Process or arc process

Step 1
$$N_2 + O_2 \xrightarrow{3000^{\circ}C} 2NO - heat$$

Step 2 $NO + O_2 \xrightarrow{} NO_2$
Step 3 $NO_2 + H_2O \xrightarrow{} HNO_2 + HNO_3$
Step 4 $HNO_2 \xrightarrow{} HNO_3 + NO + H_2O$

(ii) Ostwald's Process

Physical Properties

Nitric acid usually acquires yellow colour due to its decomposition by sunlight into NO2.

$$4HNO_3 \xrightarrow{\text{sunlight}} 4NO_2 + 2H_2O + O_2$$

The yellow colour of the acid can be removed by warming it to 60-80°C and bubbling dry air through it. it has extremely corrosive action on the skin and causes painful sores.

Chemical Properties

It is very strong acid and it exhibits usual properties of acids. It reacts with basic oxides, carbonates, bicarbonates and hydroxides forming corresponding salts.

Oxidising nature: Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

or $2HNO_3 \longrightarrow H_2O + 2NO + 3O$

- (a) Oxidation of non-metals: The nascent oxygen oxidises various non-metals to their corresponding highest oxyacids.
- (i) Sulphur is oxides to sulphuric acid

$$S + 6HNO_3 \xrightarrow{conc.and hot} H_2SO_4 + 6NO_2 + 2H_2O_3$$

(ii) Carbon is oxidised to carbonic acid

$$C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + 2H_2O$$

(iii) Phosphorus is oxidised to orthophosphoric acid.

$$2P + 10HNO_3 \xrightarrow{conc.and hot} 2H_3PO_4 + 10NO_2 + 2H_2O_3$$

(iv) Iodine is oxidised to iodic acid

$$I_2 + 10HNO_3 \xrightarrow{conc.and hot} 2HIO_3 + 10NO_2 + 4H_2O_3$$

- (b) Oxidation of metalloids: Metalloids like non-metals also form highest oxyacids
- (i) Arsenic is oxidised to arsenic acid

As + 5HNO₃
$$\xrightarrow{\text{conc.and hot}}$$
 2H₃AsO₄ + 5NO₂ + H₂O

(ii) Antimony is oxidised to antimonic acid

$$Sb + 5HNO_3 \xrightarrow{conc.and hot} 2H_3SbO_4 + 5NO_2 + H_2O_3$$

(iii) Tin is oxidised to meta-stannic acid.

$$Sn + 2HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

- (c) Oxidiation of compounds
- (i) Sulphur dioxide is oxidised to sulphuric acid

$$SO_2 + 2HNO_3 \longrightarrow H_2SO_4 + 2NO_2$$

(ii) Hydrogen sulphide is oxidised to sulphur

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

(iii) Ferrous sulphate is oxidised to ferric sulphate in presence of H₂SO₄

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O_4$$

(iv) Iodine is liberated from KI.

$$6KI + 8 HNO_3 \longrightarrow 6KNO_3 + 2NO + 3I_2 + 4H_2O$$

(v) HBr, HI are oxidised to Br_2 and I_2 , respectively.

$$2HBr + 2HNO_3 \longrightarrow Br_2 + 2NO_2 + 2H_2O$$
 Similarly
 $2HI + 2HNO_3 \longrightarrow I_2 + 2NO_2 + 2H_2O$

(vi) Ferrous sulphide is oxidised to ferric sulphate

$$FeS + 8HNO_3 \longrightarrow Fe_2(SO_4)_3 + 8NO_2 + 4H_2O$$

(vii) Stannous chloride is oxidised to stannic chloride in presence of HCl

(viii) Cane sugar is oxidised to oxalic acid

$$C_{19}H_{29}O_{11} + 36 \text{ HNO}_3 \longrightarrow 6(COOH)_2 + 36NO_2 + 23H_9O$$

Action on Metals: Nitric acid reacts with most of the metals except noble metals like gold and platinum. Towards its reaction with metals, HNO_3 acts as an acid as well as an oxidising agent. Like Other acids, HNO_3 liberate nascent H from metals which further reduces the nitric acid into number of products like NO, NO_2 , N_2O , N_2 , NH_2OH or NH_3 according to the following reactions:

The progress of the reaction is controlled by a number of factors :

- (a) The nature of the metal
- (b) The concentration of the acid,
- (c) The temperature of the reaction
- (d) The presence of other impurities

Concentration of nitric acid	Metal	Main products
Vom dilute HNO (60/)	Mg, Mn (2%)	H ₂ + Metal nitrate
Very dilute HNO ₃ (6%)	Fe, Zn, Sn	NH4NO3 + metal nitrate + H2O
	Pb, Cu, Ag, Hg	NO + metal nitrate + H ₂ O
Dilute HNO ₃ (20%)	Fe, Zn	N_2O + metal nitrate + H_2O
	Sn	$NH_4NO_3 + Sn(NO_3)_2$
Conc. HNO ₃ (70%)	Zn, Fe, Pb, Cu, Ag, Hg	NO ₂ + metal nitrate + H ₂ O
Conc. 111103(70%)	Sn	$NO_2 + H_2SnO_3$

Action on Proteins

- (a) Nitric acid attacks proteins forming a yellow nitro compound called xanthoprotein. It, therefore, stains skin and renders wool yellow. This property is utilized for the test of proteins.
- (b) Oxidation: Number of organic compound are oxidised.

