

p - BLOCK-I

The elements in which the last electron enters to the outer most p orbital are called p- block elements. As the maximum number of electrons that can be accommodated in a set of p-orbitals is six, therefore there are six groups of p - blocks in the periodic table.

Group 13 Elements : Boron Family

The Elements are B (Non metal), Al, Ga, In, Tl (Metals)

General electronic configuration [Noble gas] $ns^2 np^1$

Atomic and Physical properties

(i) **Atomic and Ionic radii**

Atomic radii: $B > Ga < Al < In < Tl$

(ii) **Ionization Enthalpies.**

$B > Tl > Ga > Al > In$ (Sum of three IE values)

(iii) **Melting and Boiling points**

M.P. $B > Al > Tl > In > Ga$

B.P. $B > Al > Ga > In > Tl$

(iv) **Electropositive Character**

Due to high IE they are less electropositive. On moving down the group metallic character increases due to decrease in IE [\therefore B is nonmetal and other elements are metals.]

$B <$	$Al < Ga < In < Tl$
Non metal	Metals

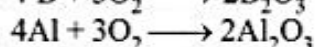
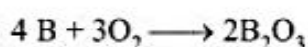
Note : Boron exists in many allotropic forms. All the allotropes have basic building B_{12} icosahedral units made up of polyhedron having 20 faces and 12 corners. For example one is the simplest form : α - rhombohedral boron.



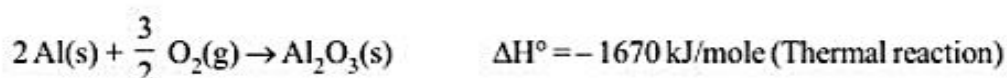
But Al, In & Tl all have close packed metal structure.

CHEMICAL PROPERTIES

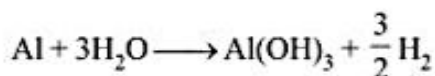
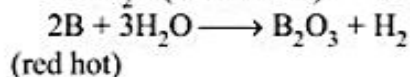
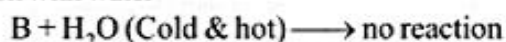
(i) **Reaction with oxygen**



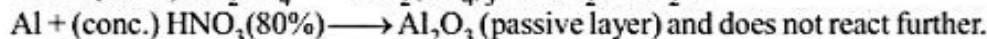
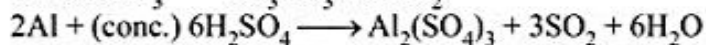
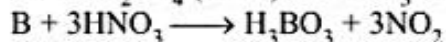
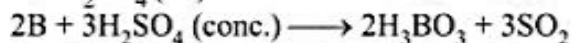
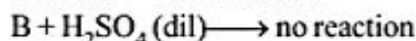
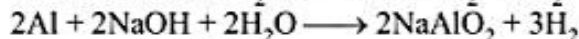
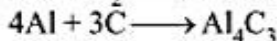
Al should react air to form a very thin oxide film (10^{-4} to 10^{-6} mm thick) on the surface and protects the metal from further attack



(ii) Reaction with water



Ga and In are attacked neither by cold water nor hot water unless oxygen is present. Tl form an oxide on surface.

(iii) $B + HCl \longrightarrow \text{no reaction}$ (iv) $2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$ (v) $2B + N_2 \longrightarrow 2BN$ $2Al + N_2 \longrightarrow 2AlN$ (vi) $3Mg + 2B \longrightarrow Mg_3B_2$ **Illustration**

1. Stability of trivalent and monovalent cation of group 13 (Boron family) will be in order :

(A) $Ga^{3+} < In^{3+} < Tl^{3+}$ (B) $Ga^{3+} > In^{3+} > Tl^{3+}$ (C) $Ga^+ > In^+ < Tl^+$ (D) $Ga^+ < In^+ < Tl^+$

Ans. (B), (D)

Sol. By inert pair effect stability of +3 state decreases and that of +1 state increases along a group.

Exercise

1. Which one of the following elements has the highest melting point

(A) Al

(B) B

(C) Ga

(D) Tl

Ans. (B)

BORON AND ITS COMPOUNDS

(i) Occurrence :

Boron does not occur free in nature .It occurs principally as borates e.g.

(i) Borax & tincal : $Na_2B_4O_7 \cdot 10H_2O$

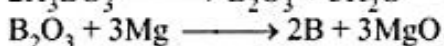
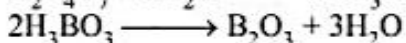
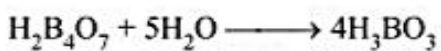
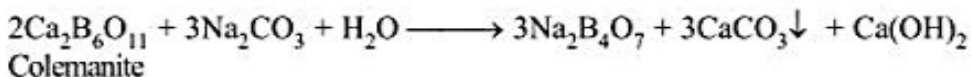
(ii) Colemanite : $Ca_2B_6O_{11} \cdot 5H_2O$

(iii) Kernite : $Na_2B_4O_7 \cdot 4H_2O$

(iv) Boric acid : H_3BO_3

(ii) **Extraction of Boron** →**Extraction from minerals :**

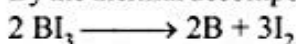
Principle → Boron may be obtained by treating borax with hot concentrated HCl, igniting the boric acid H_3BO_3 to give the oxide B_2O_3 and finally reduced with Mg.

**Crystalline Boron :****Preparation :**

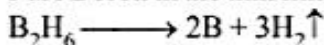
By reducing the vapour of boron tribromide (BBr_3) with hydrogen in an electric arc



By the thermal decomposition of BI_3 on a tantalum filament



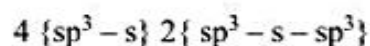
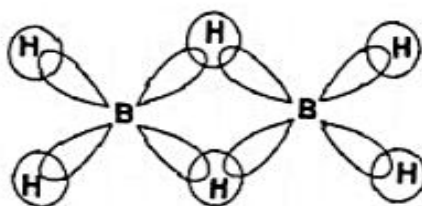
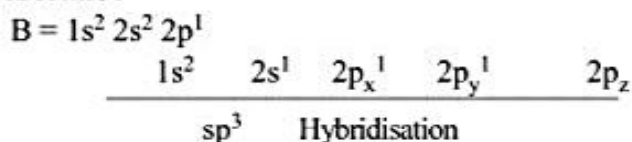
Pure Boron in the thin film can also be obtained by heating diborane to 700°C

(iii) **Physical properties**

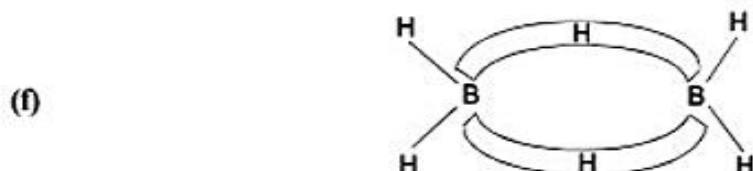
(a) It is a non-metal. Boron occurs in two different allotropic forms AMORPHOUS and CRYSTALLINE

(b) Amorphous boron has not been obtained in the pure state .

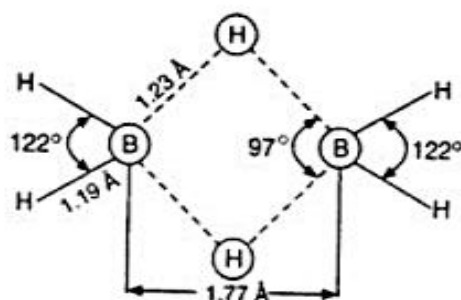
(c) Crystalline boron is a black powder , extremely hard with a metallic appearance but with very low electrical conductivity.

COMPOUNDS OF BORON**(I) B_2H_6 (Diborane)****Structure of Diborane :**

- (a) 4 Terminal H-are bonded by σ bond & remaining 2H are bridging hydrogens and of these are broken then dimer become monomer.
- (b) Boron undergoes sp^3 hybridisation 3 of its sp^3 hybridised orbitals contain one e^- each & fourth sp^3 hybrid orbital is vacant
- (c) 3 of these sp^3 hybrid orbitals get overlapped by s orbitals of 3 hydrogen atoms.
- (d) One of the sp^3 hybrid orbitals which have been overlapped by s orbital of hydrogen gets overlapped by vacant sp^3 hybrid orbital. of 2nd Boron atom and its vice versa.
- (e) By this two types of overlapping take place 4(sp^3-s) overlap bonds & 2 (sp^3-s-sp^3) overlap bonds.



