NEETJEE

Class XI







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Unit

The p-Block Elements (Group 13 and 14)

GROUP-13 ELEMENTS (BORON FAMILY)

INTRODUCTION

Group-13 of the periodic table consist of the following elements with general configuration ns^2np^1 . A new element is added to group-13 i.e., nihonium (Nh), which is radioactive.

Element	Electronic configuration
B (5)	[He] $2s^2 2p^1$
Al (13)	[Ne] $3s^2 3p^1$
Ga (31)	[Ar] $3d^{10} 4s^2 4p^1$
In (49)	[Kr] $4d^{10} 5s^2 5p^1$
Tl (81)	[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$
Nh (113)	[Rn] $5f^{14} 6d^{10} 7s^2 7p^1$

Physical Propertie

Atomic and ionic radii

The atomic/ionic radius increases from B to Tl (exception Al > Ga).

Ionisation energy

I.E. decreases down the group. Successive I.E. increases in the order:

$$\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$$

Electronegativity

Boron has the maximum electronegativity among the group-13 elements. Electronegativity first decreases from B to Al and then increases down the group.

Metallic character

B is a non-metal while Al is a metal and all other elements are almost metallic in character.

As we move down the group, density increases.

Boiling point -----

Boiling points of group-13 elements follow a regular trend and decreases down the group.

Melting point -----

The melting points decreases from B to Ga and then increases from Ga to Tl.

The melting point of boron is very high because it has giant covalent polymer structure in both solid and liquid states.

Oxidation states

B and Al show +3 oxidation states only but Ga, In and Tl show +1 and +3 oxidation states due to inert pair effect.

Inert pair effect

The two s-electrons in the outer shell tend to remain paired and will not participate in compound formation. This effect is called inert pair effect. The inert pair effect increases gradually in Ga, In and Tl compounds e.g., Ga⁺ compounds are unstable, In compounds are moderately stable, whereas Tl compounds are most stable.

Reactivity towards air

- $4M_{(s)} + 3O_{2(g)} \xrightarrow{\Delta} 2M_2O_{3(s)}$ (M = B, Al, Ga, In, Tl) $2M_{(s)} + N_{2(g)} \xrightarrow{\Delta} 2MN_{(s)} \qquad (M = B, Al)$
- On moving down the group, the acidic character of oxides decreases and the basic character increases.

Reactivity towards water

Boron is not affected by water or steam. Red hot boron decomposes steam.

$$2B + 3H_2O \longrightarrow B_2O_3 + 3H_2$$

- Aluminium can decompose the steam. $2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2$
- Ga and In are attacked by water only in the presence of oxygen.
- Tl is attacked by moist air. $4Tl + 2H_2O + O_2 \longrightarrow 4TlOH$

Chemical Properties

Reactivity towards acids and alkalies

Boron does not react with non-oxidising acids while others react with acids e.g.,

$$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2Al_{(aq)}^{3+} + 6Cl_{(aq)}^{-} + 3H_{2(g)}$$

- Conc. HNO₃ makes Al passive due to the formation of thin layer of Al_2O_3 .
- Boron resist the action of alkalies upto 773 K. $2B_{(s)} + 6KOH_{(aq)} \xrightarrow{> 773 \text{ K}} 2K_3BO_{3(s)} + 3H_{2(g)}$
- Al and Ga being amphoteric also react with aqueous alkalies.

$$2M_{(s)} + 2\text{NaOH}_{(aq)} + 6\text{H}_2\text{O}_{(l)} \longrightarrow$$

$$2\text{Na}^+ [M(\text{OH})_4]_{(aq)}^- + 3\text{H}_{2(g)}$$

$$(M = \text{Al, Ga})$$

Reactivity towards non-metals

At high temperature, B reacts directly with all non-metals except H, Ge, Te and the noble gases.

$$4B + C \xrightarrow{\Delta} B_4C$$

$$4B + 3O_2 \xrightarrow{\Delta} 2B_2O_3$$

$$2B + 3S \xrightarrow{\Delta} B_2S_3$$

Al combines with most of the non-metals on heating.

