

p-BLOCK ELEMENTS

Introduction :

Group 13 to 18 of the periodic table of elements constitute the p-block. The p-block contains metals, metalloids as well as non-metals.

The p-block elements have general valence shell electronic configuration $ns^2 np^{1-6}$.

The first member of each group from 13–17 of the p-block elements differ in many respects from the other members of their respective groups because of small size, high electronegativity and absence of d-orbitals.

The first member of a group also has greater ability to form $p\pi-p\pi$ multiple bonds to itself (e.g. $C \equiv C$, $C \equiv N$, $N \equiv N$) and to element of second row (e.g. $C = O$, $C = N$, $C \equiv N$, $N = O$) compared to the other members of the same group.

The highest oxidation of p-block element is equal to the group number minus 10. Moving down the group, the oxidation state two less than the highest group oxidation state becomes more stable in groups 13 to 16 due to inert pair effect (reluctance of s-subshell electrons to participate in chemical bonding)

TRENDS IN PROPERTIES OF p-BLOCK ELEMENTS.

Electronegativity, ionization enthalpy, oxidizing power.					
→					
Covalent radius, van der Waals' radius, metallic character	B	C	N	O	F
	Al	Si	P	S	Cl
	Ga	Ge	As	Se	Br
	In	Sn	Sb	Te	I
	Tl	Pb	Bi	Po	At
←					
↑					
Electronegativity, enthalpy of atomization (except for N_2 , O_2 , F_2), ionization enthalpy, oxidizing power.					
↑					
↓					
Covalent radius, van der Waals' radius, enthalpy of atomization (upto group 14), metallic character					



(A) GROUP 13 ELEMENTS : THE BORON FAMILY

Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium and thallium are almost exclusively metallic in character,

Electronic Configuration:

The outer electronic configuration of these elements is $ns^2 np^1$.

Atomic Radii :

On moving down the group, for each successive member one extra shell of electrons is added and therefore, atomic radius is expected to increase. Atomic radius of Ga is less than of Al. The presence of additional 10 d-electrons offer only poor screening effect for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

Ionization Enthalpy:

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group. The decrease from B to Al is associated with increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of d- and f electrons, which have low screening effect, to compensate the increase in nuclear charge. The sum of the first three ionisation enthalpies for each of the elements is very high.

Electronegativity:

Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements.

Physical Properties

Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point. Rest of the member are soft metals with low melting point and high electrical conductivity. Gallium with low melting point (303 K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures. Density of the elements increases down the group from boron to thallium.

Atomic & physical properties :

Element		B	Al	Ga	In	Tl
Atomic Number		5	13	31	49	81
Atomic Mass		10.81	26.98	69.72	114.82	204.38
Electronic configuration		[He] $2s^2 2p^1$	[Ne] $3s^2 3p^1$	[Ar] $3d^{10} 4s^2 4p^1$	[Kr] $4d^{10} 5s^2 5p^1$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$
Atomic Radius / pm		85	143	135	167	170
Ionic Radius M^{3+} / pm		–	53.5	62	80	88.5
Ionization enthalpy / (kJ mol ⁻¹)	I	800	577	578	558	590
	II	2427	1816	1979	1820	1971
	III	3659	2744	2962	2704	2877
Electronegativity		2.0	1.5	1.6	1.7	1.8
Density/[g cm ⁻³ (293 K)]		2.35	2.70	5.90	7.31	11.85
Melting point / K		2453	933	303	430	576
Boiling point / K		3923	2740	2676	2353	1730

Chemical Properties :**Oxidation state and trends in chemical reactivity :**

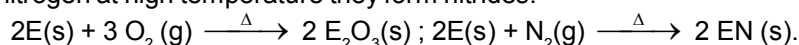
Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form + 3 ions and force it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al^{+3} ions. However, down the group, due to poor shielding, effective nuclear charge holds ns electrons tightly (responsible for inert pair effect) and thereby, restricting their participation in bonding. As a result of this only p-orbital electron may be involved in bonding. In fact in Ga, In and Tl, both + 1 and + 3 oxidation states are observed. The relative stability of + 1 oxidation state progressively increases for heavier elements: $Al < Ga < In < Tl$. In thallium +1 oxidation state is predominant and + 3 oxidation state highly oxidising in character. The compound in +1 oxidation state, as expected from energy considerations, are more ionic than those in + 3 oxidation state.

In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in BF_3) will be only six.

Such **electron deficient** molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increases in the size down the group. BCl_3 easily accepts a lone pair of electrons from ammonia to form $BCl_3 \cdot NH_3$. In trivalent state most of the compounds being covalent are hydrolysed in water. The trichloride on hydrolysis in water form tetrahedral $[M(OH)_4]^-$ species; Aluminium chloride in acidified aqueous solution form octahedral $[Al(H_2O)_6]^{3+}$ ion.

(i) Reactivity towards air

Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.



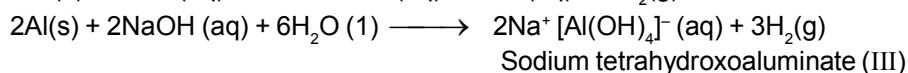
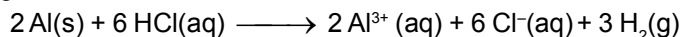
p-BLOCK ELEMENTS

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

(ii) Reactivity towards acids and alkalis

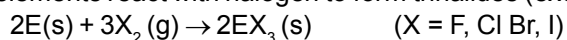
Boron does not react with acids and alkalis even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalis and thus shows amphoteric character.

Aluminium dissolved in dilute HCl and liberates dihydrogen. However, concentrated nitric acid renders aluminium passive by forming protective oxide layer on the surface. Aluminium also reacts with aqueous alkali and liberates dihydrogen.



(iii) Reactivity towards halogens

These elements react with halogen to form trihalides (except TI I_3).



IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[\text{M}(\text{OH})_4]^{-}$ and octahedral $[\text{M}(\text{H}_2\text{O})_6]^{3+}$, except in boron, exist in aqueous medium.

It is due to the absence of d orbitals that the maximum covalence of boron is 4. Since the d-orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4.

● BORON (B):

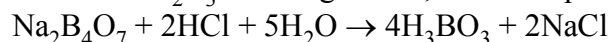
○ OCCURRENCE :

Boron occurs in nature in the form of the following minerals:

- (i) Borax $(\text{Na}^+)_2\text{B}_4\text{O}_7^{2-} \cdot 10\text{H}_2\text{O}$. (Boron is part of an anionic complex), (ii) Boric acid H_3BO_3 ,
- (iii) Kernite $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ & (iv) Colemanite $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$

○ EXTRACTION OF BORON :

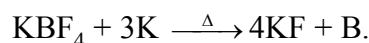
- (i) By the reduction of B_2O_3 with magnesium, sodium or potassium in the absence of air :



The product thus obtained is boiled with HCl and filtered when K_2O or MgO dissolves leaving behind elemental boron. It is thoroughly washed to remove HCl and then dried finally.

Brown amorphous powder of B is obtained in this way.

- (ii) From potassium fluoroborate (KBF_4) by heating it with potassium metal.



It is then treated with dilute HCl to remove KF and B is then washed and dried.

- (iii) In small quantities in pure form (crystalline boron) by the

- (i) Reduction of BBr_3 with H_2 on a heated titanium metal filament at 1275-1475 K

The vapours of Br_2 are absorbed in Cu and the residual vapours of boron are condensed.

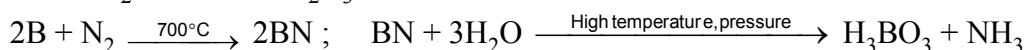
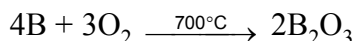
- (ii) Decomposition of BI_3 vapours by means of high tension arc (80 kV) through tungsten electrodes.



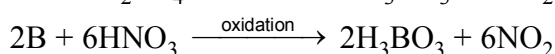
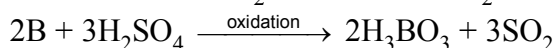
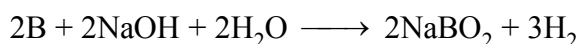
○ **PROPERTIES :**

(i) It exists in five forms, four of which are crystalline and one is amorphous. All crystalline forms are very hard made up of clusters of B_{12} units. All crystalline forms are black in appearance and chemically inert. Melting points are around 2300°C . But amorphous form is brown and chemically active.

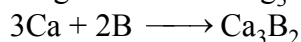
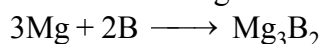
(ii) Reaction with air :



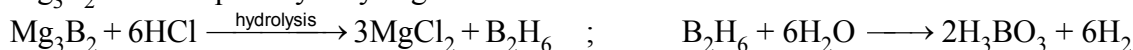
(iii) Action of alkalis and acids :



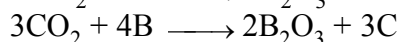
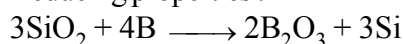
(iv) Reaction with Mg and Ca :



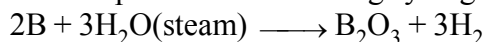
Mg_3B_2 on consequent hydrolysis gives diborane.