H is held in this bond by forces of attraction from B & This bond is called 3 centered two electron bonds. It is also called Banana bonds. Due to repulsion between the two hydrogen nuclei, the delocalised orbitals of bridges are bent away from each other on the middle giving the shape of banana.



Uses of Diborane :

- Diborane is used for preparing substances such as high energy fuel & propellents.
- Boron hydrides have been tried as rocket fuels .
- It is used as a catalyst in polymerisation reaction.
- It is used as a reducing agent in inorganic reaction.
- It is used for welding torches.

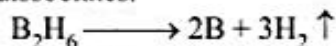
Preparation of B_2H_6 :

- $Mg_3B_2 + HCl \longrightarrow B_2H_6 + B_4H_{10} + B_5H_9$ etc.
(10%)
- $B_4H_{10} \xrightarrow[100^\circ C]{\Delta} B_2H_6 + H_2 + \text{higher borane}$
- $BCl_3 \text{ (or } BBr_3) + 6H_2 \xrightarrow[\text{discharge at low pressure}]{\text{Electric}} B_2H_6 + 6HCl$
- $3LiAlH_4 + 4BF_3 \longrightarrow 3LiF + 3AlF_3 + 2B_2H_6$
or $LiBH_4$ or $3(BF_3)$

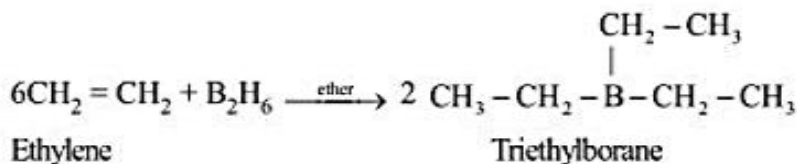
Physical properties :

- Diboranes (Melting point = $-165.5^\circ C$, Boiling point = $-92.5^\circ C$) is a colourless gas with a foul smell & is extremely toxic.
- It is an extremely reactive inflammable gas which burns in air with green flame.

- (iii) Diborane reacts with sodium amalgam to form an addition product $B_2H_6Na_2$.
 (iv) On heating to $700^\circ C$ diborane dissociates.



- (v) Diborane readily adds at $0^\circ C$ to $25^\circ C$ to the olefinic acetylene compound to form trialkylborane. The reaction is known as hydroboration.



- (vi) Diborane is electron - deficient molecule & hence it reacts with several molecule having lone pair(s) of electron (e.g. CO, ether, amines etc.) to form complex compounds.
 (vii) Boranes have great affinity for water & O_2 hence they do not occur in nature. Moreover borane cannot be prepared directly from its elements as they have positive enthalpy & positive free energy of formation.

Chemical properties

- (i) $B_2H_6 + O_2 \xrightarrow[\text{air spontaneously}]{\text{burns in}} B_2O_3 + H_2O$
 (ii) $B_2H_6 + H_2O \text{ (Cold)} \longrightarrow H_3BO_3 + 6H_2$
 (iii) $B_2H_6 + HCl \text{ (dry)} \xrightarrow[AlCl_3]{\text{anh.}} B_2H_5Cl + H_2$
 (iv) $B_2H_6 + 2N(CH_3)_3 \longrightarrow 2(CH_3)_3N + BH_3$
 (v) $B_2H_6 + 2Na \text{ (amalgam)} \longrightarrow B_2H_6Na_2$
 (vi) $6NH_3 + 3B_2H_6 \longrightarrow 2B_3N_3H_6 + 12H_2$
borazole

Illustration

1. In diborane
 (A) 4-Bridged hydrogens and two terminal hydrogens are present
 (B) 2-Bridged hydrogens and four terminal hydrogens are present
 (C) 3-Bridged and three terminal hydrogens are present
 (D) None of the above

Ans. (B)

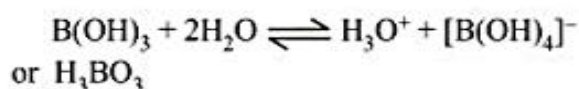
Sol. In diborane (B_2H_6) there are two bridged H atoms and four terminal H atoms which along with two B atoms lie in plane perpendicular to each other.

Exercise

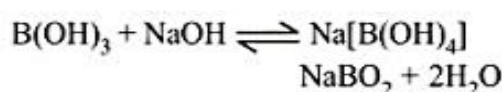
1. In the reaction $B_2O_3 + C + Cl_2 \longrightarrow A + CO$. The A is
 (A) BCl_3 (B) BCl_2 (C) B_2Cl_2 (D) CCl_2
 Ans. (A)

(II) Orthoboric Acid (H_3BO_3)

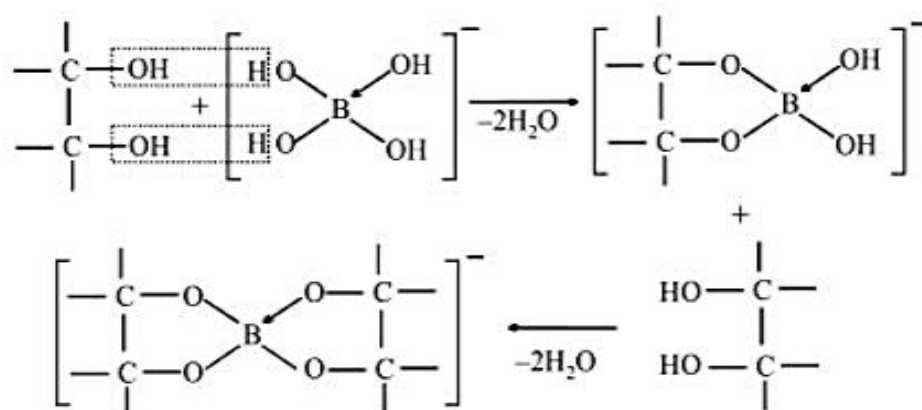
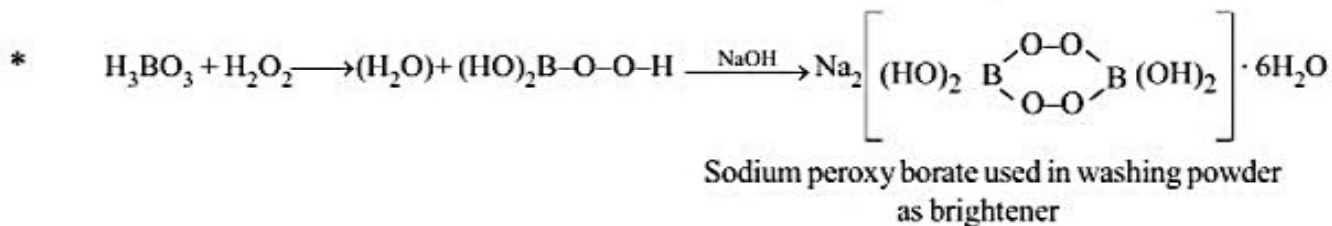
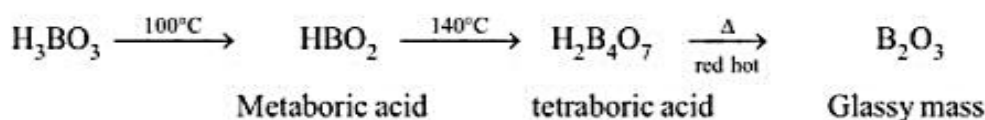
H_3BO_3 is soluble in water and behaves as weak monobasic acid. It does not donate protons but rather it accepts OH^- . Therefore it acts as a Lewis acid ($\text{B}(\text{OH})_3$)



Since $\text{B}(\text{OH})_3$ only partially reacts with water to form H_3O^+ and $[\text{B}(\text{OH})_4]^-$ it behaves as a weak acid. Thus it cannot be titrated satisfactorily with NaOH as a sharp end point is not obtained. If certain polyhydroxy compounds such as glycerol, mannitol or sugar are added to the titration mixture then $\text{B}(\text{OH})_3$ behaves as a strong monobasic acid and hence can now be titrated with NaOH and end point is diluted using phenolphthalein as indicator.



The added compound must be a cis diol to enhance the acidic properties. In this way the cis-diol forms very stable complexes with $[\text{B}(\text{OH})_4]^-$ formed in forward direction above, thus effectively removing it from solution. Hence reaction proceeds in forward direction (Le-Chatelier principle.)