Reactivity towards halogens

These elements react with halogens to form trihalides (except TlI₃).

$$2M_{(s)} + 3X_{2(g)} \longrightarrow 2MX_{3(s)}$$
 $(X = F, Cl, Br, I)$

Lewis acid character decreases down the group $BX_3 > AlX_3 > GaX_3 > InX_3$

(Due to increase in size)

Lewis acid character of boron trihalides $BI_3 > BBr_3 > BCl_3 > BF_3$

(Due to $p\pi$ - $p\pi$ back bonding)



Turning dirty aluminium foil into biofuel catalyst!

Recently, an innovative crystallization method is developed to obtain 100% pure single crystals of aluminium salts from the contaminated foil. This is the starting material for the preparation of alumina catalyst. Usually to produce this type of alumina it would have to come from bauxite ore, which in mined in countries such as West Africa, West Indies and Australia, causing huge environmental damage.

ANOMALOUS BEHAVIOUR OF BORON

Boron shows anomalous behaviour as compared to the other members of the group due to

- its smallest size and high ionization energy
- highest electronegativity
- absence of *d*-orbitals in its valence shell.

Points of Differences

- B forms only covalent compounds while others form both ionic and covalent compounds.
- Trihalides of B are monomeric while other elements have halogen bridged dimeric structures.
- B has two allotropic forms; crystalline and amorphous. Other members do not show allotropy.
- The melting and boiling points of B are much higher as compared to other members.

 Boron shows a maximum covalency of four in its compounds e.g., BH₄ while other members show a maximum covalency of six e.g., [AlF₆]³⁻.

Uses

Aluminium

- It forms many useful alloys with Cu, Mn, Mg, Si and Zn.
- It is used as a conductor for transmission of electricity.
- It is used for making silvery paints for covering iron or other materials.

Boron

- As a moderator in nuclear reactors.
- As an abrasive and a refractory material.
- As rocket fuels because of high energy/mass ratio.
- As a hardener in steel industry.

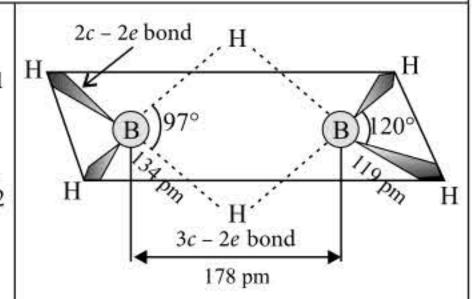
IMPORTANT COMPOUNDS OF BORON AND ALUMINIUM

	Preparation	Properties	Structure	
Borax (Na ₂ B ₄ O ₇ .10H ₂ O)	$Ca_{2}B_{6}O_{11} + 2Na_{2}CO_{3} \xrightarrow{\Delta} Na_{2}B_{4}O_{7}$ $Colemanite \qquad Borax \\ + 2NaBO_{2} + 2CaCO_{3} \downarrow $ $4NaBO_{2} + CO_{2} \longrightarrow Na_{2}B_{4}O_{7} \\ + Na_{2}CO_{3} Ha_{2}B_{4}O_{7} $ $+ 6H_{2}O + CO_{2}$	$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$ $Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$ Transparent glassy bead $Na_2B_4O_7 + 2NaOH \longrightarrow 4NaBO_2 + H_2O$ $Na_2B_4O_7 + H_2SO_4 \longrightarrow Na_2SO_4$ $+ H_2B_4O_7$	$2Na^{+}$ B_{O} B_{O} B OH OH OH OH OH OH OH OH	
	Uses: As a water softener and a cleansing agent. In the laboratory for borax bead test.			
Orthoboric acid (H ₃ BO ₃)	$Na_{2}B_{4}O_{7} + 2HCl + 5H_{2}O \longrightarrow$ $4H_{3}BO_{3} + 2NaCl$ $Na_{2}B_{4}O_{7} + H_{2}SO_{4} + 5H_{2}O \longrightarrow$ $4H_{3}BO_{3} + Na_{2}SO_{4}$ $Ca_{2}B_{6}O_{11} + 4SO_{2} + 11H_{2}O \longrightarrow$ $2Ca(HSO_{3})_{2} + 6H_{3}BO_{3}$ $B_{2}H_{6} + 6H_{2}O \longrightarrow 2H_{3}BO_{3} + 6H_{2}$ $BN + 3H_{2}O \longrightarrow H_{3}BO_{3} + NH_{3}$	H—OH + B(OH) ₃ → [B(OH) ₄] ⁻ + H ⁺ ; $pK_a = 9.25$ H ₃ BO ₃ $\xrightarrow{370 \text{ K}}$ HBO ₂ + H ₂ O $\xrightarrow{410 \text{ K}}$ H ₂ B ₄ O ₇ $\xrightarrow{Red \text{ Hot}}$ $2B_2O_3 + H_2O$ B(OH) ₃ + 3C ₂ H ₅ OH $\xrightarrow{Conc. H_2SO_4}$ $\xrightarrow{B(OC_2H_5)_3 + 3H_2O}$	H, OBO H, OBO H	