(v) Reducing properties :



(vi) It decomposes steam liberating hydrogen gas.



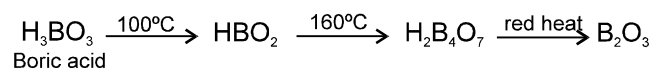
○ **USES :**

Boron is used in the construction of high impact-resistant steel and, since it absorbs neutrons, in reactor rods for controlling atomic reactions.

○ **COMPOUNDS OF BORON :**

○ **BORON TRIOXIDE (B_2O_3) :**

○ **PREPARATION :**

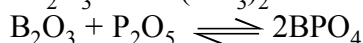
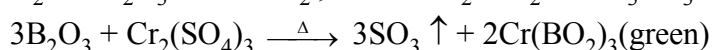


○ **PROPERTIES :**

It is a weakly acidic oxide and reacts with alkalis or bases to form borates.



It reacts with water slowly to form orthoboric acid. When heated with transition metal salts, it forms coloured compounds.



○ **ORTHOBORIC ACID (H_3BO_3) :**

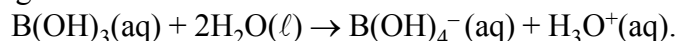
Among the oxyacids of boron are

○ **PREPARATION :**

- (i) It is precipitated by treating a concentrated solution of borax with sulphuric acid.
 $\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{SO}_4 + 5\text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 4\text{H}_3\text{BO}_3 \downarrow$
- (ii) From Colemanite: Powdered colemanite is suspended in water and excess SO_2 is passed through it. On filtering and cooling the filtrate, white crystals of H_3BO_3 are obtained.
 $\text{Ca}_2\text{B}_6\text{O}_{11} + 2\text{SO}_2 + 11\text{H}_2\text{O} \longrightarrow 2\text{Ca}(\text{HSO}_3)_2 + 6\text{H}_3\text{BO}_3$

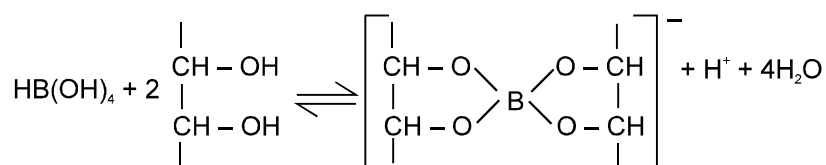
○ **PROPERTIES:**

- (i) It is a weak monobasic acid and in aqueous solution the boron atom completes its octet by removing OH^- from water molecules:

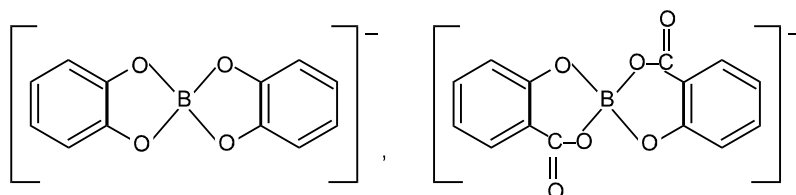


It, therefore, functions as a Lewis acid and not as a proton donor.

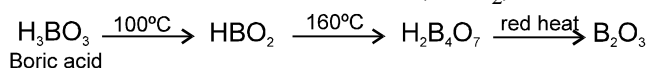
It behaves as strong acid when a polyhydroxy compound such as glycol or glycerol is added to its aqueous solution. The acidity is due to the high stability of the conjugate bone chelate complex.



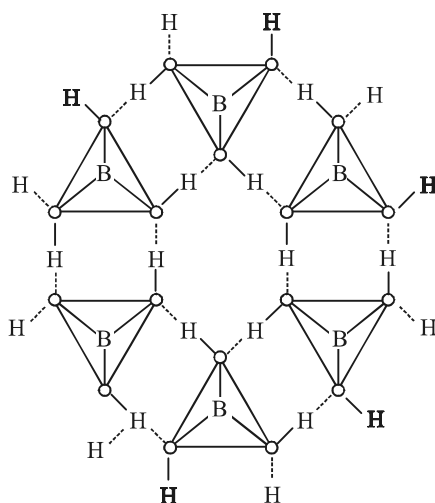
Ethanol does not form similar complex but catechol, salicylic acids form similar complexes.



When heated it first forms metaboric acid (HBO_2) and then boron trioxide.

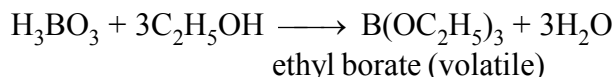


Orthoboric acid is greasy to touch less soluble in cold water but more soluble in hot water. It has a layered structure in which planar BO_3 units are joined by hydrogen bonds.



○ **TEST FOR BORATE RADICAL :**

When boric acid is heated with ethyl alcohol, the evolved gas is burned forming a green edged flame.



○ **USES :**

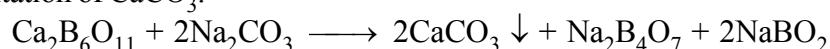
It is an antiseptic and its water solution is used as an eyewash. It is also used in glass, enamel and pottery industry.

○ **BORAX ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) :**

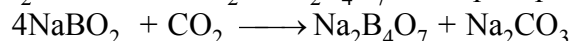
○ **PREPARATION:** It is found in nature but can also be prepared by the following methods.

(i) From Colemanite.

When colemanite powder is heated with Na_2CO_3 solution, the following reaction occurs with the precipitation of CaCO_3 .

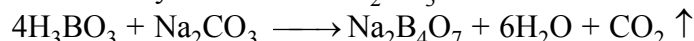


The filtrate is cooled when white crystals of borax are precipitated. The mother liquor on treatment with CO_2 converts NaBO_2 to $\text{Na}_2\text{B}_4\text{O}_7$ which precipitates out on crystallization.



(ii) From orthoboric acid.

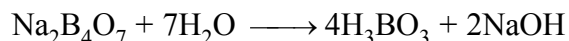
Borax is obtained by the action of Na_2CO_3 on orthoboric acid.



○ **PROPERTIES:**

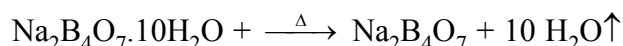
(i) Borax is a white powder, less soluble in cold water, more soluble in hot water.

(ii) Its aqueous solution is alkaline because of its hydrolysis to weak acid H_3BO_3 and strong alkali NaOH .

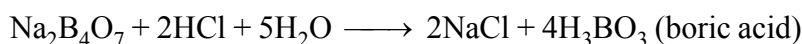


(iii) Action of heat.

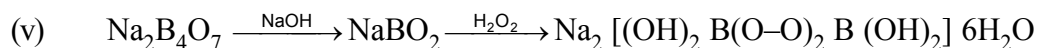
When borax powder is heated, it first swells due to loss of water in the form of steam but at 740°C it becomes converted into colourless transparent borax bead.



(iv) Action of acids :

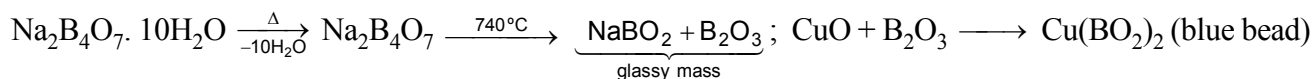


On cooking, the white flakes of boric acid are obtained



Correct formula of borax is $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$

○ **BORAX-BEAD TEST :** Boric anhydride reacts with certain metal salts such as, Ni^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Mn^{2+} etc. to form coloured metaborates. The colour of the metaborates can be used to identify the metallic ions (cations) in salts.

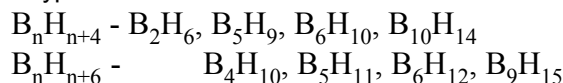


○ **USES :**

It is used

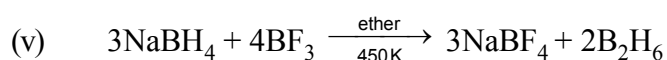
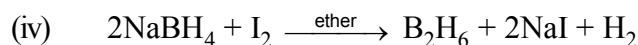
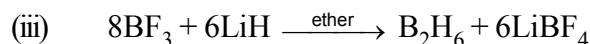
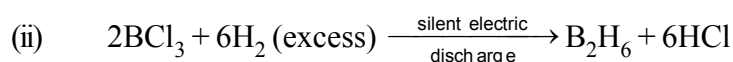
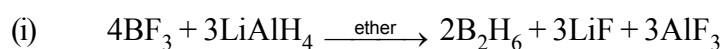
(i) in borax bead test, (ii) in purifying gold, (iii) as flux during welding of metals and (iv) in production of glass.

○ **DIBORANE (B_2H_6) :** Binary compounds of B with H are called boron hydrides or boranes. These compounds form following two types of series :



The chemistry of diborane has aroused considerable interest because of its usefulness in many synthetic reactions and also because the elucidation of its structure helped to clarify the basic concepts about the structure of electron deficient compounds.