*** Heating of boric acid :**

- Ans. (D)**

Sol. $\text{Na}_2\text{B}_4\text{O}_7 + 7\text{H}_2\text{O} \longrightarrow 2\text{B(OH)}_3 + 2\text{Na[B(OH)}_4\text{]}$
 B(OH)_3 or H_3BO_3 is an acid and does not react with acid.
Hence $\text{Na[B(OH)}_4\text{]}$ reacts with acid.

Exercise

1. Borax is converted into B by steps
 Borax I $\text{H}_3\text{BO}_3 \xrightarrow{\Delta} \text{B}_2\text{O}_3$ — II \rightarrow B
 I and II reagents are :
 (A) Acid, Al (B) Acid, C (C) Acid, Fe (D) Acid, Mg
- Ans. (D)

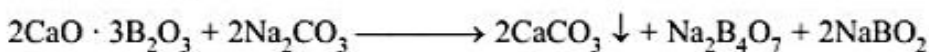
(III) Borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ or Tincal :

- (a) It is also named as sodium tetra borate decahydrate.
(b) Common Indian name is Suhaga.
(c) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ is known as Jeweller's
(d) $\text{Na}_2\text{B}_4\text{O}_7$ is known as Boron glass

(b) Preparation :

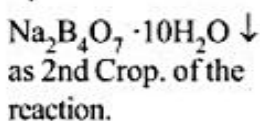
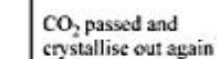
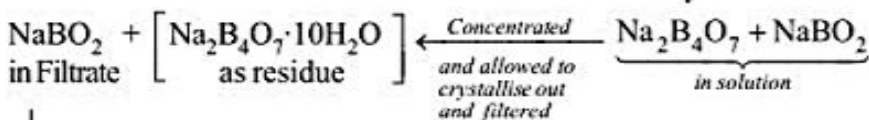
Form colemanite :

Preparation of Borax :



Colemanite

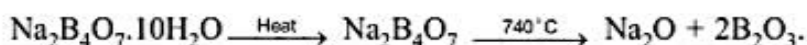
Filtered
– CaCO₃ (as residue)



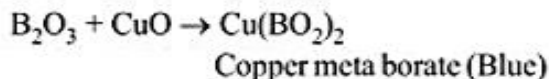
Uses of borax: (i) In making glass, enamel and glaze of pottery.
(ii) As antiseptic in medicinal soaps preparation.

Chemical Properties :**Action of Heat on Borax :**

- (i) Borax swells up on heating.
 (ii) On heating borax loses water and swells into a white mass which on further heating melts to form transparent glassy solid called Borax glass and Borax bead.

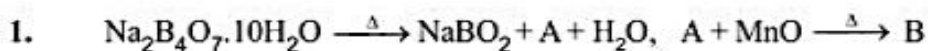


- (iii) The borax bead is due to the formation of B_2O_3 which when fused with metal salts form corresponding metaborate.



- (iv) Colour of meta borates

Cu	Fe	Co	Ni	Cr
Blue	Green	Blue	Brown	Green

Illustration

A and B are :

(A) Na_3BO_3 , $\text{Mn}_3(\text{BO}_3)_2$

(B) $\text{Na}_2(\text{BO}_2)_2$, $\text{Mn}(\text{BO}_2)_2$

(C) B_2O_3 , $\text{Mn}(\text{BO}_2)_2$

(D) None is correct

Ans. (C)

Sol. $\text{A} = \text{B}_2\text{O}_3$, $\text{B} = \text{MnO} + \text{B}_2\text{O}_3 \rightarrow \text{Mn}(\text{BO}_2)_2$

Exercise

1. Borax is used as a buffer since :
 (A) Its aqueous solutions contains equal amount of weak acid and its salt
 (B) It is easily available
 (C) Its aqueous solution contains equal amount of strong acid and its salt
 (D) Statement that borax is a buffer, is wrong

Ans. (A)

Aluminium and its compounds

- Aluminium does not occur free in nature. It is most abundant metal in the earth's crust.
- Important minerals are :

(i) Bauxite : $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	(ii) Diaspore : $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
(iii) Corundum : Al_2O_3	(iv) Cryolite : Na_3AlF_6
(v) Feldspar : KAlSi_3O_8 or $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	
- Among binary compounds of Al only AlF_3 & Al_2O_3 are ionic.
- Extraction of Al is done from bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) by electrolysis. The process involves:

(a) Purification of bauxite.	(b) Electrolytic reduction of alumina.
(c) Purification of Al.	
- Bauxite is associated with impurities of Fe_2O_3 , SiO_2 & TiO_2 . The method of purification depends upon the nature of impurity.

COMPOUNDS OF ALUMINIUM

(I) Al_2O_3 (Corundum)

Preparation :

- (i) $2\text{Al}(\text{OH})_3 \xrightarrow{300^\circ\text{C}} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$
- (ii) $\text{Al}_2(\text{SO}_4)_3 \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 3\text{SO}_3$
- (iii) $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O} \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 2\text{NH}_3 + 4\text{SO}_3 + 25\text{H}_2\text{O}$

Properties

- (1) It is very stable and unreactive
- (2) Melting point $\longrightarrow 2050^\circ\text{C}$
Boiling point $\longrightarrow 2980^\circ\text{C}$
- (3) It is amphoteric oxide :

$$\text{Al}_2\text{O}_3 + 6\text{HCl} \longrightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O}$$

$$\text{Al}_2\text{O}_3 + 2\text{NaOH} \longrightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}$$
- (4) Reaction with carbon :

$$2\text{Al}_2\text{O}_3 + 9\text{C} \xrightarrow{2000^\circ\text{C}} \text{Al}_4\text{C}_3 + 6\text{CO}$$

$$4\text{Al}(\text{OH})_3 + 3\text{CH}_4 \xleftarrow{12\text{H}_2\text{O}}$$

Uses :

- (i) It is used as a refractory material.
- (ii) In chromatography for separation of mixture.
- (iii) In preparation of Artificial gems.

(II) AlCl_3

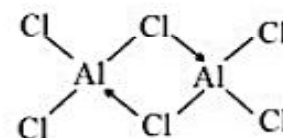
Preparation:

- (i) $2\text{Al} + 6\text{HCl}(\text{vap.}) \xrightarrow[\text{dry}]{(\text{over heated})} 2\text{AlCl}_3 + 3\text{H}_2$
- (ii) $\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 \xrightarrow[1000^\circ\text{C}]{\Delta} 2\text{AlCl}_3(\text{vap.}) + 3\text{CO}$

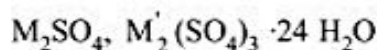
$$\downarrow \text{Cooled}$$
Solid anh. AlCl_3

Props:

- (i) Its anhydrous form is deliquescent and fumes in air.
- (ii) It sublimes at 180°C .
- (iii) It is covalent and exists in the form of dimer even if in non polar solvents e.g. alc., ether, benzene, where it is soluble in fair extent.



- Uses:** (i) Friedel-Craft reaction
(ii) Dyeing, drug. & perfumes etc.

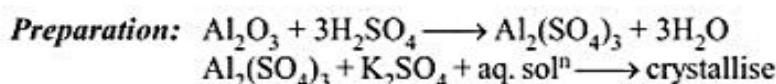
(III) Alums:

Props: Swelling characteristics

where $M = Na^+, K^+, Rb^+, Cs^+, As^+, Tl^+, NH_4^+$

$M' = Al^{+3}, Cr^{+3}, Fe^{+3}, Mn^{+3}, Co^{+3}$

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Potash alum
$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Ammonium alum
$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$	Chrome alum
$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$	Ferric alum



Uses: (i) Act as coagulant (ii) Purification of water
 (iii) Tanning of leather (iv) Mordant in dying (v) Antiseptic

Illustration

1. Generally the atomic and ionic radii increase with increase in atomic number down the group. But the atomic size of aluminium and gallium is almost the same. This is because
 (A) The nuclear charge of Ga is higher than that of Al
 (B) Gallium contains intervening d-electrons which do not screen the valence electrons effectively
 (C) The ionization energies of Ga and Al are comparable
 (D) All the three above.