Sawdust catches fire when nitric acid is poured on it. Turpentine oil bursts into flames when treated with fuming nitric acid. Toluene is oxidised to benzoic acid with dil. HNO₃.

Structure

Nitric acid is a monobasic acid, i.e. the molecule consist of one hydroxyl group as it is formed by the hydrolysis of nitryl chloride, NO_2Cl . It may be structurally represented as below:



Gaseous nitric acid is a planar molecule. The bond lengths and bond angles as present in the molecule are represented in the figure :

6. ALLOTROPIC MODIFICATIONS OF PHOSPHORUS

Phosphorus exists in a number of allotropic forms. These forms are :

- (a) Yellow or white phosphorus
- (b) Red phosphorus
- (c) Black phosphorus

(a) White or yelllow phosphorus

Preparation

(i) Bone ash or Apatite rock both have same formula
$$\begin{array}{c|c} Ca_3(PO_4)_2 + 3SiO_2 \xrightarrow{1200^{\circ}C} 3CaSiO_3 + P_2O_5 \\ 2P_2O_5 + 10C \xrightarrow{1500^{\circ}C} P_4 + 10CO \\ (Coke) & \text{white 'P'} \end{array}$$

(ii)
$$Ca_3(PO_4)_2 + 3H_2SO_4 \xrightarrow{conc.} 3CaSO_4 + 2H_3PO_4$$

 $H_3PO_4 \xrightarrow{320^{\circ}C} HPO_3$

meta phosphoric acid

$$12C + 4HPO_3 \xrightarrow{1000°C} 2H_2^{\uparrow} + 12CO^{\uparrow} + P_4$$

Coke white 'P'

Properties

- (i) It has characteristic garlic smell and is poisonous in nature. Persons working with phosphorus develop a disease in which the jaw bones decay. This disease is knwon as **phossy jaw**.
- (ii) In contact with air, it undergoes slow combustion and glows in dark. This property is called **phosphorescence**.
- (iii) Its ignition temperature is low (about 30 °C). It readily catches fire giving dense fumes of phosphorus pentoxide. It is, therfore, kept in water.

$$P_4 + 5O_2 \longrightarrow P_4O_{10} \text{ or } 2P_2O_5$$



(b) Red phosphorus

Preparation

Red phosphorus is formed by heating yellow phosphorus, between 240-250 C, in presence of an inert gas.

Structure of red phosphorus :- It is regarded as a polymer consisting of chains of P_4 tetrahedral linked together by covalent bond.

$$--P \left(\begin{array}{c} P \\ P \end{array} \right) P --P \left(\begin{array}{c} P \\ P \end{array} \right) P --P \left(\begin{array}{c} P \\ P \end{array} \right) P --P \left(\begin{array}{c} P \\ P \end{array} \right)$$

proposed molecular structue of red phosphorus

(c) Black P

Preparation: This is most stable form of Phosphorus

White(P)
$$\xrightarrow{\text{at high P}}$$
 Black P

Black P contain zig-zag & double layered structure.

Order of density & mp

Black > Red > White

Comparison between White and Red Phosphorus

Property	White phosphorus	Red phosphorus
Physical state	Soft waxy solid.	Brittle powder.
Colour	White when pure.	Red.
	Attains yellow colour	
	on standing.	
Odour	Garlic	Odourless.
Solubility in water	Insoluble.	insoluble
Solubility in ${ m CS}_2$	Soluble.	Insoluble.
Physiological action	Poisonous.	Non-poisonous.
Chemical activity	Very active.	Less active.
Stability	Unstable.	Stable.
Phosphorescence	Glows in dark	Does not glow in dark.
Reaction with NaOH	Evolves phosphine.	No action.
Molecular formula	P_4	Complex polymer.

7. PHOSPHINE GAS (PH₃)

Preparation

(a)
$$4H_3PO_3 \xrightarrow{\Delta} PH_3 + 3H_3PO_4$$

(b)
$$PH_4I + KOH \longrightarrow KI + PH_3 + H_2O$$

 $(PH_3 + HI)$
(c) $2AIP + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + PH_3 \uparrow$ $}$ purest PH_3

Physical properities

- (a) It is having 'rotten fish' smell.
- (b) It is soluble in ${\rm CS}_2$ and insoluble in water.

$$(PH_3 + H_2O \longrightarrow PH_4^{\dagger} + OH^{-})$$
in s-orbital, so donating capacity is less

Note: PH_4^+ is formed with acids.