○ **PREPARATION :**



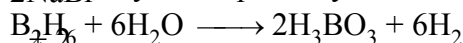
(vi) It can also be prepared by treating NaBH_4 with concentrated H_2SO_4 or H_3PO_4 .



○ **PROPERTIES :**

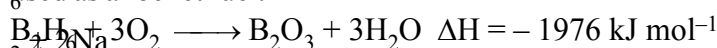
(i) Diborane is a colourless gas (boiling point 183 K).

(ii) It is rapidly decomposed by water with the formation of H_3BO_3 & H_2 :



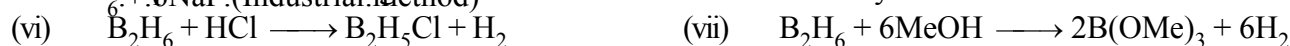
(iii) Mixtures of diborane with air or oxygen inflame spontaneously producing large amount of heat.

Diborane has a higher heat of combustion per unit weight of fuel than most other fuels. It is therefore used as a rocket fuel.

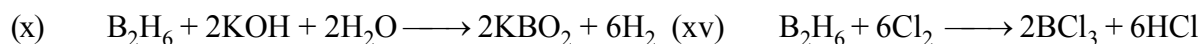
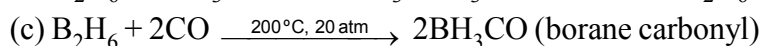


(iv) Pyrolysis of B_2H_6 in sealed vessels at temperatures above 375 K is an exceedingly complex process producing a mixture of various boranes, eg, B_4H_{10} , B_5H_9 , B_6H_{12} , and $\text{B}_{10}\text{H}_{14}$.

(v) Diborane undergoes a facile addition reaction with alkenes and alkynes in ether solvents at room temperature to form organoboranes. This reaction is known as hydroboration reaction.



(vii) Cleavage reactions



● ALUMINIUM (Al) :

○ EXTRACTION (HALL-HEROULT PROCESS):

The aluminium is extracted from ore bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$). The ore is first purified by Bayer's process. The anhydrous Al_2O_3 is mixed with Na_3AlF_6 & CaF_2 & then fused. The fused mixture is subjected to electrolytic reduction when aluminium is obtained at cathode.



Aluminium is purified by Hoope's process

○ PROPERTIES:

- (i) It is a silvery metal with a density of 2.7 g/cc, having a melting point of 660°C , and is a good conductor of heat and electricity. It is malleable and ductile.
- (ii) Action of air: Dry air has no action on aluminium. But moist air forms a thin layer of Al_2O_3 on its surface and it loses its luster. At very high temperatures it burns to form Al_2O_3 and AlN .
- (iii) Reaction with halogens: When gaseous halogens are passed over aluminium, its halide are formed in an anhydrous form. $2\text{Al} + 3\text{Cl}_2 \longrightarrow 2\text{AlCl}_3$
- (iv) Action of alkalis: When warmed with concentrated NaOH , it liberates H_2 gas and a colourless solution of sodium aluminate is formed.

$$2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaAlO}_2 + 3\text{H}_2\uparrow$$
- (v) Action of acids: Aluminium reacts with dilute H_2SO_4 and dilute HCl but concentrated HNO_3 does not react with aluminium because aluminium becomes passive by the action of concentrated HNO_3 forming a protective oxide layer on the surface.

$$2\text{Al} + 3\text{H}_2\text{SO}_4 \longrightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2\uparrow ; \quad 2\text{Al} + 6\text{HCl} \longrightarrow 2\text{AlCl}_3 + 3\text{H}_2\uparrow$$
- (vi) Reaction with N_2 : When N_2 gas is passed over heated aluminium, aluminium nitride is formed. Hot aluminium thus acts as an absorbing agent for N_2

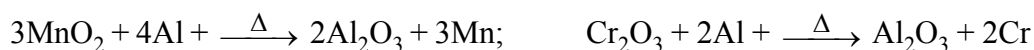
$$2\text{Al} + \text{N}_2 \longrightarrow 2\text{AlN}$$

AlN reacts with hot water to form $\text{Al}(\text{OH})_3$ and NH_3
- (vii) Reaction with water: Aluminium does not react with cold water. It is very slowly attacked by boiling water or steam.

$$2\text{Al} + 3\text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + 3\text{H}_2\uparrow$$
- (viii) Action of HgCl_2 solution: When aluminium is added to HgCl_2 solution mercury is liberated.

$$3\text{HgCl}_2 + 2\text{Al} \longrightarrow 2\text{AlCl}_3 + 3\text{Hg}\downarrow$$

- (ix) Reduction of oxides of metals: When oxides of less reactive metal than aluminium is heated with aluminium, the other metal is liberated.



○ **USES :**

It is extensively used

- (i) for manufacture of cooking and household utensils.
- (ii) as aluminium plating for tanks, pipes, iron bars and other steel objects to prevent corrosion.
- (iii) for manufacture of aluminium cables.
- (iv) for making precision instruments, surgical apparatus, aircraft bodies, rail coaches, motorboats, car

○ **COMPOUNDS OF ALUMINIUM :**

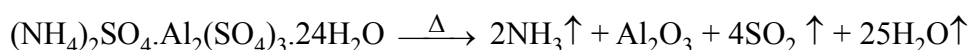
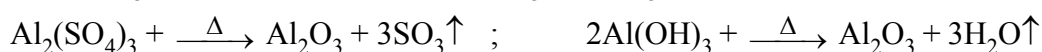
○ **ALUMINIUM OXIDE (Al_2O_3) :**

It is also called alumina. It occurs in nature in the form of bauxite and corundum. It is also found in the form of gems. Some important aluminium oxide gems are:

(A) Topaz-yellow, (B) Sapphire-blue, (C) Ruby-red, (D) Amethyst-violet, (E) Emerald-green

○ **PREPARATION:**

Pure Al_2O_3 is obtained by igniting $\text{Al}_2(\text{SO}_4)_3$, $\text{Al}(\text{OH})_3$ or ammonium alum.



○ **PROPERTIES :**

It is a white amorphous powder insoluble in water but soluble in acids (forming eg., AlCl_3) as well as alkalis (forming NaAlO_2), Thus amphoteric in nature. It is a polar covalent compound.

○ **USES :**

It is used

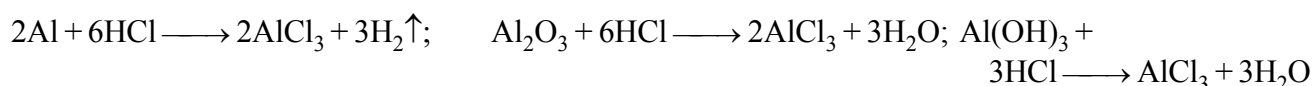
- (i) for the extraction of aluminium.
- (ii) for making artificial gems.
- (iii) for the preparation of compounds of aluminium.
- (iv) in making furnace linings. It is a refractory material.
- (v) as a catalyst in organic reactions.

○ **ALUMINIUM CHLORIDE ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) :**

It is a colourless crystalline solid, soluble in water. It is covalent. Anhydrous AlCl_3 is a deliquescent white solid.

○ **PREPARATION :**

- (i) By dissolving aluminium, Al_2O_3 , or $\text{Al}(\text{OH})_3$ in dilute HCl :



The solution obtained is filtered and crystallized when the crystals of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ are obtained.

- (ii) Anhydrous AlCl_3 is obtained by the action of Cl_2 on heated aluminium.
 - (iii) By heating a mixture of Al_2O_3 and coke and passing chlorine over it.
- $$\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 \longrightarrow 2\text{AlCl}_3 (\text{anhydrous}) + 3\text{CO}\uparrow$$

○ **PROPERTIES :**

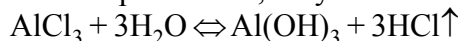
(i) Action of heat:

Hydrated salt when heated strongly is converted to Al_2O_3 .



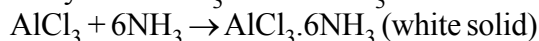
(ii) Action of moisture on anhydrous AlCl_3 :

When exposed to air, anhydrous AlCl_3 produces white fumes of HCl



(iii) Action of NH_3 :

Anhydrous AlCl_3 absorbs NH_3 since the latter is a Lewis acid.



(iv) Action of NaOH solution:

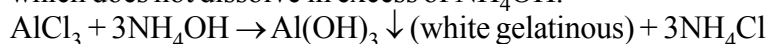
When NaOH solution is added dropwise to an aqueous AlCl_3 solution, a gelatinous precipitate of $\text{Al}(\text{OH})_3$ is first formed which dissolves in excess of NaOH solution to give a colourless solution of sodium aluminate.



This reaction is important as a test to distinguish between an aluminium salt from salts of Mg , Ca , Sr , and Ba . (When NaOH solution is added to their salt solutions, a white precipitate of hydroxide forms which does not dissolve in excess of NaOH).