Ans. (B)

Sol. Due to the poor shielding (screening) effect of d-electrons in case of Ga, the valence electrons are attracted more strongly and hence the size is not increased.

2. Which of the following statements is incorrect about aluminium ?
 (A) It liberates H_2 from acids (B) It liberates H_2 from bases
 (C) It liberates H_2 from both acids and bases (D) It liberates H_2 from acids but not from bases

Ans. (D)

Sol. Al liberates H_2 from both acids and alkalies. For example,
 $2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$; also refer to.

Exercise

1. Which of the following reactions forms the basis of Goldschmidt aluminothermite process ?
 (A) $2Al + N_2 \longrightarrow 2AlN$ (B) $2Al + 3Cl_3 \longrightarrow 2AlCl_3$
 (C) $2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$ (D) $2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$.

Ans. (D)

2. Aluminium becomes passive in
 (A) Conc. HNO_3 (B) H_2CrO_4 (C) $HClO_4$ (D) All

Ans. (D)

Group 14 Elements (Carbon Family)

The Elements are C [Non metals], Si, Ge [Metalloids], Sn, Pb, [Metals]

General electronic configuration [noble gas] $ns^2 np^2$

(I) Atomic and Physical properties

(i) Atomic Radii

Covalent radii : $C < Si < Ge < Sn < Pb$

(ii) Ionizations Enthalpies

$C > Si > Ge > Pb > Sn$ (IE_1 values)

(iii) Melting and Boiling Points

M.P. $C > Si > Ge > Pb > Sn$

B.P. $Si > Ge > Sn > Pb$

(iv) Metallic Character

$C < Si < Ge < Sn < Pb$ (Metallic character)

C, Si [Non metal]

Ge [Metalloid]

Sn, Pb [Metal]

(II) Allotropes

Carbon have two types of Allotropic forms

(1) Crystalline (2) Amorphous

(1) Crystalline : Diamond, Graphite and Fullerene

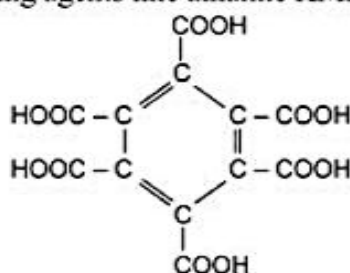
(i) Diamond :

- (1) Each carbon is linked to another atom and so very closed packing in structure of Diamond.
- (2) Density and hardness is very much greater for diamond because of closed packing in diamond due to sp^3 hybrid and are tetrahedrally arranged around it.
- (3) Diamond has sharp cutting edges that's why it is employed in cutting of glass.
- (4) Diamond crystals are non conductor of electricity because of not presence of mobile electron.
- (5) 1 carat of diamond = 200 mgm.
- (6) Diamond powder if consumed is fatal and causes death in minutes.

(ii) Graphite :

- (1) In graphite carbon are sp^2 hybridised and due to this carbon exist as hexagonal layer.
- (2) Each carbon is lined with 3 carbons and one carbon will be left and form a two dimensional shed like structure.
- (3) Distance between two layers is very large so no regular bond is formed between two layers. The layers are attached with weak vander waal force of attraction.
- (4) The carbon have unpaired electron so graphite is a good conductor of current.
- (5) C-C bond length in Graphite is shorter (1.42 \AA) than that of Diamond (1.54 \AA).
- (6) Graphite has high melting point so it is employed in manufacture of crucible.

- (7) Graphite when heated with oxidising agents like alkaline KMnO_4 forms metallic acid.



Benzene hexa carboxylic acid

(iii) **Buckminster Fullerene :**

- (1) It has the formula C_{60} and is made from interlocking hexagonal and pentagonal rings of carbon atoms.
- (2) Such molecules are now thought to exist even in chimney root or candle smoke.
- (3) The structure of C_{60} is similar to the surface of a football which has also set of interlocking hexagons and pentagons.
- (4) Another molecule C_{70} has been recently discovered.
- (5) These and similar large carbon molecules are sometimes referred as "bucky balls".

(2) **Amorphous Allotropic Forms of Carbon :**

(A) **Lamp Black :**

- (i) Obtained by incomplete combustion of compounds which contains higher % of carbon, benzene, turpentine, acetylene etc. These all on combustion form black carbon called lamp black.
- (ii) Black blue ink, printing ink, black paints, varnishes are made from lamp black.

(B) **Coke :**

- (i) Obtained by destructive distillation of coal
- (ii) Coke is usually employed as weak reducing agent with compared to CO.

(C) **Wood Charcoal :**

- (i) Obtained by incomplete combustion of wood.
- (ii) Used to decolourise organic compound.

Allotropic forms of Tin :

- (i) It has three allotropic forms
 - (a) White tin :
 - (i) Used in containers of oil.
 - (ii) White tin is more stable and having maximum density.
 - (b) Grey tin :
 - (c) Rhombic tin :
- (ii) At low temp. (18°C) white tin converts to Grey tin.
- (iii) At temp. of 160°C (above) white tin converts to Rhombic tin.
- (iv) White tin forms grey tin which is obtained as powdery substance and with formation of this thickness of white tin container decreases. This is called Tin pest or Tin disease or Tin plague.
- (v) When tin sheets are folded, they given a peculiar sound which is called as Tin cry.

(3) Catenation

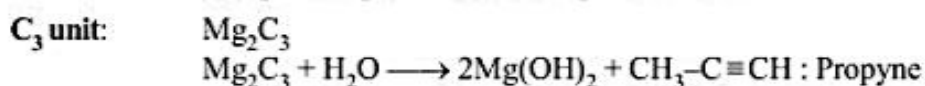
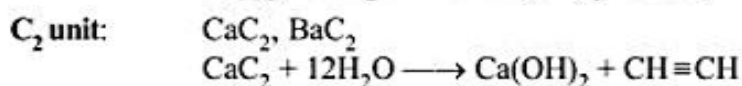
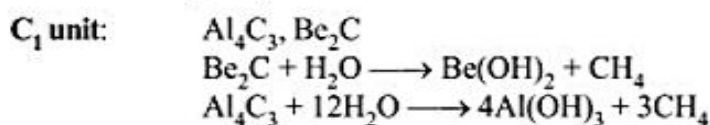
The property of forming bonds with atoms of the same element or tendency to self linking called catenation. Carbon shows maximum catenation. On moving down the group catenation tendency decreases. This because the strength of C – C bond is very high and in case of other elements, strength of M – M (where M = Si, Ge, Sn, Pb) bond is decreases down the group.

Bond	Bond Energy (kJmol ⁻¹)
C – C	348
Si – Si	297
Ge – Ge	260
Sn – Sn	240

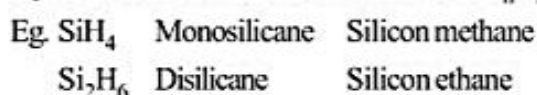
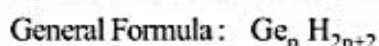
COMPOUNDS OF CARBON FAMILY**(1) Carbide****Types of Carbide****(i) Ionic and salt like:**

Classification on basis of
no. of carbon atoms
present in hydrocarbon
found on their hydrolysis

- (a) C₁ unit
(b) C₂ unit
(c) C₃ unit

**(ii) Covalent carbide : SiC & B₄C****(iii) Interstitial carbide : MC (Transition element or inner transitional elements forms this kind of carbide)**

Interstitial carbide formation doesn't affect the metallic lusture and electrical conductivity. (Q no chemical bond is present, no change in property)

(2) Hydrides :**(i) Carbon form large number of hydrides eq. Alkanes, Alkenes.****(ii) Hydrides of Si are silanes with formula Si_nH_{2n+2}. These are also called as Silicon alkanes.****(iii) Silanes with 'n' up to 8 are known.****(iv) Hydrides of Ge are called Germaines.**

- (v) Tin has only two hydrides i.e.
 (a) Stannane – SnH_4
 (b) Distannane – Sn_2H_6
- (vi) Lead has only one hydride i.e.
 Plumbane – PbH_4
- (vii) Thermal stability of hydrides ↓ Decreases, Because ($\Delta \text{E.N}$ decreases)

(3) Oxides :

Carbon reacts with oxygen to form three types of oxides-

- (a) Carbon monoxide CO (b) Carbon dioxide CO_2 (c) Carbon suboxide C_3O_2

(a) Carbon monoxide CO

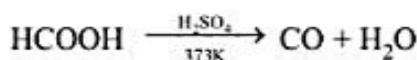
- (i) By incomplete combustion of carbon



- (ii) Reduction of oxides of heavy metals with carbon

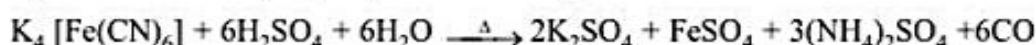


- (iii) By dehydration of formic acid with conc. H_2SO_4
 (laboratory method)



Formic acid (pure)

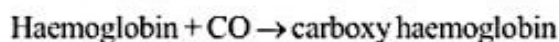
- (iv) By action of conc. H_2SO_4 on potassium ferrocyanide



pot. ferrocyanide

Physical Properties :

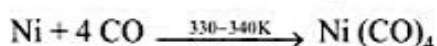
- (i) It is a neutral oxide.
 (ii) Colourless & odourless gas, slightly soluble in water.
 (iii) Poisonous nature due to its ability to form a stable complex with the haemoglobin present in the red blood cells.



