FOCUS NEET/JEE 2019

Class XI

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UNIT - 6 : The *p*-Block Elements (Group 13 & 14)

- The elements in which the last electron enters into any of the outermost *p*-orbitals are called *p*-block elements.
- The general outer electronic configuration of the *p*-block elements is ns^2np^{1-6}.
- The elements belonging to the group 13 to 18 of the long form of periodic table are *p*-block elements. The *p*-block elements include metals, non-metals and metalloids.

Group 13 elements (Boron Family)

- Group 13 of the periodic table contains six elements boron (B), aluminium (Al), gallium (Ga), indium (In), thallium (Tl) and Nihonium (Nh). Aluminium is the most abundant of these elements. Boron occurs rather sparsely and gallium, indium, thallium are not found in concentrated deposits.

Electronic Configuration

Element	Symbol	Electronic configuration [noble gas] ns^2np^1
Boron	$_5B$	$[He]2s^22p^1$
Aluminium	$_{13}Al$	$[Ne]3s^23p^1$
Gallium	$_{31}Ga$	$[Ar]3d^{10}4s^24p^1$
Indium	$_{49}In$	$[Kr]4d^{10}5s^25p^1$
Thallium	$_{81}Tl$	$[Xe]4f^{14}5d^{10}6s^26p^1$
Nihonium	$_{113}Nh$	$[Rn]5f^{14}6d^{10}7s^27p^1$

Atomic and Physical Properties

Increasing trends	Decreasing trends
Atomic radii Ionic radii Stability of + 1 oxidation state (Inert pair effect) Ionic character Electropositive character Density	Ionisation energies M.P./B.P. Stability of + 3 oxidation state Covalent character Electronegativity

Chemical Properties

- All the elements of group 13 form trioxides (E_2O_3) when heated in dioxygen (Tl also forms some Tl_2O).
  $4E_{(s)} + 3O_{2(g)} \xrightarrow{\Delta} 2E_2O_{3(s)}$ (E = element)
  The nature of oxides varies down the group.
  B_2O_3 (Acidic), Al_2O_3, Ga_2O_3 (Amphoteric), In_2O_3, Tl_2O_3, Tl_2O (Basic)
- Boron and aluminium form nitrides when heated with nitrogen at high temperature.
  $2E_{(s)} + N_{2(g)} \xrightarrow{\Delta} 2EN_{(s)}$ (E = element)
- Boron does not react with acids and alkalies even at moderate temperature, but aluminium dissolves in mineral acids and aqueous alkalies and thus, shows amphoteric character. However, concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface.

- Group 13 elements react with halogens to form trihalides except TlI_3.
$2E_{(s)} + 3X_{2(g)} \longrightarrow 2EX_{3(s)}$ (X = F, Cl, Br, I)
- The covalent trihalides *e.g.*, BF_3 being electron deficient are strong Lewis acids and the tendency to behave as Lewis acids decreases with increase in size down the group.