(c) Like NH_3 , PH_3 also can form addition product.

$$\mathrm{CaCl_2} \bullet \mathrm{8NH_3}, \; \mathrm{Cu_2Cl_2} \bullet \mathrm{2PH_3}, \; \mathrm{AlCl_3} \bullet \mathrm{2PH_3}, \; \mathrm{SnCl_4} \bullet \mathrm{2PH_3}$$

 $\ensuremath{\mathsf{PH}}_3$ can be absorbed by Ca(OCl)Cl.

$$\mathsf{PH}_3 \, + \, \mathsf{3Ca(OCl)Cl} \, + \, \mathsf{3H}_2\mathsf{O} \longrightarrow \mathsf{PCl}_3 \, + \, \mathsf{3HCl} \, + \, \mathsf{3Ca(OH)}_2$$

$$2NH_3 + 3Ca(OCl)Cl \longrightarrow N_2 + 3CaCl_2 + 3H_2O$$

Chemical properties

(a)
$$PH_3 + O_3 \xrightarrow{150^{\circ}} P_2O_5 + H_2O$$

(b)
$$PH_3 + 3Cl_2 \longrightarrow PCl_3 + 3HCl_3$$

(c)
$$PH_3 + 4N_2O \xrightarrow{electrical} H_3PO_4 + 4N_2$$

(d)
$$2PH_3 + 3CuSO_4 \longrightarrow Cu_3P_2 \downarrow + 3H_2SO_4$$

Detection of PH_3 Black ppt.

(e)
$$PH_3 + 6AgNO_3 \longrightarrow \left[Ag_3P \cdot 3AgNO_3 \downarrow\right] + 3HNO_3$$

Yellow ppt.

$$Ag_3 P \cdot 3AgNO_3 + 3H_2O \longrightarrow 6Ag \downarrow + 3HNO_3 + H_3PO_3$$

(f) $PH_3 + 4HCHO + HCl \longrightarrow [P(CH_2OH)_4]^+Cl^-$ (which is used for making fire-proof cotton fabrics) white/colourless solid

8. OXIDES OF PHOSPHORUS

It forms three important oxides which exist in dimeric forms.

Phosphorus trioxide (P_4O_6)

Preparation

Phosphorus trioxides is formed when phosphorus is burnt in a limited supply of air.

$$P_4 + 3O_2$$
 (limited) \longrightarrow P_4O_6

Properties

(a) Heating in air: On heating in air, it forms phosphorus pentoxide.

$$P_4O_6 + 2O_2 \longrightarrow P_4O_{10}$$

Phosphorus (V) oxide

(b) Action of water: It dissolves in cold water to give phosphorus acid.

$$P_4O_6 + 6H_2O \text{ (cold)} \longrightarrow 4H_3PO_3$$

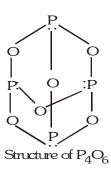
Phosphorus acid

It is, therefore, considered as anhydride of phosphorus acid.

Note: With hot water, it gives phosphoric acid and inflammable phosphine.

Structure

- (a) Each atom of phosphorus in P_4O_6 is present at the corner of a tetrahedron
- (b) Each phosphorus atom is covalently bonded to three oxygen atoms and each oxygen atom is bonded to two phosphorus atoms.
- (c) It is clear from the structure that the six oxygen atoms lie along the edges of the tetrahedron of P atoms.



Phosphorus (V) oxide (P_4O_{10})

Preparation: It is prepared by heating white phosphorus in excess of air.

$$P_4 + 5O_2$$
 (excess) $\xrightarrow{\Delta} P_4O_{10}$

Properties

- (a) It is snowy white solid.
- (b) Action with water: It readily dissolves in cold water forming metaphosphoric acid.

$${\rm P_4O_{10}} \ + \ 2{\rm H_2O} \ ({\rm Cold}) \longrightarrow \ 4{\rm HPO_3}$$

Metaphosphoric acid.

With hot water it gives phosphoric acid.

$$P_4O_{10} + 6H_2O \text{ (Hot)} \longrightarrow 4H_3PO_4$$

Phosphoric acid

- (c) **Dehydrating nature**: Phosphorus pentoxide has strong affinity for water and, therefore, acts as a powerful dehydrating agent. It extracts water from many inorganic and organic compounds.
- (d) P_4O_{10} is a very strong dehydrating agent and extracts water from many compounds including sulphuric acid and nitric acid.

$$2\text{HClO}_4 \ \xrightarrow{\quad P_4O_{10} \quad } \text{Cl}_2O_7$$

Chlorine (VII) oxide

$$2CH_{3}CONH_{2} \xrightarrow{P_{4}O_{10}} CH_{3}CN$$

Acetamide

Methyl cyanide

Structure

- (a) Its structure is similar to that of P_4O_6 .
- (b) In addition, each phosphorus atom forms a double bond with oxygen atom as shown in figure.