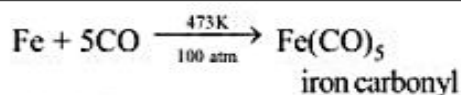
Due to formation of stable complex with CO, Haemoglobin loses its O_2 carrying capacity which causes death.

Chemical properties

- (i) Formation of metal carbonyls

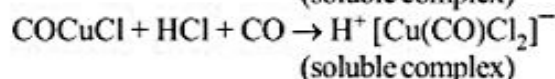
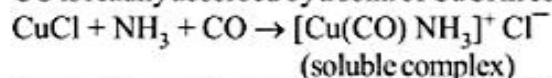
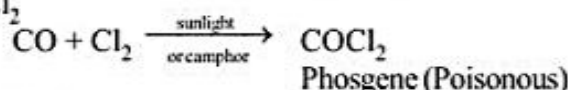


Nickel carbonyl

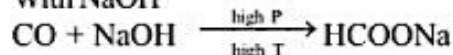


(ii) Absorption

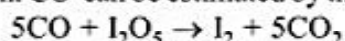
CO is readily absorbed by a soln. of CuCl in conc. HCl or NH₃ due to the formation of soluble complexes

(iii) With Cl₂

(iv) With NaOH

**Estimation of carbon monoxide :**

- (i) It reduces iodine pentoxide to iodine & this iodine can be titrated with standard sodium thio sulphate solution. CO can be estimated by this method.



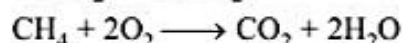
- (ii) CO does not support combustion but itself burns in air with a blue flame producing carbonsuboxide.

Tests of carbon monoxide :

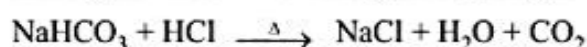
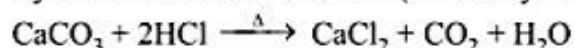
- (i) It burns with blue flame.
 (ii) Filter paper soaked with PdCl₂ is turned pink, green or black. PdCl₂ is reduced to the metal.
 (iii) It reduces iodine penta oxide into free iodine, which give colour with CCl₄, CS₂ or CHCl₃.

(b) Carbon dioxide CO₂**Preparation**

- (i) By burning carbon, fossil fuels & other org. Compounds in air



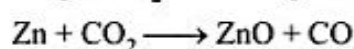
- (ii) By action of HCl on carbonates (laboratory method)

**Physical Properties :**

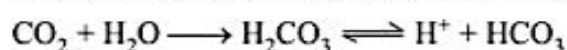
- (i) Colourless & odourless gas (about 1.5 time heavier than air)
 (ii) Not poisonous, but does not support life.

Chemical properties

- (i) Non combustible nature (certain active metals Na, K, Mg burn in it)



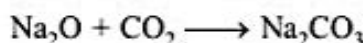
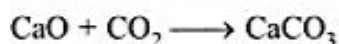
- (ii) Acidic nature : It dissolves in water to some extent to form carbonic acid.



carbonic acid

(weak dibasic acid) $2\text{H}^+ + \text{CO}_3^{2-}$

it reacts with metallic oxides

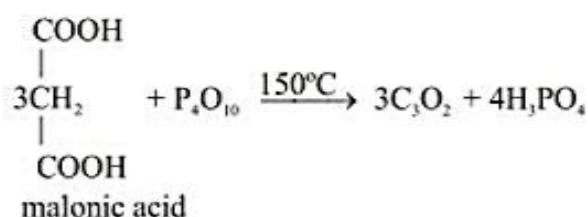


(c) **Carbon suboxide** C_3O_2

(i) Structure: $\text{O} = \text{C} = \text{C} = \text{O}$ (Linear)

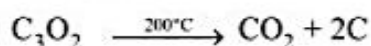
Preparation :

By heating malonic acid with phosphorus penta oxide



Properties :

- (i) Colourless gas, B.P. 60°C
- (ii) Very readily polymerises to give coloured salts.
- (iii) It decomposes at 2000°C

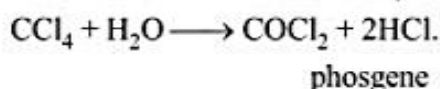


(4) **Oxyacids :**

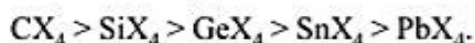
- (i) Oxyacids are formed by C & Si.
- (ii) Main inorganic oxyacid is H_2CO_3
- (iii) H_2SiO_3 is silica acid.

(5) **Halides :**

- (i) They form tetra halides MX_4 except PbBr_4 & PbI_4 .
- (ii) The non existence of PbBr_4 and PbI_4 is due to that Pb^{+4} is a strong oxidising agent while Br^- & I^- are highly reducing agent.
- (iii) All MX_4 are covalent except SnF_4 . It is Ionic.
- (iv) The tetrahalides of carbon cannot undergo hydrolysis due to non availability of vacant 'd' orbitals



- (v) The tetrahalides of silicon like SiF_4 can form SiF_6^{2-} . In this ion silicon undergoes sp^3d^2 hybridisation where carbon cannot form this type of ion.
- (vi) Dihalides of these elements are more ionic than their corresponding tetrahalides.
- (vii) Thermal stability of tetrahalides



Illustration

1. Which element-element bond has the highest bond dissociation energy?

- (A) C—C (B) Si—Si (C) Ge—Ge (D) Sn—Sn

Ans. (A)

Sol. C—C bond dissociation energy is 355 kJ mol⁻¹ which is highest amongst the carbon family members.

2. In graphite, electrons are

- (A) Localised on every third C-atom (B) Present in anti-bonding orbital
(C) Localised on each C-atom (D) Spread out between the structure.

Ans. (D)

Sol. In graphite, each carbon is sp²-hybridized and forms four covalent bonds with other C-atoms overlap side wise to give π-electron cloud which is delocalized and thus the electrons are spread out between the structure.

Exercise

1. Consider following statements :

I : In diamond, each carbon atom is linked tetrahedrally to four other carbon atoms by sp³ bonds.

II : Graphite has planar hexagonal layers of carbon atoms held together by weak vander Waals forces

III : Silicon exists only in diamond structure due to its tendency to form p_p — p_p bonds to itself.

In this :

- (A) Only I and II are correct (B) Only I is correct
(C) Only II and III are correct (D) All are correct statements

Ans. (D)

2. Select correct statement :

(A) Oxides of carbon family (MO₂) are all network solids with octahedral coordination

(B) Silicon dioxide (silica) is a network solid with tetrahedral coordination and is a giant molecule

(C) GeO₂, SnO₂ and PbO₂ are all network solids with octahedral coordination

(D) None appears correct

Ans. (B), (C)

SILICON (Si)**Occurrence**

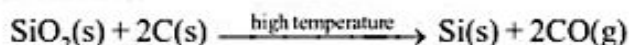
Silicon is the second most abundant (27.2%) element after oxygen (45.5%) in the earth's crust. It does not occur free in nature but in the combined state, it occurs widely in form of silica and silicates. All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or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

- (i) Feldspar — K₂O. Al₂O₃. 6SiO₂
(ii) Kaolinite — Al₂O₃. 2SiO₂. 2H₂O
(iii) Asbestos — CaO. 3MgO. 4SiO₂

Preparation

- (i) From silica (sand): Elemental silicon is obtained by the reduction of silica (SiO_2) with high purity coke in an electric furnace.