Preparation, Properties and Uses of Boron

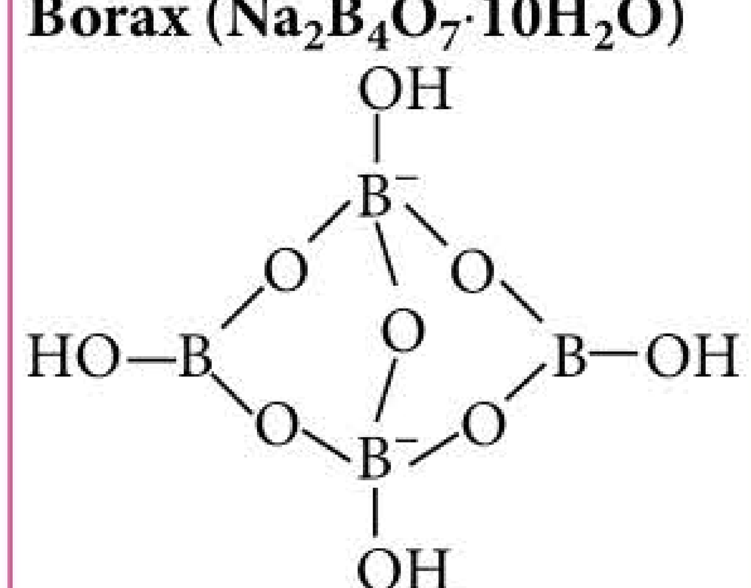
Preparation	Physical properties	Chemical properties	Uses
$B_2O_3 + 3Mg \xrightarrow{\text{Heat}} 3MgO + 2B_{(s)}$	• It is extremely hard solid.	$2B + 3X_2 \longrightarrow 2BX_3$	• In making filaments which are used in making light composite materials for aircraft.
$2BX_3 + 3H_2 \xrightarrow[\text{Ta or W}]{1270\text{ K}} 2B + 6HX$	• It is non-metallic.	$B + \underset{\text{(conc.)}}{3HNO_3} \longrightarrow H_3BO_3 + 3NO_2\uparrow$	• As semiconductor in making electronic devices.
$KBF_4 \xrightarrow{\text{Electrolysis}} K^+ + B^{3+} + 4F^-$	• It has two allotropes : – **Crystalline boron :** Black and chemically inert. It is very hard in nature. – **Amorphous boron:** Brown and chemically active.	$2B + \underset{\text{(conc.)}}{3H_2SO_4} \longrightarrow 2H_3BO_3 + 3SO_2\uparrow$ $4B + 3O_2 \longrightarrow 2B_2O_3$ $2B + N_{2(g)} \longrightarrow 2BN_{(s)}$	• In preparation of metal borides which are used as protective shields and control rods in nuclear reactors.
$B_2H_6 \xrightarrow[1773\text{ K}]{\text{Heat}} 2B + 3H_2$	• It is poor conductor of heat and electricity. • It has two isotopes : ${}^{10}_{5}B$(20%) and ${}^{11}_{5}B$(80%).	$2B + 6NaOH \xrightarrow{>773\text{ K}} 2Na_3BO_3 + 3H_2$ $\underset{\text{(Red hot)}}{2B} + \underset{\text{(Steam)}}{3H_2O} \longrightarrow B_2O_3 + 3H_2$	• In steel industry for increasing the hardness of steel.

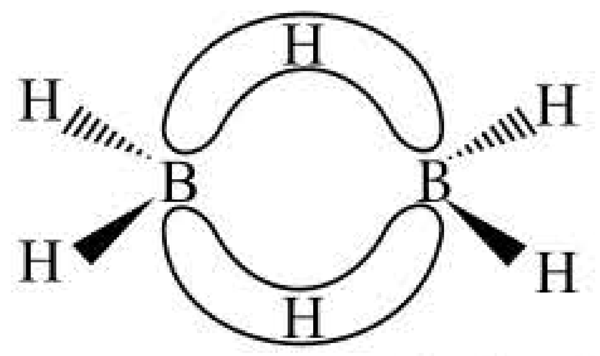
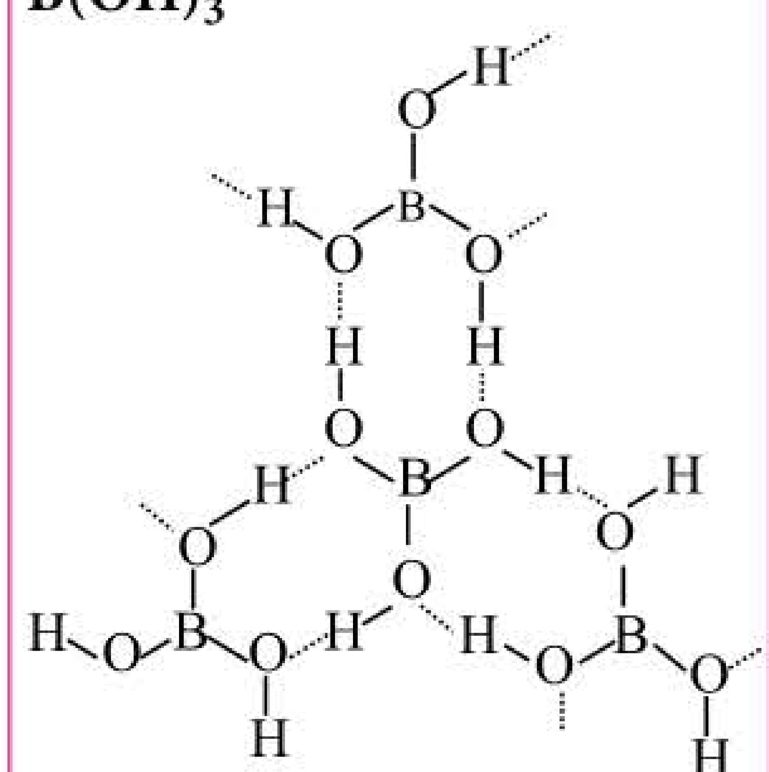
Anomalous Properties of Boron

- Due to the smallest size, high ionisation energy, absence of vacant *d*-orbitals and high electronegativity boron shows anomalous behaviour as compared to other members of the group.