(v) Action of NH_4OH solution:

When NH_4OH solution is added to a solution of AlCl_3 , a white precipitate of $\text{Al}(\text{OH})_3$ is formed which does not dissolve in excess of NH_4OH .



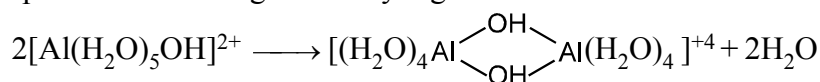
This reaction is important as a test to distinguish an Al salt from a Zn salt. (With a Zn salt a white precipitate of $\text{Zn}(\text{OH})_2$ is formed which dissolves in excess of NH_4OH solution).

(vi) Hydrolysis with water:

When AlCl_3 is dissolved in water, it undergoes hydrolysis rapidly to produce $\text{Al}(\text{OH})_3$ which is a weak base and HCl which is a strong acid. Hence the solution is acidic to litmus.



The complex cation has a high tendency to get dimerised.



(vii) $4\text{LiH} + \text{AlCl}_3 \longrightarrow \text{LiAlH}_4 + 3\text{LiCl}$

○ **USES :**

It is used :

- (i) as catalyst for cracking of petroleum.
- (ii) as catalyst in Friedel-Crafts reactions.
- (iii) for preparing aluminium compounds.

○ **ALUMS ; $\text{M}_2\text{SO}_4 \cdot \text{M}'_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ OR $\text{MM}'(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$**

Alums are transparent crystalline solids having the above general formula where M is a univalent metal or positive radical and M' is a trivalent metal. Some important alums are:

(i) Potash alum $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (ii) Chrome alum $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

(iii) Ferric alum $\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (iv) Ammonium alum $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

Alums are double salts which when dissolved in water produce metal ions(or ammonium ions) and the sulphate ions.

○ PREPARATION :

Alums can be prepared by fusing M_2SO_4 & $M'_2(SO_4)_3$ in 1 : 1 molar ratio & the resulting mass is dissolved into water. From the solution thus obtained, alums are crystallised.

○ USES :

It is used

- (i) as a mordant in dye industry
- (ii) as a germicide for water purification
- (iii) as a coagulating agent for precipitating colloidal impurities from water.

**(B) GROUP 14 ELEMENTS : THE CARBON FAMILY**

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C . In addition to these two isotopes, ^{14}C is also present, it is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is a very important component of ceramics, glass and cement. Germanium exists only in traces. Tin occurs mainly as cassiterite, SnO_2 and lead as galena, PbS . Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

Electronic Configuration :

The valence shell electronic configuration of these elements is $ns^2 np^2$.

Covalent Radius :

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled d and f orbitals in heavier members.

Ionization Enthalpy :

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electron is visible here also. In general the ionisation enthalpy decreases down the group. Small decreases in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effects of intervening d and f-orbitals and increases in size of the atom.

Electronegativity :

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity value for elements from Si to Pb are almost the same.

Physical Properties :

All group 14 members are solids. Carbon and silicon are non-metals, germanium is metalloid whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

ATOMIC & PHYSICAL PROPERTIES

Element		C	Si	Ge	Sn	Pb
Atomic Number		6	14	32	50	82
Atomic Mass		12.01	28.09	72.60	118.71	207.2
Electronic configuration		[He] $2s^2 2p^2$	[Ne] $3s^2 3p^2$	[Ar] $3d^{10} 4s^2 4p^2$	[Kr] $4d^{10} 5s^2 5p^2$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$
Atomic Radius / pm		77	118	122	140	146
Ionic Radius M^{+4} / pm		–	40	53	69	78
Ionization enthalpy / (kJ mol ⁻¹)	I	1086	786	761	708	715
	II	2352	1577	1537	11411	1450
	III	4620	3228	3300	2942	3081
Electronegativity		2.5	1.8	1.8	1.8	1.9
Melting point / K		4373	1693	1218	505	600
Boiling point / K		–	3550	3123	2896	2024

Chemical Properties :

Oxidation states and trends in chemical reactivity :

The group 14 elements have four electrons in their outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon does not exhibit negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence $Ge < Sn < Pb$. It is due to the inertness of ns^2 electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group. Carbon cannot exceed its covalence more than 4. Other elements of the group can do so. It is because of the presence of d orbitals in them. Due to this, their hydrides undergo disproportionation and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like $[SiF_6]^{2-}$, $[GeI_6]^{2-}$, $[Sn(OH)_6]^{2-}$ exist.

(i)

Reactivity towards oxygen :

All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e. monoxide and dioxide of formula MO and MO_2 respectively. SiO does not exist at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation state. The dioxides – CO_2 , SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

(ii)

Reactivity towards water :

Carbon, silicon and germanium are not affected by water. Tin decomposes slowly to form dioxide and dihydrogen gas. Lead is unaffected by water, probably because of a protective oxide film formation.

(iii)

Reactivity towards halogen :

These elements can form hydrides of formula MX_2 and MX_4 (where $X = F, Cl, Br, I$). Except carbon all other members react directly with halogen under suitable conditions to make hydrides. Most of the MX_4 are covalent in nature. Exceptions are SnF_4 and PbF_4 , which are ionic in nature. PbI_4 does not exist because $Pb-I$ bond is too weak to form during the reaction. It does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbitals to have four unpaired electrons around lead atom. Heavier members Ge to Pb are able to make hydrides of formula MX_2 . Stability of hydrides increases down the group. Except SnI_4 other tetrahalides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecules in d orbitals.

IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of d orbitals. Accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of d orbitals, Carbon also has unique ability to form $p\pi-p\pi$ multiple bonds with itself and with other atoms of small size and high electronegativity. Few example of multiple bonding are $C=C$, $C\equiv C$, $C=O$, $C=S$ and $C\equiv N$. Heavier elements do not form $p\pi-p\pi$ bonds because their atomic orbital are too large and diffuse to have effective overlapping.

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is because $C-C$ bonds are very strong. Down the group the size increases tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is $C > Si > Ge \approx Sn$. Lead does not show catenation. Due to the property of catenation and $p\pi-p\pi$ bonds formation, carbon is able to show allotropic forms.

ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985 third form of carbon known as **fullerenes** was discovered by H.W. Kroto, E Smalley and R.F.Curl.

Diamond :

It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The $C-C$ bond length is 154 pm. The structure extends in space and produces a rigid three dimensional network of carbon atoms. In this structure directional covalent bonds are presents throughout the lattice.

It is very difficult to break extended covalent bonding and therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools in making dyes and in the manufacture of tungsten filament for electric light bulbs.

Graphite :

Graphite has layered structure. Layers are held by van der Waal's forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. $C-C$ bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and make three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet. Electrons are mobile and, therefore graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

Fullerenes :

Fullerenes are made by the heating of graphite in an electrical arc in the presence of inert gases such as helium or argon. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called **Buckminsterfullerene**. It contains twenty six -membered rings and twelve five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon atom is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with $C-C$ distance of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called bucky balls in short. It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H^\ominus$ values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol^{-1} , respectively. Carbon black is obtained by burning hydrocarbons in a limited supply of air.

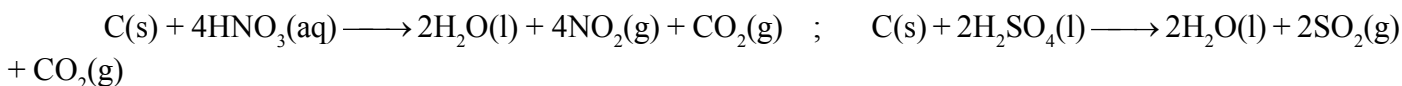
Uses of carbon :

Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalis. Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminants and in air conditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy. Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg.).

○ **PROPERTIES OF CARBON :**

- (i) Carbon in any form will react with oxygen at a sufficiently high temperature to give carbon dioxide; in a deficiency of oxygen, carbon monoxide is formed as well.
- (ii) $C(s) + 2S(s) \longrightarrow CS_2(l)$ (iii) $Ca(s) + 2C(s) \longrightarrow CaC_2(s)$
- (iii) $C(s) + 2F_2(g) \longrightarrow CF_4(g)$
- (iv) It will reduce steam, forming water gas, and many oxides of metals; these reductions are of industrial importance.

$$C + H_2O(g) \xrightarrow{\Delta} CO + H_2 ; Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
- (v) It is not attacked by dilute acids, but concentrated nitric acid and sulphuric acid are reduced if warmed with carbon according to the equations:



● **OXIDES OF CARBON :**

○ **CARBON DIOXIDE (CO₂) :**

○ **PREPARATION :**

- (i) In the laboratory it can be conveniently made by the action of dilute hydrochloric acid on marble chips:
 $CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O(l)$
- (ii) Industrially it is produced as a by-product during the manufacture of quicklime and in fermentation processes:
 $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) ; C_6H_{12}O_6(aq) \{ \text{glucose} \} \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$

○ **PROPERTIES:**

- (i) It is a colourless, odourless and heavy gas which dissolves in its own volume of water at ordinary temperature and pressure. Like all gases, it dissolves much more readily in water when the pressure is increased and this principle is used in the manufacture of soda water and fizzy drinks.
- (ii) CO₂ is easily liquefied (critical temperature = 31.1°C) and a cylinder of the gas under pressure is a convenient fire extinguisher. When the highly compressed gas is allowed to expand rapidly solid carbon dioxide ('dry ice') is formed. Solid carbon dioxide sublimates at -78°C and, since no massy liquid is produced, it is a convenient means of producing low temperatures.