- (ii) From silicon tetrachloride (SiCl_4) or silicon chloroform (SiHCl_3): Silicon of very high purity required for making semiconductors is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen followed by purification by zone refining.

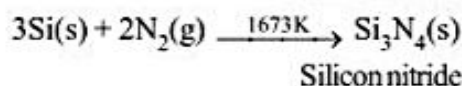
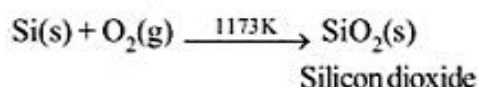
**Physical Properties :**

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

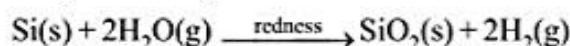
Chemical Properties:

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

- (i) **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,.



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

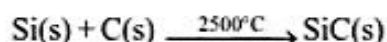


- (iii) **Reaction with halogens:** It burns spontaneously in fluorine gas at room temperature to form silicon tetrafluoride (SiF_4).



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

- (iv) **Reaction with carbon :** Silicon combines with carbon at 2500 °C forming silicon carbide (SiC) known as carborundum.



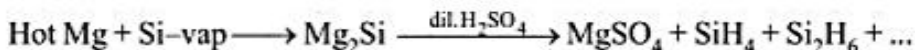
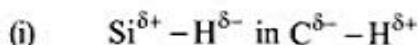
Carborundum is an extremely hard substance next only to diamond. It is mainly used as an abrasive and as a refractory material.

USES:

- (i) 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.
 (ii) High purity silicon is used as semiconductors in electronic devices such as transistors.
 (iii) It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

Compounds of Silicon :**(1) Hydride**Silane $\text{Si}_n\text{H}_{2n+2}$ (SiH_4 & Si_2H_6)

Only these two are found

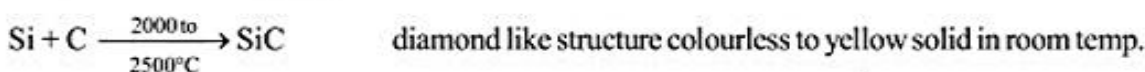
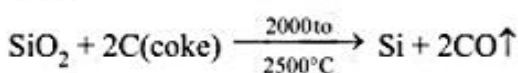
Higher molecules are not formed. \therefore Si can't show catanation property**Ques.** SiH_4 is more reactive than CH_4 . ExplainReasons

C - electro-ve than H

Si less electro-ve than H

So bond polarity is reversed when Nu^- attacks, 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.**(2) SiC (Carborundum)****Preparation**

↓

when impurity is present

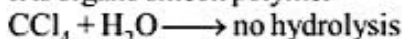
Properties

(i) It is very hard and is used in cutting tools and abrasive powder (polishing material)

(ii) It is very much inert

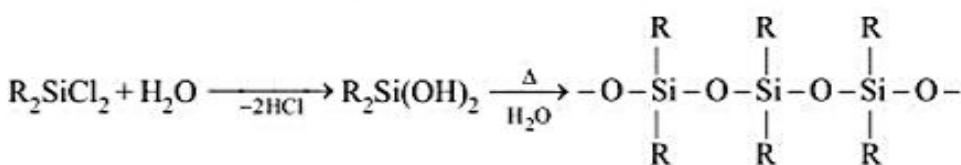
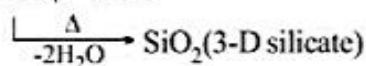
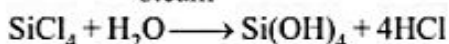
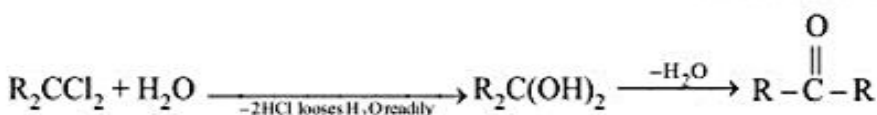
(iii) It is not being affected by any acid except H_3PO_4 **(3) Silicones**

It is organo silicon polymer

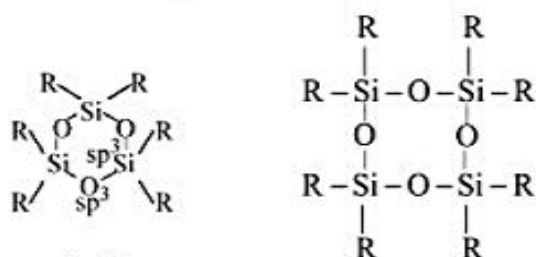


super heated

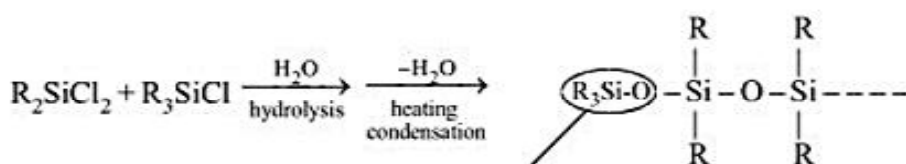
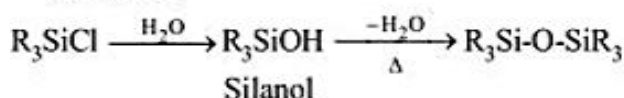
steam

**Linear silicone**

Silicones may have the cyclic structure also having 3, 4, 5 and 6 nos. of silicon atoms within the ring. Alcohol analogue of silicon is known as silanol

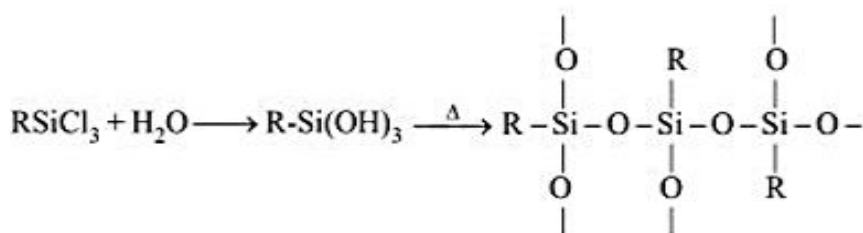


cyclic silicone
not planar



This end of the chain can't be extended hence
 R_3SiCl is called as chain stopping unit

* Using R_3SiCl in a certain proportion we can control the chain length of the polymer



cross linked silicone 3 dimensional network

It provides the crosslinking among the chain making the polymer more hard and hence controlling the proportion of RSiCl_3 we can control the hardness of polymer.

Uses

- (1) It can be used as electrical insulator (due to inertness of Si-O-Si bonds)
- (2) It is used as water repellant (\because surface is covered) eg. car polish, shoe polish, massonary works in buildings
- (3) It is used as antifoaming agent in sewage disposal, beer making and in cooking oil used to prepare potato chips.
- (4) As a lubricant in the gear boxes.

(4) Silica (SiO_2)

Occurrence:

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 : $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, Kaolinite : $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ etc.

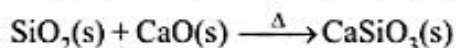
PROPERTIES:

- (i) Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.

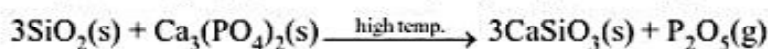
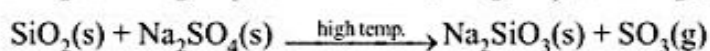
- (ii) Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.

$$\text{SiO}_2(\text{s}) + 4\text{HF}(\text{l}) \longrightarrow \text{SiF}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l})$$

- (iii) It also combines with metallic oxides at high temperature giving silicates e.g.



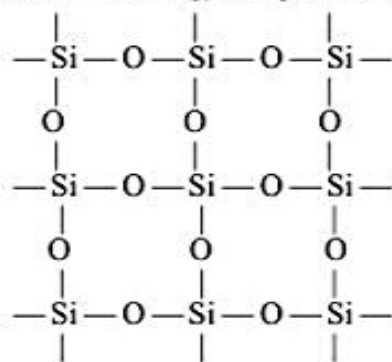
- (iv) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.



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 :**

- (i) Sand is used in large quantities to make mortar and cement.
- (ii) 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.
- (iii) Powdered quartz is used for making silica bricks.
- (iv) Silica gel ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$) is used as a desiccant (for absorbing moisture) and as an adsorbent in chromatography.