Property	Boron	Other elements of group 13
Metallic behaviour	Non-metal	Metals
Covalency	Maximum-4	Maximum-6
Allotropy	Exhibits	Do not exhibit
Oxidation states	Only +3	+1, +3
Compounds	Only covalent	Both ionic and covalent
Halides	Monomeric	Polymeric
Oxides and hydroxides	Acidic	Mainly basic
Combination with metals	Forms boride	Do not combine (form alloy)

Some Important Compounds of Boron

Compound	Preparation	Properties	Uses
Borax ($Na_2B_4O_7 \cdot 10H_2O$)  $[B_4O_5(OH)_4]^{2-}$	• $\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \longrightarrow \underset{\text{Cal. carbonate}}{2CaCO_3\downarrow} + \underset{\text{Borax}}{Na_2B_4O_7} + \underset{\text{Metaborate}}{2NaBO_2}$ $4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$ • $4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + CO_2\uparrow + 6H_2O$	• $Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\text{Strong alkali}}{2NaOH} + \underset{\text{Weak acid}}{4H_3BO_3}$ • $Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$ $Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + \underset{\text{(Glassy mass)}}{B_2O_3}$ $CuSO_4 \longrightarrow CuO + SO_3\uparrow$ $CuO + B_2O_3 \longrightarrow \underset{\text{(Bluish green bead)}}{Cu(BO_2)_2}$	• in borax bead test • as a flux for soldering and welding • in making glazes and enamels • in making borosilicate glass • used as a water softener and cleaning agent.

Diborane (B_2H_6)  Four 2*c*-2*e* B–H terminal bonds Two 3*c*-2*e* B–H bridging bonds	• $4BF_3 + 3LiAlH_4 \xrightarrow[\text{ether}]{\text{Diethyl}} 2B_2H_6 + 3LiF + 3AlF_3$ • **Laboratory Method** $2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$ • **Industrial Method** $2BF_3 + 6NaH \xrightarrow{450\ K} B_2H_6 + 6NaF$	• $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$ • $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$ • $B_2H_6 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$ • $B_2H_6 + 2NMe_3 \longrightarrow 2BH_3\cdot NMe_3$ $B_2H_6 + 2CO \longrightarrow 2BH_3\cdot CO$	• for preparing a number of borohydrides such as $LiBH_4$, $NaBH_4$, etc. • as a reducing agent in organic reactions.
Orthoboric acid (H_3BO_3) or $B(OH)_3$ 	• **From borax :** $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$ $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + Na_2SO_4$ • **By hydrolysis of boron compounds :** $BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$ $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$ $BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$	• It is a weak monobasic acid. It is not a protonic acid but acts as Lewis acid. $B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$ • **Action of heat :** $\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{370\ K} \underset{\text{Metaboric acid}}{HBO_2} + H_2O$ $\underset{\text{Metaboric acid}}{4HBO_2} \xrightarrow[-H_2O]{410\ K} \underset{\text{Tetraboric acid}}{H_2B_4O_7}$ $\xrightarrow[\text{heat}]{\text{Red}} \underset{\text{Boron trioxide}}{2B_2O_3} + H_2O$	• 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*.

Group 14 Elements (Carbon Family)

- Group 14 of the periodic table contains six elements which are carbon, silicon, germanium, tin, lead and Flerovium. Carbon is an essential constituent of all organic matter while silicon is the main constituent of inorganic matter.