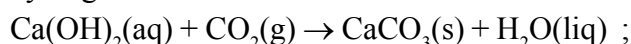
- (iii) Carbon dioxide is the acid anhydride of carbonic acid, which is a weak dibasic acid and ionises in to steps as follows :



$\text{H}_2\text{CO}_3 / \text{HCO}_3^-$ buffer system helps to maintain pH of blood between 7.26 to 7.42.

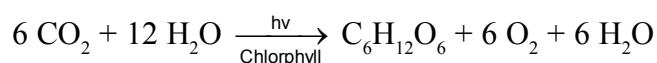
A solution of carbonic acid in water will slowly turn blue litmus red and when the solution is boiled, all the CO_2 is evolved.

- (iv) Carbon dioxide readily reacts with alkalies forming the carbonate and, if CO_2 is in excess, the hydrogen carbonate. This is the basis of the lime-water test for CO_2 gas.



The above reaction accounts for the formation of temporarily hard water.

- (v) Carbon dioxide, which is normally present to the extent of $\sim 0.03\%$ by volume in the atmosphere, is removed from it by the process known as photosynthesis. It is the process by which green plants convert atmospheric CO_2 into carbohydrates such as glucose. The overall chemical change can be expressed as :



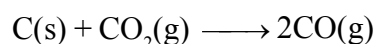
By this process plants make food for themselves as well as for animals and human beings. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO_2 content of the atmosphere. This may lead to increase in green house effect and thus, raise the temperature of the atmosphere which might have serious consequences.

- (vi) Gaseous CO_2 is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher. A substantial amount of CO_2 is used to manufacture urea.

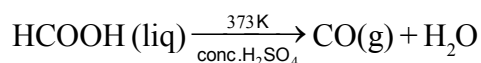
○ CARBON MONOXIDE (CO) :

○ PREPARATION:

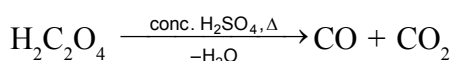
- (i) It forms together with CO_2 , when carbon or carbonaceous matter is oxidized by air or oxygen. It is also produced when CO_2 is reduced by red-hot carbon; this reaction is of importance in metal extractions.



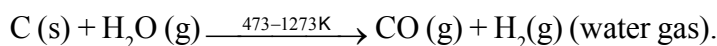
- (ii) In the laboratory it can be prepared by dehydrating methanoic acid with concentrated sulphuric acid:



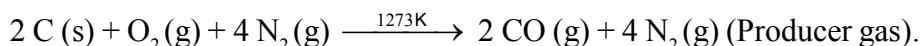
- (iii) If oxalic acid is dehydrated in the same way, CO_2 is formed as well.



- (iv) On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H_2 thus produced is known as water gas or synthesis gas.



When air is used instead of steam, a mixture of CO and N₂ is produced, which is called producer gas.



Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

- (v) $\text{Zn} + \text{CO}_2 \longrightarrow \text{ZnO} + \text{CO}$
- (vi) $\text{K}_4\text{Fe(CN)}_6 + 6\text{H}_2\text{SO}_4 \text{ (conc.)} + 6\text{H}_2\text{O} \xrightarrow{\Delta} 2\text{K}_2\text{SO}_4 + \text{FeSO}_4 + 3(\text{NH}_4)_2\text{SO}_4 + 6\text{CO}$
- (vii) $\text{HCN} + 2\text{H}_2\text{O} \longrightarrow \text{HCOOH} + 2\text{NH}_3 \text{ (absorbed by H}_2\text{SO}_4\text{)}$
 $\text{HCOOH} \xrightarrow{\Delta} \text{H}_2\text{O} + \text{CO}$

○ PROPERTIES :

- (i) Carbon monoxide is a colourless, odourless gas which burns in air with a blue flame, forming CO₂. It is exceedingly poisonous, combining with the haemoglobin in the blood more readily than oxygen, so that normal respiration is impeded very quickly. Ordinary gas masks are no protection against the gas, since it is not readily adsorbed on active charcoal. In the presence of air, a mixture of manganese (IV) oxide and copper(II) oxide catalytically oxidizes it to CO₂, and this mixed catalyst is used in the breathing apparatus worn by rescue teams in mine disasters.
- (ii) Carbon monoxide is a powerful reducing agent, being employed industrially in the extraction of iron and nickel:

$$\text{Fe}_2\text{O}_3\text{(s)} + 3\text{CO(g)} \longrightarrow 2\text{Fe(s)} + 2\text{CO}_2\text{(g)} ; \quad \text{NiO(s)} + \text{CO(g)} \longrightarrow \text{Ni(s)} + \text{CO}_2\text{(g)}$$
- (iii) It reacts with many transition metals, forming volatile carbonyls; the formation of nickel carbonyl followed by its decomposition is the basis of the Mond's process for obtaining very pure nickel:

$$\text{Ni(s)} + 4\text{CO(g)} \xrightarrow{90^\circ\text{C}} \text{Ni(CO)}_4\text{(liq)} \xrightarrow{180^\circ\text{C}} \text{Ni(s)} + 4\text{CO(g)}$$
- (iv) In addition to reacting with oxygen, carbon monoxide combines with sulphur to give carbonyl sulphide and with chlorine in the presence of light to give carbonyl chloride (phosgene), used in the production of polyurethane foam plastics. Phosgene is an exceedingly poisonous gas.

$$\text{CO(g)} + \text{S(s)} \longrightarrow \text{COS(s)} \text{ (carbonyl sulphide)} ; \quad \text{CO(g)} + \text{Cl}_2\text{(g)} \longrightarrow \text{COCl}_2\text{(g)} \text{ (carbonyl chloride)}$$
- (v) Although carbon monoxide is not a true acid anhydride since it does not react with water to produce an acid, it reacts under pressure with fused sodium hydroxide to give sodium methanoate:

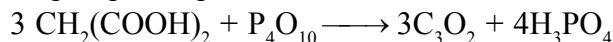
$$\text{NaOH(liq)} + \text{CO(g)} \longrightarrow \text{HCOONa(s)} \xrightarrow{\text{dil. HCl}} \text{HCOOH(aq)}$$
- (vi) With hydrogen under pressure and in the presence of zinc oxide or chromium (III) oxide catalyst it reacts to give methanol; this reaction is of industrial importance.

$$\text{CO(g)} + 2\text{H}_2\text{(g)} \longrightarrow \text{CH}_3\text{OH(liq)}$$
- (vii) CO is readily absorbed by an ammoniacal solution of copper (I) chloride to give CuCl.CO.2H₂O. It reduces an ammoniacal solution of silver nitrate to silver (black) and, in the absence of other gaseous reducing agents, this serves as a test for the gas. It can be estimated by reaction with iodine pentoxide, the iodine which is produced quantitatively being titrated with standard sodium thiosulphate solution.

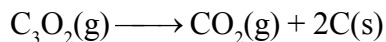
$$5\text{CO(g)} + \text{I}_2\text{O}_5\text{(s)} \longrightarrow \text{I}_2\text{(s)} + 5\text{CO}_2\text{(g)}$$

○ **CARBON SUBOXIDE (C₃O₂) :**

This is an evil-smelling gas and can be made by dehydrating propanedioic acid (malonic acid), of which it is the anhydride, with phosphorus pentoxide:



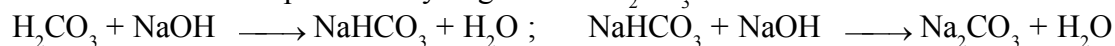
When heated to about 200°C, it decomposes into CO₂ and C:



The molecule is thought to have a linear structure: O=C=C=C=O.

○ **CARBONATES (CO₃²⁻) AND BICARBONATES (HCO₃⁻)**

Carbonic acid is a dibasic acids giving rise to two series of salts, carbonates (normal salts) and bicarbonates (acid salts) due to successive removal of the replaceable hydrogens from H₂CO₃.

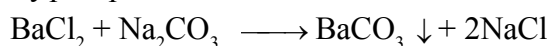


○ **PREPARATION :**

(i) With NaOH :



(ii) By precipitation :



○ **CARBIDES :**

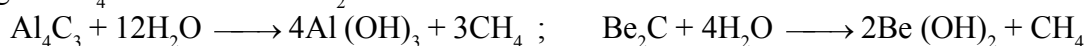
The binary compounds of carbon with other elements (less electronegative or of similar electronegativity) are called carbides. They are classified into following 3 categories :

(i) Ionic (ii) Covalent (iii) Interstitial (or metallic)

(i) Ionic carbides (or salt like carbides) : Generally formed by elements of I, II & III group (Boron is exception). Based on the product obtained on hydrolysis, they are further sub-classified into three types.