Illustration

1. In silicon dioxide
 (A) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms
 (B) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms
 (C) Silicon atom is bonded to two oxygen atoms
 (D) There are double bonds between silicon and oxygen atoms

Ans. (A)

Sol.

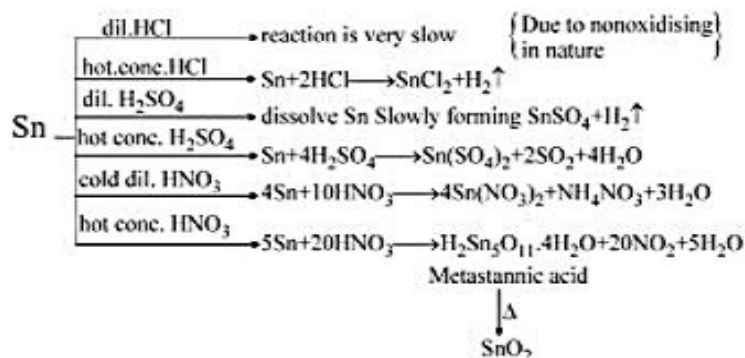
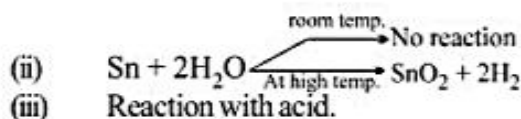
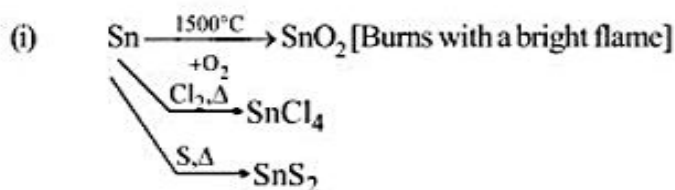


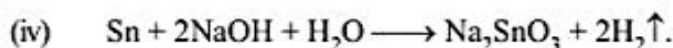
Exercise

1. Which is/are true statement(s) about silicones ?
 (A) They are repeating units (SiO_4) in silicates
 (B) They are synthetic polymers containing repeated R_2SiO_2 units
 (C) They are formed by hydrolysis of R_2SiCl_2 units
 (D) None is correct

Ans. (B), (C)

TIN & ITS COMPOUND





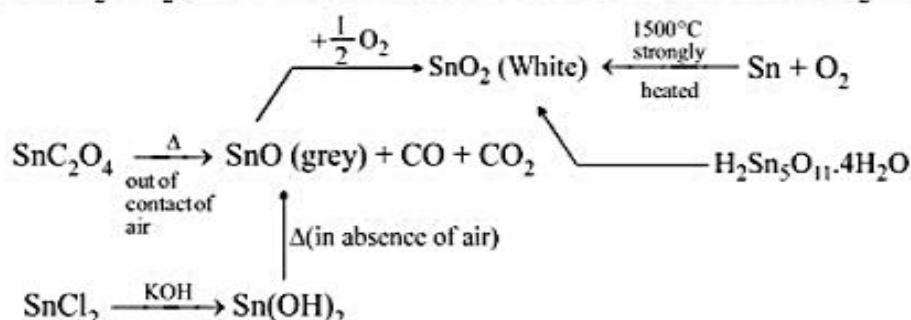
or

KOH [In absence of air Na_2SnO_2 forms and in contact with air it readily converts into Na_2SnO_3]

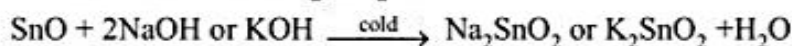
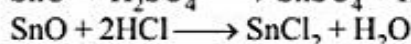
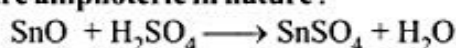
Oxides:

SnO (grey)

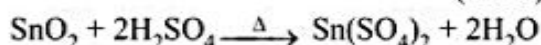
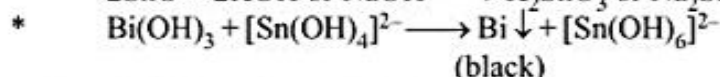
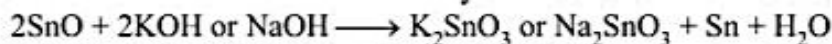
& SnO_2 (white)



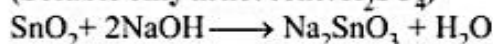
Both are amphoteric in nature :



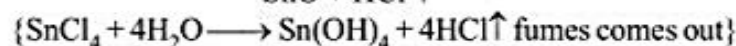
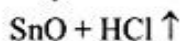
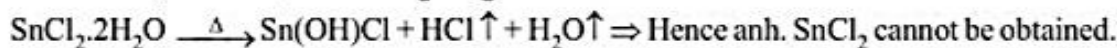
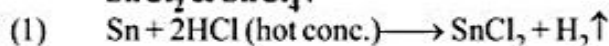
But conc. hot alkali behaves differently.



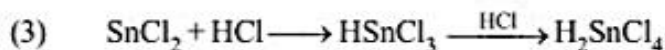
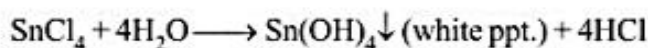
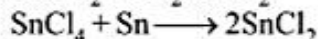
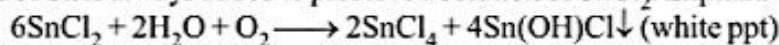
(Soluble only in hot conc. H_2SO_4)



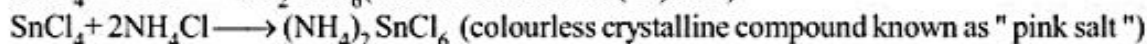
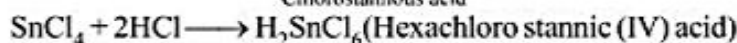
SnCl_2 & SnCl_4 :



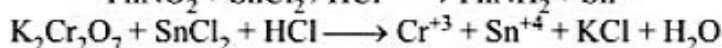
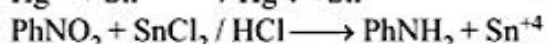
(2) A piece of Sn is always added to preserve a solution of SnCl_2 . Explain.



Chlorostannous acid



(4) **Red Prop. of SnCl_2 :**



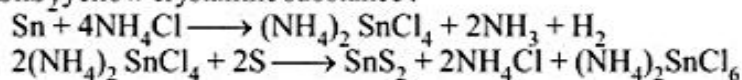
- (5) Readily combines with $I_2 \Rightarrow SnCl_2I_2 \Rightarrow$ This reaction is used to estimate tin.

Formation of $SnCl_4$:

- (i) $Sn + Cl_2 \xrightarrow[\text{(dry)}]{\text{(Excess)}}$ $SnCl_4$ (molten) (ii) $2HgCl_2 + SnCl_2 \longrightarrow 2Hg \downarrow + SnCl_4$
 (iii) $Sn + Aq. \text{ rigia} \longrightarrow SnCl_4 + NO + H_2O$

- * $SnCl_4 \cdot 5H_2O$ is known as butter of tin \Rightarrow used as mordant.
 $(NH_4)_2 SnCl_6$ is known as 'pink salt' \Rightarrow used as calico printing.