Uses:

- It is used in the manufacture of heat resistant borosilicate glass.
- The aqueous solution of boric acid is used as a mild antiseptic especially as eye wash under the name boric lotion.

$$2NaBH_4 + I_2 \xrightarrow{Diglyme} B_2H_6 + 2NaI + H_2 2BF_3 + 6NaH \xrightarrow{450 \text{ K}} B_2H_6 + 6NaF 4BF_3.Et_2O + 3LiAlH_4 \xrightarrow{Diethyl} 2B_2H_6 + 3LiF + 3AlF_3 + 4Et_2O$$



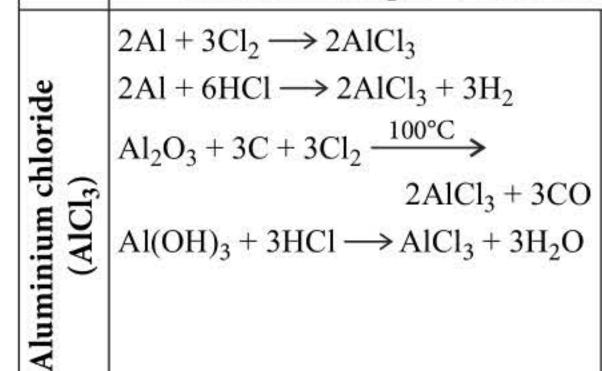
Due to the resemblance of three centre two electron bond to a banana, it is also called banana bond.

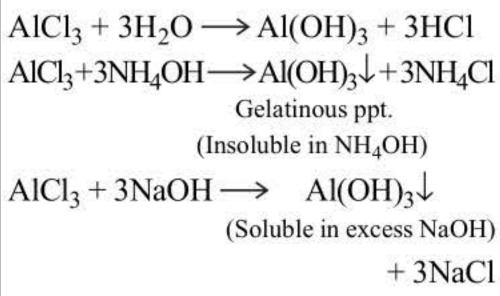
Uses:

• For preparing a number of borohydrides reducing agent such as LiBH₄, NaBH₄, etc, in organic reaction.

Borazine

To make bullet-proof vests and light composite material for aircrafts.

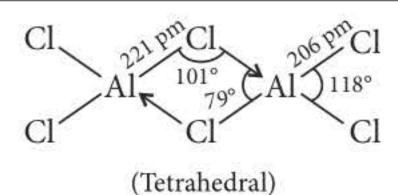




 $Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$

(Soluble

meta-aluminate)



AlCl₃ achieves stability by forming dimer.

Uses:

- Anhydrous AlCl₃ is used as a catalyst in Friedel-Crafts reaction and in cracking of petroleum.
- It is extensively used in manufacture of dyes, drugs and perfumes.

GROUP-14 ELEMENTS (CARBON FAMILY)

INTRODUCTION

Group-14 is transition between metals and non-metals. C is the most versatile element. Organic chemistry is devoted to carbon containing compounds. A new element is added to group-14, *i.e.*, Flerovium (Fl) which is radioactive.

Group-14 contains the following elements with general electronic configuration $ns^2 np^2$.

Element	Electronic configuration
Carbon (6)	[He] $2s^2 2p^2$
Silicon (14)	[Ne] $3s^2 3p^2$
Germanium (32)	[Ar] $3d^{10} 4s^2 4p^2$
Tin (50)	[Kr] $4d^{10} 5s^2 5p^2$
Lead (82)	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$
Flerovium (114)	[Rn] $5f^{14} 6d^{10} 7s^2 7p^2$

Physical Properties

Covalent and ionic radii

Covalent radii of group-14 elements regularly increases with increase in atomic number. The same trend is observed with ionic radius in their +2 and +4 oxidation states.

lonisation energy

First *I.E.* decreases from C to Sn but the decrease is not regular, decrease is very sharp from C to Si, but from Si onwards the decrease is very little due to poor shielding effect of 3d- and 4d- electrons in Ge and Sn. Pb is having a little more *I.E.* than Sn but less than Ge due to lanthanide contraction. Thus, the first *I.E.* of group-14 elements follow the order: C > Si > Ge > Sn < Pb

Electronegativity

C is the most electronegative element in this group. Electronegativity decreases from C to Si and remain constant from Si to Sn and then slightly increases for Pb.