(a) Methanides

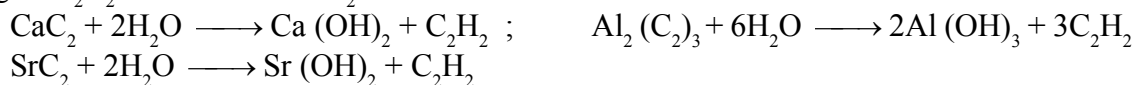
These give CH₄ on reaction with H₂O.



These carbides contain C⁴⁻ ions in their constitution.

(b) Acetylides

These give C₂H₂ on reaction with H₂O.



Such compounds contain C₂²⁻ [:C≡C:]²⁻ ions.

(c) Alkylides

These give 1-propyne on reaction with H₂O.



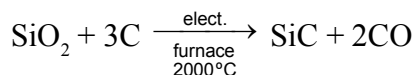
Such compounds contain C₃⁴⁻ [:C≡C—C:]⁴⁻ ions.

(ii) Covalent carbides

Compounds like CH₄, CO₂, CS₂ can be considered to be covalent carbides. Besides these, some giant molecules like SiC are also examples of covalent carbides.

(iii) Interstitial or metallic carbides

Such carbides are formed by transition metals in which carbon atoms occupy interstitials in the crystal structure of metals.

○ **CARBORUNDUM (SiC) :**○ **PREPARATION:**○ **PROPERTIES :**

- (i) It is a very hard substance (Hardness = 9.5 Moh)
- (ii) On heating it does not melt rather decomposes into elements.
- (iii) Not attacked by acids. However, it gives the following two reactions at high temperature.

$$\text{SiC} + 2\text{NaOH} + 2\text{O}_2 \xrightarrow{\Delta} \text{Na}_2\text{SiO}_3 + \text{CO}_2 + \text{H}_2\text{O} ; \text{SiC} + 4\text{Cl}_2 \xrightarrow{\Delta} \text{SiCl}_4 + \text{CCl}_4$$

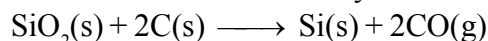
☞ It has a diamond like structure in which each atom is sp^3 hybridized. Therefore each atom is tetrahedrally surrounded by 4 atoms of other type.

○ **SILICON :**

Silicon is the second most abundant element occurring in the earth's crust (about 28 per cent by weight) as the oxide, silica, in a variety of forms, e.g., sand, quartz and flint, and as silicates in rocks and clays.

○ **PREPARATION :**

- (i) The element is obtained from silica by reduction with carbon in an electric furnace:



Extremely pure silicon is obtained from 'chemically' pure silicon by the method of zone refining.

- (ii) $\text{SiO}_2 + 2\text{Mg} \xrightarrow{\Delta} 2\text{MgO} + \text{Si}$

○ **PROPERTIES :**

Silicon is a very high melting-point solid with the same structure as diamond. The non-existence of an allotrope with the graphite structure clearly shows the inability of silicon atoms to multiple bond with themselves. In the massive form, silicon is chemically rather unreactive but powdered silicon is attacked by the halogens and alkalis:

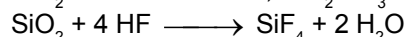
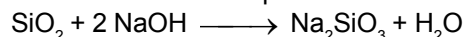
- (i) $\text{Si}(\text{powdered}) + 2\text{Cl}_2(\text{g}) \longrightarrow \text{SiCl}_4(\text{liq})$
- (ii) $\text{Si}(\text{powdered}) + 2\text{OH}^-(\text{aq}) + \text{H}_2\text{O}(\text{liq}) \longrightarrow \text{SiO}_3^{2-}(\text{aq}) + 2\text{H}_2(\text{g})$
- (iii) It is not attacked by acids except hydrofluoric acid, with which it forms hexafluorosilicic acid:

$$\text{Si}(\text{s}) + 6\text{HF}(\text{g}) \longrightarrow \text{H}_2\text{SiF}_6(\text{aq}) + 2\text{H}_2(\text{g})$$
- (iv) $\text{Si} + 2\text{KOH} + \text{H}_2\text{O} \longrightarrow \text{K}_2\text{SiO}_3 + 2\text{H}_2$
- (v) $\text{Na}_2\text{CO}_3 + \text{Si} \xrightarrow{\Delta} \text{Na}_2\text{SiO}_3 + \text{C}$
- (vi) $2\text{Mg} + \text{Si} \xrightarrow{\Delta} \text{Mg}_2\text{Si}$ (Magnesium silicide)

● **COMPOUNDS OF SILICON:****Silicon Dioxide SiO_2**

Silicon dioxide, commonly known as silica, occurs in several crystallographic forms. Quartz, cristobalite and tridymite are some of the crystalline forms of silica, and they are interconvertible at suitable temperature. Silicon dioxide is a covalent, three-dimensional network solid in which each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon atoms. Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight

membered rings are formed with alternates silicon and oxygen atoms. Silica in its normal form is almost non-reactive because of very high Si – O bond enthalpy. It resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures. However it is attacked by HF and NaOH.



Quartz is extensively used as a piezoelectric material ; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel used as a drying agent and as a support for chromatographic materials and catalysts. Kieselghur, an amorphous form of silica is used in filtration plants.

○ SILICATES :

Binary compounds of silicon with oxygen are called silicates but they contain other metals also in their structures.

(i) Since the negativity difference b/w O & Si is about 1.7, so Si–O bond can be considered 50% ionic & 50% covalent.

(ii) If we calculate the radius ratio $\frac{r_{\text{Si}^{+4}}}{r_{\text{O}^{2-}}} = 0.29$

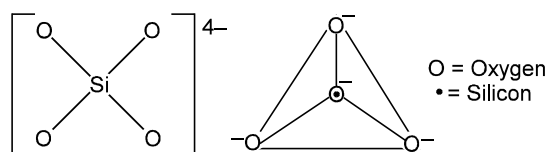
It suggests that the co-ordination no. of silicon must be 4 and from VBT point of view we can say that Si is sp^3 hybridized. Therefore silicate structures must be based upon SiO_4^{4-} tetrahedral units

(iii) SiO_4^{4-} tetrahedral units may exist as discrete units or may polymerise into larger units by sharing corners.

● CLASSIFICATION OF SILICATES :

(A) Orthosilicates :

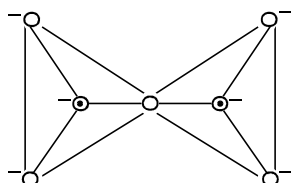
These contain discrete $[\text{SiO}_4]^{4-}$ units i.e., there is no sharing of corners with one another as shown in figure.



e.g. Zircon (ZrSiO_4), Forsterite of Olivine (Mg_2SiO_4), Willemite (Zn_2SiO_4)

(B) Pyrosilicate :

In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving $[\text{Si}_2\text{O}_7]^{6-}$ units.

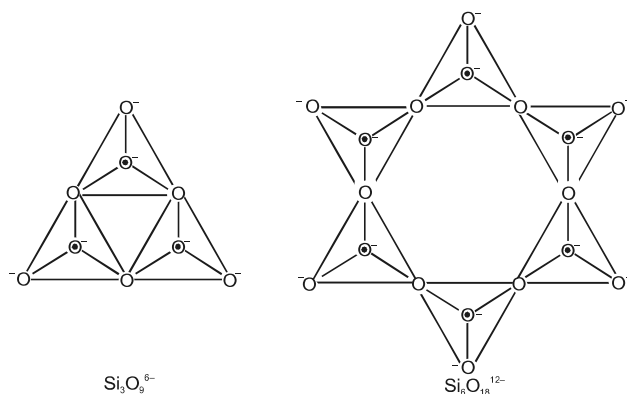


☞ (–) charge will be present on the oxygen atoms which is bonded with one Si atom.

e.g. Thortveitite ($\text{Sc}_2\text{Si}_2\text{O}_7$), Hemimorphite ($\text{Zn}_3(\text{Si}_2\text{O}_7)\text{Zn}(\text{OH})_2\text{H}_2\text{O}$)

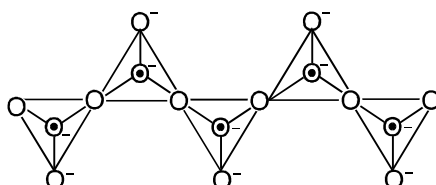
(C) Cyclic silicates :

If two oxygen atoms per tetrahedron are shared to form closed rings such that the structure with general formula $(\text{SiO}_3^{2-})_n$ or $(\text{SiO}_3)_{2n}^{2n-}$ is obtained, the silicates containing these anions are called cyclic silicates. $\text{Si}_3\text{O}_9^{6-}$ and $\text{Si}_6\text{O}_{18}^{12-}$ anions are the typical examples of cyclic silicates.