Element	Symbol	Electronic configuration
Carbon	$_6C$	$[He]2s^22p^2$
Silicon	$_{14}Si$	$[Ne]3s^23p^2$
Germanium	$_{32}Ge$	$[Ar]3d^{10}4s^24p^2$
Tin	$_{50}Sn$	$[Kr]4d^{10}5s^25p^2$
Lead	$_{82}Pb$	$[Xe]4f^{14}5d^{10}6s^26p^2$
Flerovium	$_{114}Fl$	$[Rn]5f^{14}6d^{10}7s^27p^2$

Physical Properties

Atomic or covalent radii	C < Si < Ge < Sn < Pb
Ionisation energy	C > Si > Ge > Sn > Pb
Electronegativity	C > Si ≃ Ge ≃ Sn < Pb
Oxidation state	Stability of +4 oxidation state decreases down the group while that of +2 increases.
Melting and boiling points	Decrease from carbon to lead.
Density	Increases from C to Pb
Allotropy	All elements show allotropy

Reactivity of the Elements of Group 14

- Elements in this group are relatively unreactive but reactivity increases down the group. Pb often appears more noble than expected due to a surface coating of oxide and partly due to high over potential for the reduction of H^+ to H_2 at a lead surface.

Reagent	Reactivity
H_2O	C, Si, Ge, Pb are unaffected by H_2O.
	$Sn + \underset{\text{(steam)}}{2H_2O} \longrightarrow SnO_2 + 2H_2$

Dilute acids	C, Si, Ge are unaffected by dilute acids.
	Pb does not dissolve in dilute H_2SO_4 due to formation of $PbSO_4$ coating.
Concentrated acids	Diamond is unaffected by concentrated acids, but graphite is oxidised by concentrated HNO_3 to give graphitic acid ($C_{11}H_4O_5$) which is an insoluble yellowish green substance and to graphite oxide with hot concentrated HF/HNO_3.
	Si is oxidised and changes to SiF_4 by hot concentrated HNO_3/HF.
	Pb does not dissolve in concentrated HCl due to formation of $PbCl_2$ coating.
Alkalies	Carbon is unaffected by alkalies.
	Sn and Pb are slowly attacked by cold alkali, and rapidly by hot alkali, giving stannates $Na_2[Sn(OH)_6]$ and plumbates $Na_2[Pb(OH)_6]$.
Complex formation	Si, Ge, Sn and Pb can show coordination number more than 4. *e.g.*, Si, Ge (6), Sn, Pb (8)
Halogens	Diamond is unreactive, but graphite reacts forming $(CF)_n$.
	Si and Ge form volatile SiX_4 and GeX_4 respectively.
	Sn and Pb are less reactive. Sn reacts with Cl_2 and Br_2 in cold, and with F_2 and I_2 on warming. Lead reacts with F_2 in cold and with Cl_2 on heating forming PbX_2.