Density

C (diamond) has more density than Si. Except carbon, the density of group-14 element increases with increase in atomic number.

Melting point and boiling point

The m.pt. and b.pt. decreases as we move down the group due to corresponding decrease in the interatomic forces of attraction. However, exceptionally the m.pt. of Sn is lower than that of Pb.

The m.pt. and b.pt. of group-14 elements are higher than the corresponding group-13 elements due to the formation of four covalent bonds with each other resulting in strong binding forces between their atoms in solid as well as in liquid state.

Metallic and non-metallic character

Metallic character increases with increase in atomic number.

C Si Ge Sn Pb
Non-metal Metalloid Metal



Carbon Nanotube Hybrid Structure!

To introduce and control the temperature coefficient of resistance (TCR) of metal matrix composite, relatively thick and short multi-walled carbon nanotubes (MWCNTs) were introduced in the metal matrix with *in-situ* formation of chromium carbide (Cr₇C₃) at the CNT/copper (Cu) interface. Incompatible properties such as electrical conductivity and TCR can be achieved simultaneously by introducing MWCNTs in the Cu matrix, with control of the interfacial resistivity using the MWCNT/Cr₇C₃-Cu system.

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Chemical Properties

Oxidation states

• C and Si both show an oxidation state of +4 while all other elements of group-14 show two oxidation states of +2 and +4 due to inert pair effect. The stability of +2 oxidation state 2+ 2+ 2+ increases from Ge to Pb *i.e.*, Ge < Sn < Pb, while the stability of +4 oxidation state decreases from 4+ 4+ 4+ 4+ 4+ 4+ 4+ C to Pb *i.e.*, C > Si > Ge > Sn > Pb

-

Oxidising and reducing properties

- Order of the reduction power in +2 oxidation state:
 C > Si > Ge > Sn > Pb
- Order of oxidation power in +4 oxidation state :
 C < Si < Ge < Sn < Pb

Reactivity towards oxygen

- They form oxides when heated in oxygen but do not react with oxygen at ordinary temperature.
- Group-14 elements form monoxides (MO) and dioxides (MO₂). SiO exists only at high temperature.
- Acidic nature of oxides :

Pb can from Pb₃O₄ (trilead tetraoxide), known as red lead or sindhur, on heating PbO (litharge) with excess of air at 673 K.
 6PbO + O₂ 673 K 2Pb₃O₄

Anomalous Behaviour of Carbon

C differs from the rest of the members of group-14 because of

- its small atomic size
- its high electronegativity
- its property of catenation
- absence of *d*-orbitals in its valence shell.

Points of Differences

• The m.pt. and b.pt., *I.E.* and electronegativity of C is very high as compared to the other members of its family.

Reactivity towards water

 C, Si and Ge are not affected by water. Sn decomposes steam.

$$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$$

- Pb is unaffected by water on its surface probably because of a protective oxide film formation.
- Pb dissolved slowly in water containing dissolved oxygen. This is called plumbosolvency.
 2Pb + 2H₂O + O₂ → 2Pb(OH)₂

Reactivity towards halogen

- These elements can form halides of formula MX_2 and MX_4 (X = F, Cl, Br, I).
- Except carbon, all other members react directly with halogen.
- Stability of dihalides increases down the group.
- Except CCl₄, other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in vacant d-orbitals.

Reducing character

 Carbon is a powerful reducing agent, it can reduces oxides of various elements e.g.,

$$SnO_2 + 2C \xrightarrow{\Delta} Sn + 2CO$$

$$CO_2 + C \xrightarrow{\Delta} 2CO$$

$$Fe_2O_3 + 3CO \xrightarrow{250^\circ-700^\circ C} 2Fe + 3CO_2$$

- Si is also used as deoxidizer in the manufacture of steel in the form of ferrosilicon.
- Sn also acts as a good reducing agent.
- Carbon in its diamond form, is one of the hardest known element.
- It has maximum tendency to show catenation.
- Carbon has strong tendency to form pπ-pπ multiple bonds either with itself or with other elements like N, O, S, etc. Other members of the family form pπ-dπ bonds and that to a lesser extent.
- CO₂ is a gas while the dioxides of all other members are solids.
- Carbon shows a maximum covalency of four while other members of the family may expand their covalency beyond 4 e.g., [SiCl₆]²⁻.