Mosaic gold: SnS_2 yellow crystalline substance:



- * **Distinction of Sn^{+2} / Sn^{+4} :**

- (i) H_2S (ii) Hg^{+2} (iii) $Fe^{+3} + K_3[Fe(CN)_6] \xrightarrow{Sn^{+2}} \text{Blue ppt.}$

Illustration

1. Which of the following statements is not true -
 (A) $SnCl_2$ is ionic solid (B) $SnCl_4$ is reducing in nature
 (C) $SnCl_2$ is reducing in nature (D) $SnCl_4$ is covalent liquid

Ans. (B)

Sol. Sn^{+4} is more stable than Sn^{+2}

Exercise

1. When tin is boiled with alkali solution, the product is -
 (A) SnO_2 (B) $Sn(OH)_2$ (C) $Sn(OH)_4$ (D*) SnO_3^{2-}
 Ans. (D)

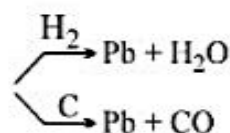
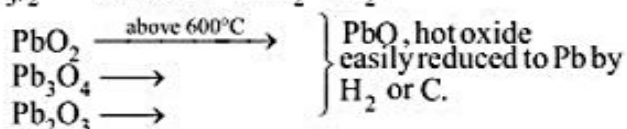
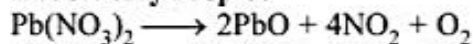
COMPOUNDS OF LEAD

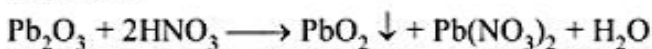
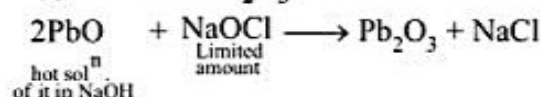
Oxides of lead:

- (i) PbO (ii) Pb_3O_4 (Red)
 (iii) Pb_2O_3 (reddish yellow) (Sesquioxide) (iv) PbO_2 (dark brown)

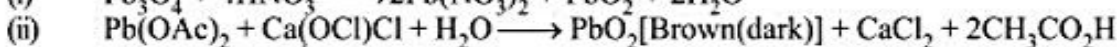
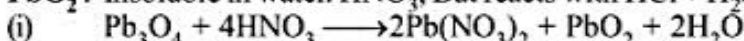
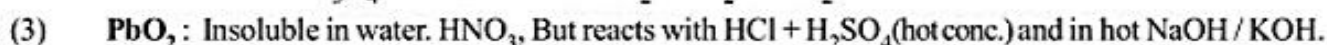
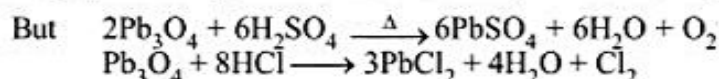
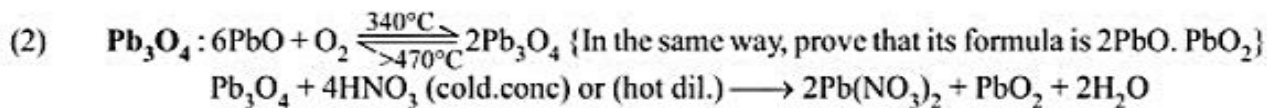
- (1) $PbO \begin{cases} \rightarrow \text{Yellow (Massicot)} \\ \rightarrow \text{Reddish yellow (litharge)} \end{cases} \xrightarrow[\text{and powdered}]{\text{fused, cooled}} \text{Litharge}$

Laboratory Prepⁿ:

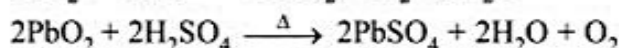


Preparation of Pb_2O_3 :

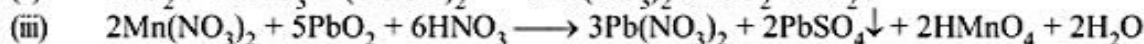
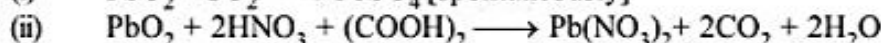
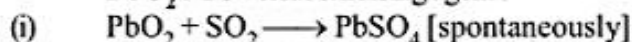
This reaction suggests that Pb_2O_3 contains PbO_2 .



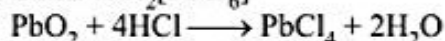
↓
Excess bleaching powder
is being removed by stirring with
 HNO_3



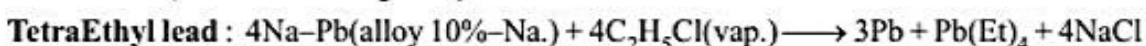
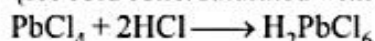
PbO_2 : Powerful oxidising agent :



PbCl_4 : Exists as $\text{H}_2[\text{PbCl}_6]$



{ice cold conc. saturated with Cl_2 }



It is antiknocking agent.

Illustration

1. PbF_4 , PbCl_4 exist but PbBr_4 and PbI_4 do not exist because of -

- (A) Large size of Br^- and I^- (B) Strong oxidising character of Pb^{4+}
 (C) Strong reducing character of Pb^{4+} (D) Low electronegativity of Br^- and I^-

Ans. (C)

Sol. Due to the inert pair effect Pb^{+2} is more stable than Pb^{+4} but F & Cl act as a oxidant so PbF_4 & PbCl_4 exist. I & Br act as a reducing agent so PbBr_4 and PbI_4 do not exist.

Exercise

1. Sindoor used by women is an oxide of lead with the formula -

- (A) PbO (B) PbO_2 (C) Pb_3O_4 (D) Pb_2O_3

Ans. (C)

SOLVED EXAMPLE

Q.1 Choose the correct order of extent of polymerization is

- (A) $\text{SiO}_4^{4-} > \text{PO}_4^{3-} > \text{ClO}_4^- > \text{SO}_4^{2-}$ (B) $\text{PO}_4^{3-} > \text{ClO}_4^- > \text{SO}_4^{2-} > \text{SiO}_4^{4-}$
 (C) $\text{SiO}_4^{4-} > \text{SO}_4^{2-} > \text{ClO}_4^- > \text{PO}_4^{3-}$ (D) $\text{SiO}_4^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{ClO}_4^-$

Ans. (D)

Sol. A extent of double bond formation of M–O bond increases due to which extent of polymerization reduces.

Q.2 Group 13 elements exhibit

- (A) Only +3 oxidation state (B) Only +1 oxidation state
 (C) Both +1 and +3 oxidation states (D) +1, +2 and +3 oxidation states.

Ans. (C)

Sol. As there are electrons in the valence shell of group 13 elements they show +3 oxidation state. Also in case of heavier members, due to inert pair effect, +1 oxidation state is most stable.

Q.3 Boron compounds behave as Lewis acids because of their

- (A) Acidic nature (B) Covalent nature
 (C) Electron deficient character (D) Ionization property

Ans. (C)

Sol. Boron compounds are electron deficient and therefore, behave as Lewis acids.

Q.4 Moissan boron is

- (A) Amorphous boron of ultra purity (B) Crystalline boron of ultra purity
 (C) Amorphous boron of low purity (D) Crystalline boron of low purity

Ans. (C)

Sol. Moissan boron is amorphous boron, obtained by reduction of B_2O_3 with Na or Mg. It has 95-98% boron and is black in colour.

Q.5 Both boron and aluminium show difference in properties from the remaining members of group 13. This is because

- (A) Both B and Al have smaller size as compared to other members of the family.
 (B) Both B and Al have high values of ionization energy
 (C) Both B and Al have only the valence electrons ($ns^2 np^1$) outside the noble gas core while the remaining elements have filled d and f-orbitals in between the noble gas core and the valence electrons
 (D) None of the above.

Ans. (C)

Sol. The difference in properties of B and Al from the remaining members of group 13 is due to the difference in their electronic configuration as stated.

Q.6 Aluminothermy used for on the spot welding of large iron structures is based upon the fact that

- (A) As compared to iron, aluminium has greater affinity for oxygen
 (B) As compared to aluminium, iron has greater affinity for oxygen
 (C) Reaction between aluminium and oxygen is endothermic
 (D) Reaction between iron and oxygen is endothermic

Ans. (A)

Sol. Al is more electropositive and has greater affinity for oxygen than iron. This fact is made use of in aluminothermy.

Q.7 Aluminium chloride exists as a
(A) Monomer (B) Dimer (C) Trimer (D) Polymer

Ans. (B)

Sol. AlCl_3 is electron deficient. Al completes its octet by forming a dimer Al_2Cl_6 .

Q.8 Which property is not exhibited by carbon in its compounds ?
(A) Forming bonds to other carbon atoms
(B) Forming multiple bonds
(C) Exhibiting allotropic forms
(D) Forming compounds with coordination number beyond four.

Ans. (D)

Sol. Carbon cannot expand its coordination number beyond four due to the absence of d-orbitals.

Q.9 A solid element (symbol Y) conducts electricity and forms two chlorides YCl_n (a colourless volatile liquid) and YCl_{n-2} (a colourless solid). To which one of the following groups of the periodic table does Y belong ?

(A) 13 (B) 14 (C) 15 (D) 16

Ans. (B)

Sol. Element Y belongs to group 14 of the periodic table which forms two chlorides YCl_4 (a colourless, volatile liquid) and YCl_2 (a colourless solid).