Crystalline Allotropes of Carbon

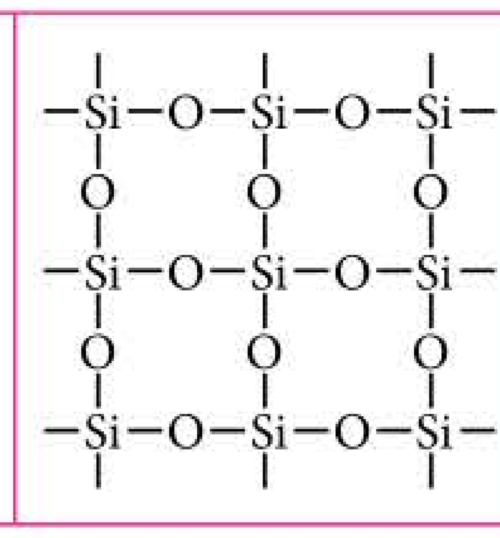
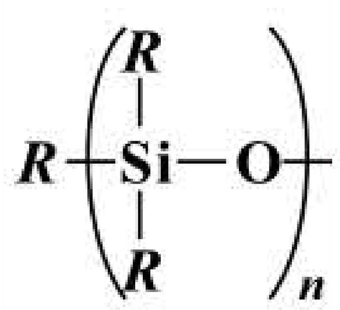
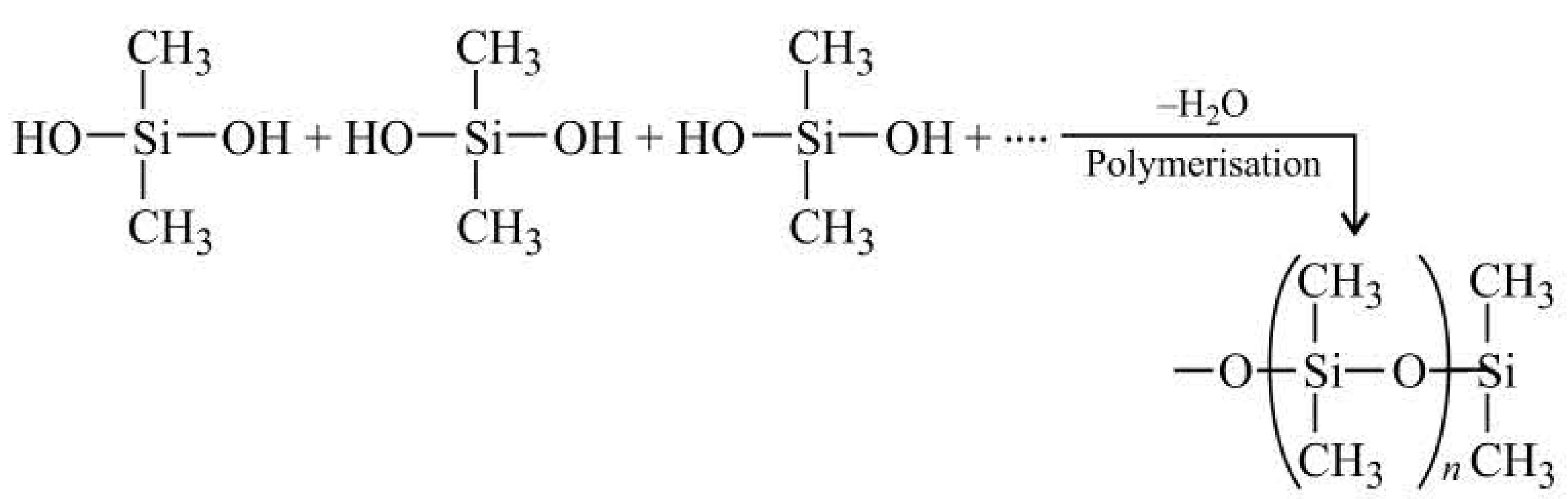
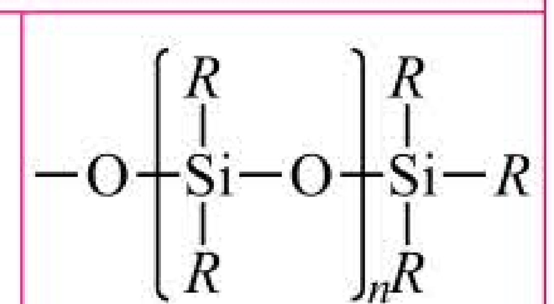
- **Diamond :** A rigid three-dimensional network of sp^3 hybridised carbon atoms, hardest substance known and used as an abrasive.
- **Graphite :** Most stable allotrope, having layered structure in which each layer has sp^2 hybridised carbon atoms in hexagonal rings and adjacent layers are held together by van der Waals' forces, soft, slippery, conductor of electricity and used as lubricant in machines.
- **Fullerenes :** Pure form of carbon, consists mainly of C_{60}, have shape like soccer ball (also called Buckminsterfullerene) which contains 20 six-membered rings and 12 five-membered rings and all carbon atoms are sp^2 hybridised.

Amorphous Allotropes of Carbon

- Carbon black, coke and charcoal are all impure forms of graphite or fullerenes.