ALLOTROPES OF CARBON

- Diamond: In diamond, C-atom is sp³ hybridised and has three dimensional network structure. Since, no free electron is available, it is a bad conductor of electricity.
- **Graphite:** C-atom is sp^2 hybridised and each carbon is directly bound to three other C-atoms. Thus, graphite has a delocalized π -electron cloud, which is responsible for its high electrical conductivity. It possesses layer structure.
- Fullerenes: It consists 12 pentagons and 20 hexagons folded into a sphere, so that it looks like a soccer ball, called 'bucky ball'.

All the carbon atoms are equal and they undergo sp^2 hybridisation.

USES OF CARBON

- Graphite is used as a lubricant, electrodes for dry cell, moderator for fast moving neutrons in nuclear reactor.
- Graphite is used in lead pencils.
- Diamond is used for cutting glass and other cutting and drilling tools. It is also used for making precious gems and jewellery.
- Being highly porous, activated charcoal is used in adsorbing poisonous gases, also used in water filters to remove organic contaminators and in air conditioning system to control odour.

IMPORTANT COMPOUNDS OF CARBON AND SILICON

	Preparation	Properties	Structure
Carbon	$2C + O_2 \xrightarrow{\Delta} 2CO$	$2CO + O_2 \longrightarrow 2CO_2$:C=Q: ◆◆_:C≡Q
monoxide	$HCOOH \xrightarrow{373 \text{ K}} H_2O$	$3CO + Fe_2O_3 \xrightarrow{\Delta} 2Fe + 3CO_2$	or :C≒O:
(CO)	$2C + O_2 \xrightarrow{\Delta} 2CO$ $HCOOH \xrightarrow{373 \text{ K}} H_2O$ $+ CO$	$CO + ZnO \xrightarrow{\Delta} Zn + CO_2$	(Linear structure with
	$C + H_2O \xrightarrow{473 - 1273 \text{ K}}$	$4\text{CO} + \text{Ni} \xrightarrow{80^{\circ}\text{C}} [\text{Ni}(\text{CO})_4]$	<i>sp</i> hybridisation)
	CO+H ₂	$5\text{CO} + \text{Fe} \xrightarrow{180^{\circ}\text{C}} [\text{Fe}(\text{CO})_5]$	
	Water gas	CO is highly poisonous gas as it forms a	
	$2C + O_2 + 4N_2 \xrightarrow{473 - 1273 \text{ K}}$	complex with haemoglobin (Hb) which is	
	$2C + O_2 + 4N_2$ $2CO + 4N_2$	300 times more stable than O_2 –Hb complex.	
		Thus, it prevents haemoglobin to carry oxygen	
	Producer gas	from the lungs to other parts of the body.	

Uses:

- As a fuel in the form of water gas, producer gas etc.
- In the extraction of iron as reducing agent.

Carbon	$C + O_2 \xrightarrow{\Delta} CO_2$	$CO_2 + 2Mg \longrightarrow 2MgO + C$	- A C+
dioxide	$CH_4 + 2O_2 \xrightarrow{\Delta} CO_2 + 2H_2O$	$CO_2 + H_2O \rightleftharpoons H_2CO_3$:Ö <u>+</u> C≡O:
(CO ₂)	1307 GT 1000	$CO_2 + K_2CO_3 + H_2O \longrightarrow 2KHCO_3$:Ö¥Ç=Ö:
	$CaCO_3 + 2HCl \longrightarrow CaCl_2$	$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$	1
	1,000	$CO_2 + CaCO_3 + H_2O \longrightarrow Ca(HCO_3)_2$:†o≡c−ö:¯
	06111706	$CO_2 + Zn \longrightarrow ZnO + CO$	(Linear structure with
	+ 2CO ₂	$6CO_2 + 6H_2O \xrightarrow{hv} C_6H_{12}O_6 + 6O_2$	sp hybridisation)