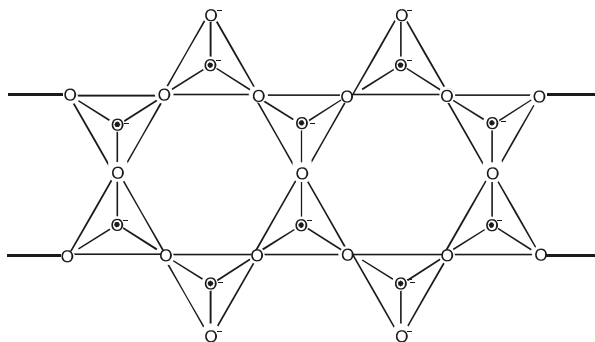
**(D) Chain silicates :**

Chain silicates may be further classified into simple chain & double chain compounds.

In case of simple chains two corners of each tetrahedron are shared & they form a long chain of tetrahedron. Their general formula is also same as the cyclic silicates i.e. $(\text{SiO}_3)_n^{2n-}$



Similarly, double chain silicates can be drawn in which two simple chains are joined together by shared oxygen. Such compounds are also known as amphiboles. The asbestos mineral is a well known example of double chain silicates. The anions of double chain silicates have general formula $(\text{Si}_4\text{O}_{11})_n^{6n-}$.



e.g., Synthetic silicates (Li_2SiO_3 , Na_2SiO_3), Spondumene ($\text{LiAl}(\text{SiO}_3)_2$),
Enstatite (MgSiO_3), Diopside ($\text{CaMg}(\text{SiO}_3)_2$), Tremolite ($\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$), etc.

(E) Two dimensional sheet silicates :

In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedrals. Such sharing forms two dimension sheet structure with general formula $(\text{Si}_2\text{O}_5)_n^{2n-}$

e.g. Talc ($\text{Mg}(\text{Si}_2\text{O}_5)_2$), Mg(OH)₂, Kaolin $\text{Al}_2(\text{OH})_4(\text{Si}_2\text{O}_5)$

(F) Three dimensional sheet silicates :

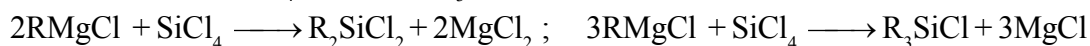
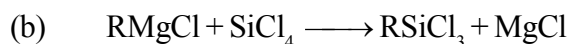
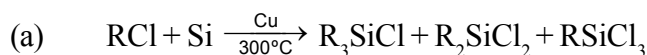
These silicates involve all four oxygen atom in sharing with adjacent SiO_4^{4-} tetrahedral units.

e.g. Quartz, Tridymite, Cristobalite, Feldspar, Zeolite and Ultramarines.

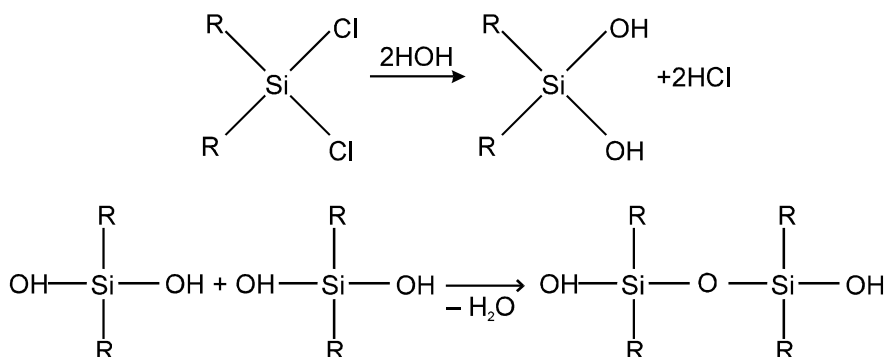
● **SILICONES :**

Silicones are synthetic organosilicon compounds having repeated R_2SiO units held by $Si-O-Si$ linkages. These compounds have the general formula $(R_2SiO)_n$ where R = alkyl or aryl group.

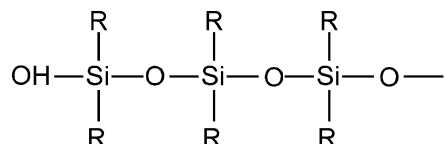
The silicones are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation. The alkyl or aryl substituted chlorosilanes are prepared by the following reactions.



After fractional distillation, the silane derivatives are hydrolysed and the 'hydroxides' immediately condense by intermolecular elimination of water. The final product depends upon the number of hydroxyl groups originally bonded to the silicon atom:

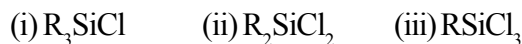


In this manner several molecules may combine to form a long chain polymer whose both the ends will be occupied by $-OH$ groups. Such compounds are generally represented from the following formula.

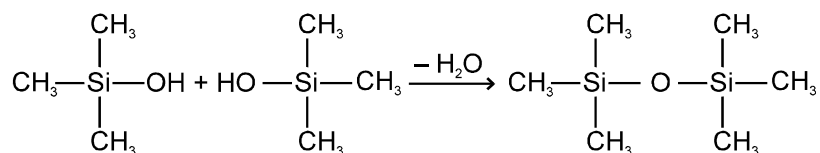
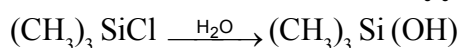


The polymer chain depicted above is terminated by incorporating a small quantity of the monochlorosilane derivative into the hydrolysis mixture.

☞ Silicones can be prepared from the following types of compounds only.

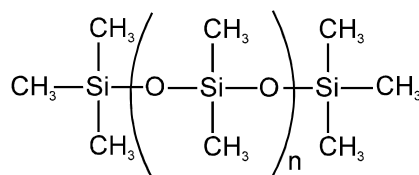


☞ Silicones from the hydrolysis of $(CH_3)_3SiCl$



☞ Silicones from the hydrolysis of a mixture of $(CH_3)_3SiCl$ & $(CH_3)_2SiCl$

The dichloro derivative will form a long chain polymer as usual. But the growth of this polymer can be blocked at any stage by the hydrolysis product of mono-chloro derivative.



☞ Silicones from the hydrolysis of trichloro derivative

When a compound like CH_3SiCl_3 undergoes hydrolysis, a complex cross-linked polymer is obtained.

☞ The hydrocarbon layer along the silicon-oxygen chain makes silicones water-repellent.

Products having the physical properties of oils, rubbers, and resins can be produced using silicones. Silicone fluids (say as hydraulic systems of planes) are thermally stable and their viscosity alters very little with temperature, and silicone rubbers retain their elasticity at much lower temperatures than ordinary rubber. Silicone varnishes are such excellent insulators and so heat-resistant that insulating wiring with them enabled motors to work over-loads that would have set fire to the insulation formerly used. A whole new field of chemistry and technology, civilian as well as military, has been opened up by the development of silicones.



TIN AND LEAD :

○ COMPOUNDS OF TIN :

○ STANNOUS OXIDE (SnO) :

○ PREPARATION:

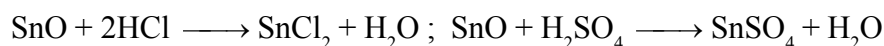
- (i) By heating stannous hydroxide, $\text{Sn}(\text{OH})_2$, in absence of air.

$$\text{Sn}(\text{OH})_2 \longrightarrow \text{SnO} + \text{H}_2\text{O} \uparrow$$
- (ii) By heating stannous oxalate, SnC_2O_4 in absence of air.

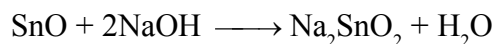
$$\text{SnC}_2\text{O}_4 \longrightarrow \text{SnO} + \text{CO} \uparrow + \text{CO}_2 \uparrow$$

○ PROPERTIES:

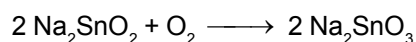
- (i) SnO is an amphoteric dark grey or black solid oxide, insoluble in water. It dissolves in acids to form stannous salts.



- (ii) SnO dissolves in hot NaOH solution to form (soluble) sodium stannite and water.



stannites are only known in aqueous solutions. Stannites absorb oxygen from air and are oxidised to stannate which are stable in nature.

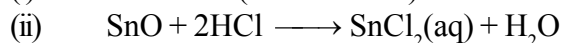


○ USES :

For the preparation of stannous chloride and stannous sulphate.

○ STANNOUS CHLORIDE ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) :

It is a colourless solid soluble in water. Its solution becomes milky on standing due to its hydrolysis to $\text{Sn}(\text{OH})_2$ and HCl . Its aqueous solution is acidic to litmus. It is a strong reducing agent. It is soluble in alcohol and ether also.