Important Compounds of Carbon and Silicon

Compound	Preparation	Properties	Structure
Carbon monoxide (CO)	$2C_{(s)} + O_{2(g)} \xrightarrow{\Delta} 2CO_{(g)}$ $HCOOH \xrightarrow[\text{Conc. } H_2SO_4]{373\text{ K}} H_2O + CO$ **Commercial Preparation :** $C_{(s)} + H_2O_{(g)} \xrightarrow{473-1273\text{ K}} \underbrace{CO + H_2}_{\text{Water gas}}$ $2C + O_2 + 4N_2 \xrightarrow{473-1273\text{ K}} \underbrace{2CO + 4N_2}_{\text{Producer gas}}$	$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}; \Delta H = -12.68$ kcal $3CO_{(g)} + Fe_2O_{3(s)} \xrightarrow{\Delta} 2Fe_{(s)} + 3CO_{2(g)}$ $CO_{(g)} + ZnO_{(s)} \xrightarrow{\Delta} Zn_{(s)} + CO_{2(g)}$ $4CO + Ni \xrightarrow{80°C} [Ni(CO)_4]$ $5CO + Fe \xrightarrow{180°C} [Fe(CO)_5]$ Highly poisonous due to the fomation of a complex with haemoglobin (Hb) which is 300 times more stable than O_2–Hb complex thus, prevents Hb in the RBCs from carrying O_2 around the body.	$:C{=}\ddot{O}: \leftrightarrow {}^{-}:C{\equiv}\overset{+}{O}:$ or $:C{\equiv}O:$
Carbon dioxide (CO_2)	$C_{(s)} + O_{2(g)} \xrightarrow{\Delta} CO_{2(g)}$ $CH_{4(g)} + 2O_{2(g)} \xrightarrow{\Delta} CO_{2(g)} + 2H_2O_{(g)}$ **Laboratory Method :** $CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$	$CO_2 + Mg \longrightarrow 2MgO + C$ $CO_2 + H_2O \rightleftharpoons H_2CO_3$ $CO_2 + Ca(OH)_2 \longrightarrow \underset{\text{(Insoluble)}}{CaCO_3} + H_2O$ $CO_2 + CaCO_3 + H_2O \longrightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$ $CO_2 + C \longrightarrow 2CO$ $6CO_2 + 6H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2$	${}^{-}:\ddot{O}{-}C{\equiv}\overset{+}{O}: \leftrightarrow :\ddot{O}{=}C{=}\ddot{O}: \leftrightarrow :\overset{+}{O}{\equiv}C{-}\ddot{O}:^{-}$

<table>
<tr><td colspan="3">Uses : It is used
• In the manufacture of soda.
• As carbogen [mixture of $O_2 + CO_2$ (5-10%)] in artificial respiration especially for pneumonia patients and victims of CO poisoning.
• As a fire extinguisher.</td></tr>
<tr><td>Silicon dioxide (SiO_2)</td><td>Covalent, three dimensional network solid.
Almost non-reactive due to high Si—O bond enthalpy.
However, it is attacked by HF and NaOH.
$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$
$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$</td><td></td></tr>
<tr><td colspan="3">Uses :
• 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 is used as a drying agent and as a support for chromatographic materials and catalysts.
• Kieselguhr, an amorphous form of silica is used in filtration plants.</td></tr>
<tr><td>Silicones

where R = alkyl or phenyl group</td><td>• Synthetic organosilicon polymers containing repeated R_2SiO units held by Si—O—Si linkage.
• They are water repelling due to non-polar alkyl groups.
$2CH_3Cl + Si \xrightarrow[570\ K]{Cu\ power} (CH_3)_2SiCl_2 \xrightarrow[-2HCl]{+2H_2O} (CH_3)_2Si(OH)_2$

Silicone straight chain</td><td></td></tr>
<tr><td colspan="3">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 plants.</td></tr>
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Different Types of Silicates

1. **Orthosilicates :** Basic unit : SiO_4^{4-}, *e.g.*, Zircon–$ZrSiO_4$, Forsterite–Mg_2SiO_4
2. **Pyrosilicates or islands :** Basic unit : $Si_2O_7^{6-}$, *e.g.*, Thortveitite–$Sc_2Si_2O_7$, Hemimorphite- $Zn_3(Si_2O_7)\cdot Zn(OH)_2\cdot H_2O$
3. **Cyclic or ring silicates :** Basic unit : $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$, *e.g.*, Wollastonite–$Ca_3Si_3O_9$, Beryl–$Be_3Al_2Si_6O_{18}$
4. **Chain silicates :** Basic unit : $(SiO_3)_n^{2n-}$ or $(Si_4O_{11})_n^{6n-}$, *e.g.*, Spodumene–$LiAl(SiO_3)_2$, Diopside–$CaMg(SiO_3)_2$
5. **Sheet silicates (two-dimensional) :** Basic unit : $(Si_2O_5)_n^{2n-}$ or $(Si_2O_5^{2-})_n$, *e.g.*, Kaolin–$Al_2(OH)_4(Si_2O_5)$, Talc–$Mg(Si_2O_5)_2Mg(OH)_2$
6. **Three-dimensional silicates :** These silicates involve all four oxygen atoms in sharing with adjacent SiO_4^{4-} tetrahedra, *e.g.*, Zeolites, Quartz, Feldspar, Ultramarines, etc.