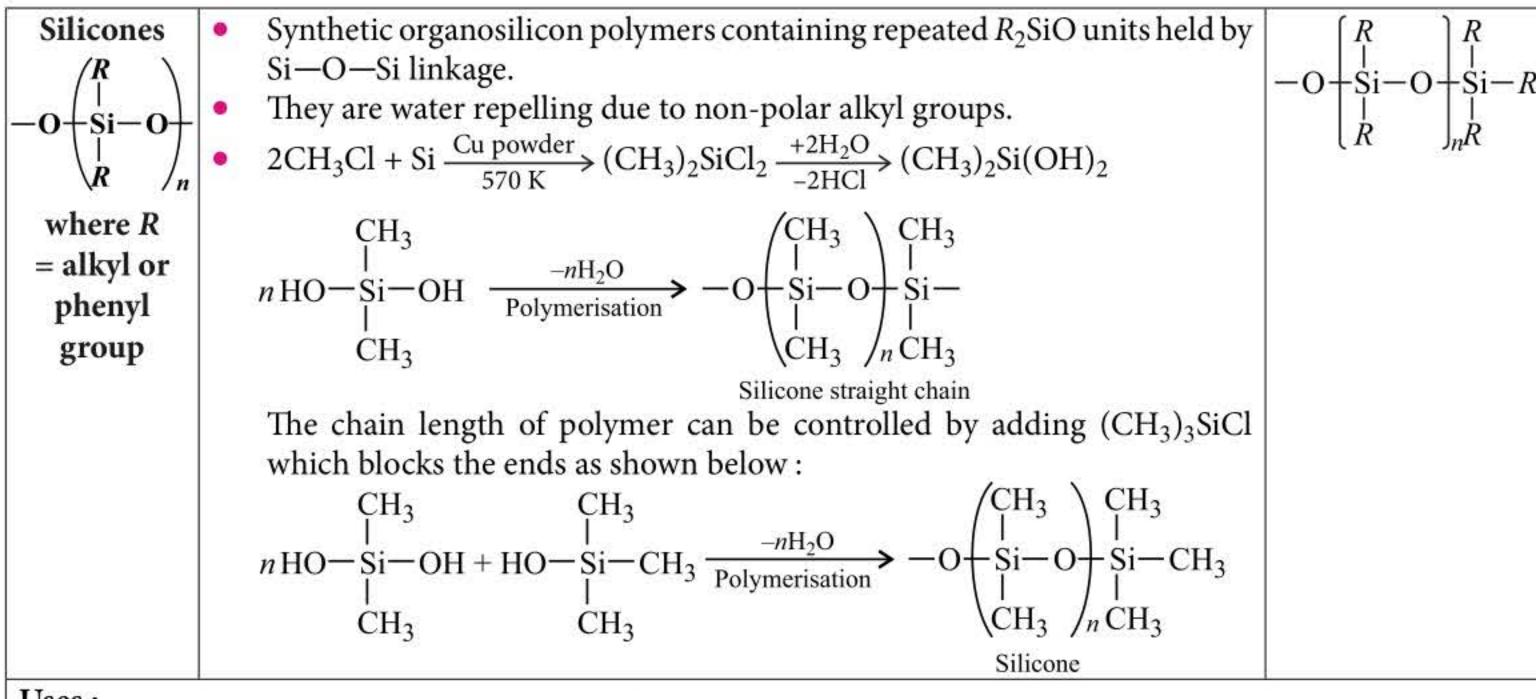
Uses:

- As carbogen [mixture of O_2 ($\approx 95\%$) + CO_2 ($\approx 5-10\%$)] in artificial respiration especially for pneumonia patients and victims of CO poisoning.
- As a fire extinguisher.