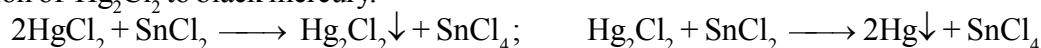
○ PREPARATION :

The solution on crystallization gives colourless crystals of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

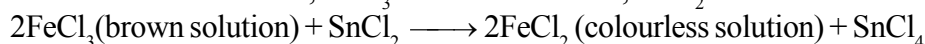
○ PROPERTIES :

- (i) Reaction with Hg_2Cl_2 solution: When SnCl_2 solution is added to an aqueous solution of mercuric chloride, a

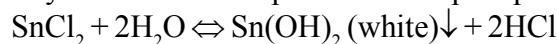
silky white precipitate of mercurous chloride, Hg_2Cl_2 is formed which turns black due to further reduction of Hg_2Cl_2 to black mercury.



- (ii) It reduces ferric chloride, FeCl_3 to ferrous chloride, FeCl_2 .



- (iii) It is hydrolysed with water to produce white precipitate of $\text{Sn}(\text{OH})_2$



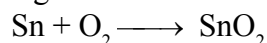
As it produces a weak base and strong acid its aqueous solution is acidic. Its hydrolysis can be prevented by adding concentrated HCl to it during the process of its preparation.

○ USES :

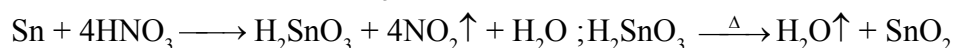
- (i) In dye industry as a reducing agent.
- (ii) For the test of mercuric salt.
- (iii) For the preparation of other stannous compounds.

○ STANNIC OXIDE (SnO_2) :**○ PREPARATION:**

- (i) By burning Sn in air



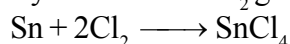
- (ii) By heating Sn with concentrated HNO_3

**○ PROPERTIES :**

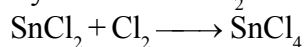
- (i) It is a white solid insoluble in water. It is weakly acidic
- (ii) It dissolves in conc. H_2SO_4 to form stannic sulphate.
$$\text{SnO}_2 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Sn}(\text{SO}_4)_2 + 2\text{H}_2\text{O}$$
- (iii) It also dissolves in conc. Alkalies to form alkali metal stannate solution.
$$\text{SnO}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SnO}_3(\text{sodium stannate}) + \text{H}_2\text{O}$$

○ STANNIC CHLORIDE (SnCl_4) :**○ PREPARATION:**

- (i) By the action of Cl_2 gas on heated Sn



- (ii) By the action of Cl_2 on stannous chloride



○ **PROPERTIES :**

- (i) It is a colourless fuming liquid, Bp = 114°C. It is covalent.
- (ii) Action of moisture: It absorbs moisture and becomes converted into hydrated stannic chlorides, $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 6\text{H}_2\text{O}$, and $\text{SnCl}_4 \cdot 8\text{H}_2\text{O}$. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ is known as “butter of tin” or “oxymercurate of tin”.
- (iii) Hydrolysis with water: It easily gets hydrolysed in water and produces strong acid HCl. Hence its aqueous solution is acidic to litmus. It hydrolyses more rapidly than SnCl_2

$$\text{SnCl}_4 + 4\text{H}_2\text{O} \longrightarrow \text{H}_4\text{SnO}_4 (\text{colloidal white precipitate}) + 4\text{HCl}$$
- (iv) SnCl_4 is a Lewis acid. Hence it has a tendency to accept lone pair of electrons from NH_3 , PH_3 etc and form adducts such as $\text{SnCl}_4 \cdot 4\text{NH}_3$
- (v) It dissolves in concentrated HCl forming H_2SnCl_6 and in presence of ammonium chloride, it forms ammonium salts of this acid.

$$\text{SnCl}_4 + 2\text{HCl} \longrightarrow \text{H}_2\text{SnCl}_6$$

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

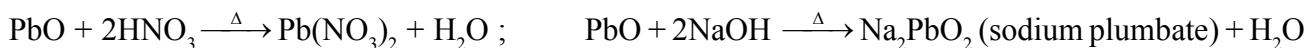
○ **USES :** For the preparation of stannic compounds.

○ **COMPOUNDS OF LEAD :**

○ **LITHARGE (PbO) :**

PbO is prepared by heating Pb at 180°C. It is a volatile yellow compound. $2\text{Pb} + \text{O}_2 \xrightarrow{\Delta} 2\text{PbO}$

It is an amphoteric oxide and dissolves in acids as well as in alkalis



It is used in rubber industry and in the manufacture of flint glasses, enamels, and storage batteries.

○ **LEAD DIOXIDE (PbO₂) :**

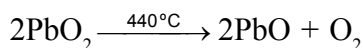
The fact that it does not liberate H_2O_2 by the action of dilute HCl suggest the above formula (It is a dioxide not a peroxide)

○ **PREPARATION :**

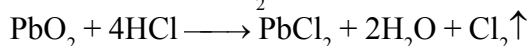
- (i) $\text{PbO} + \text{NaOCl} \xrightarrow{\Delta} \text{PbO}_2 (\text{insoluble}) + \text{NaCl}$
- (ii) $\text{Pb}_3\text{O}_4 + 4\text{HNO}_3 (\text{dilute}) \longrightarrow 2\text{Pb}(\text{NO}_3)_2 + \text{PbO}_2 + 2\text{H}_2\text{O}$

○ **PROPERTIES :**

- (i) It is a chocolate coloured insoluble powder. On heating at 440°C it gives the monoxide:



- (ii) It oxidizes HCl to Cl_2 :



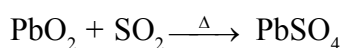
- (iii) It dissolves in conc. NaOH solution:



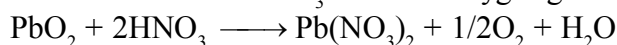
- (iv) It oxidises Mn salt to permanganic acid:



- (v) It reacts with SO_2 at red heat to form lead sulphate:



- (vi) It reacts with conc. HNO_3 to evolve oxygen gas.



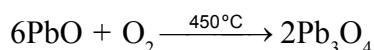
○ **USES :**

It is used in match industry for making ignition surface of match boxes and in the preparation of KMnO_4 .

○ **RED LEAD (Pb_3O_4) :**

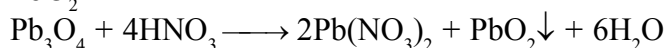
○ **PREPARATION:**

It is prepared by heating PbO at 450°C for a long time.

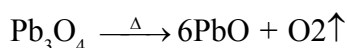


○ **PROPERTIES :**

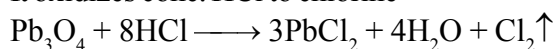
- (i) It is a red powder insoluble in water but when heated with conc. HNO_3 it gives a red precipitate of PbO_2



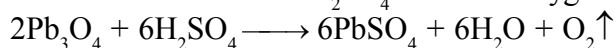
- (ii) When heated above 550°C , it decomposes into PbO



- (iii) It oxidizes conc. HCl to chlorine



- (iv) When heated with conc. H_2SO_4 it evolves oxygen

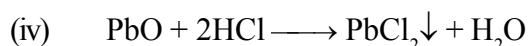
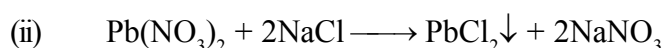
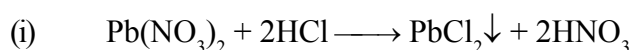


○ **USES :**

It is used as an oxidizing agent, for making red paint, for making special lead cement and for making flint glass.

○ **LEAD CHLORIDE (PbCl_2) :**

○ **PREPARATION:**



○ **PROPERTIES :**

It is a white crystalline solid, insoluble in cold water but soluble in boiling water. It dissolves in concentrated HCl forming a complex ion.



○ **USES :**

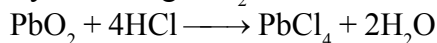
It is used for making pigments for paints.

○ LEAD TETRACHLORIDE (PbCl₄) :

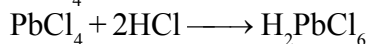
○ PREPARATION:

It is prepared by the following methods:

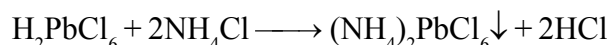
- (i) By dissolving PbO₂ in cold conc. HCl



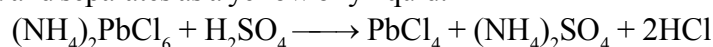
PbCl₄ dissolves in excess of HCl to form a stable solution of H₂PbCl₆.



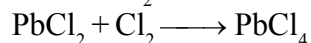
- ☞ When NH₄Cl is added to a solution of chloroplumbic acid, a yellow precipitate of ammonium chloroplumbate is formed.



- ☞ When crystals of ammonium chloroplumbate is added to ice cold conc. H₂SO₄, lead tetrachloride is formed and separates as a yellow oily liquid.



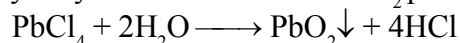
- (ii) By the action of Cl₂ on a solution of PbCl₂ in conc. HCl



○ PROPERTIES :

- (i) It is a yellow oily liquid which solidifies at -10°C and is soluble in organic solvents like ethanol and benzene.

- (ii) Rapid hydrolysis with water forms PbO₂ precipitate



○ USES :

It is used for making stannic compounds.