Silicon	It is a covalent, three dimensional network solid, almost non-reactive due to	
dioxide	high Si—O bond enthalpy. However, it is attacked by HF and NaOH.	
(SiO ₂ , Silica)	$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$	-\si-O-\si-O-\si-
	$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$	
		-\$i-O-\$i-O-\$i-

Uses:

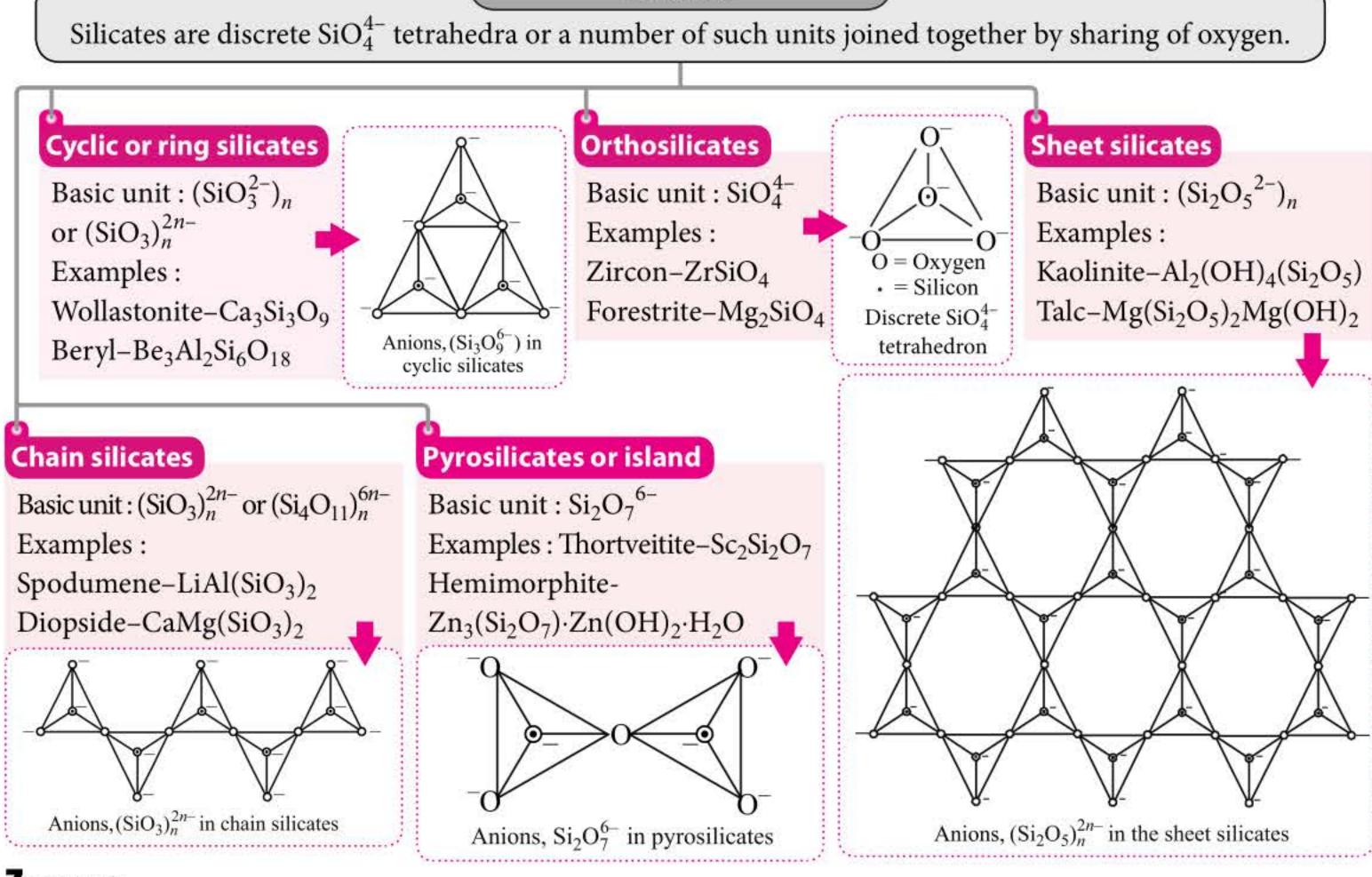
- Quartz (crystallographic form of silica) is extensively used as a piezoelectric material.
- Silica gel is used as a drying agent and as a supporter for chromatographic materials and catalysts.
- Kieselguhr, an amorphous form of silica, is used in filtration plants.



Uses:

They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible
they are also used in surgical and cosmetic implants.

Silicates



ZEOLITES

- Zeolites are hydrated 3-dimensional aluminosilicates which are formed by replacing some of the silicon atoms by Al^{3+} ions. Their general formula is $M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot mH_2O$.
- Zeolites are used as catalysts in petrochemical industries. They are also used as molecular sieves and softening
 of water by ion-exchange method.