

NEET/JEE 2019

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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	${}_5\text{B}$	$[\text{He}]2s^22p^1$
Aluminium	${}_{13}\text{Al}$	$[\text{Ne}]3s^23p^1$
Gallium	${}_{31}\text{Ga}$	$[\text{Ar}]3d^{10}4s^24p^1$
Indium	${}_{49}\text{In}$	$[\text{Kr}]4d^{10}5s^25p^1$
Thallium	${}_{81}\text{Tl}$	$[\text{Xe}]4f^{14}5d^{10}6s^26p^1$
Nihonium	${}_{113}\text{Nh}$	$[\text{Rn}]5f^{14}6d^{10}7s^27p^1$

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).
 $4E_{(s)} + 3O_{2(g)} \xrightarrow{\Delta} 2E_2O_{3(s)}$ ($E = \text{element}$)
 The nature of oxides varies down the group.
 B_2O_3 Al_2O_3 , Ga_2O_3 In_2O_3 , Tl_2O_3 , Tl_2O
 Acidic Amphoteric Basic
- Boron and aluminium form nitrides when heated with nitrogen at high temperature.
 $2E_{(s)} + N_{2(g)} \xrightarrow{\Delta} 2EN_{(s)}$ ($E = \text{element}$)
- 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. 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
$B_2O_3 + 3Mg \xrightarrow{\text{Heat}} 3MgO + 2B_{(s)}$ $2BX_3 + 3H_2 \xrightarrow[Ta \text{ or } W]{1270 K} 2B + 6HX$ $KBF_4 \xrightarrow{\text{Electrolysis}} K^+ + B^{3+} + 4F^-$ $B_2H_6 \xrightarrow[1773 K]{\text{Heat}} 2B + 3H_2$	<ul style="list-style-type: none"> It is extremely hard solid. It is non-metallic. It has two allotropes : <ul style="list-style-type: none"> Crystalline boron: Black and chemically inert. It is very hard in nature. Amorphous boron: Brown and chemically active. It is poor conductor of heat and electricity. It has two isotopes : $^{10}_5B$(20%) and $^{11}_5B$(80%). 	$2B + 3X_2 \longrightarrow 2BX_3$ $B + 3HNO_3 \xrightarrow{\text{(conc.)}} H_3BO_3 + 3NO_2 \uparrow$ $2B + 3H_2SO_4 \xrightarrow{\text{(conc.)}} 2H_3BO_3 + 3SO_2 \uparrow$ $4B + 3O_2 \longrightarrow 2B_2O_3$ $2B + N_{2(g)} \longrightarrow 2BN_{(s)}$ $2B + 6NaOH \xrightarrow{>773 K} 2Na_3BO_3 + 3H_2$ $2B + 3H_2O \xrightarrow{\text{(Red hot) (Steam)}} B_2O_3 + 3H_2$	<ul style="list-style-type: none"> In making filaments which are used in making light composite materials for aircraft. As semiconductor in making electronic devices. In preparation of metal borides which are used as protective shields and control rods in nuclear reactors. In steel industry for increasing the hardness of steel.

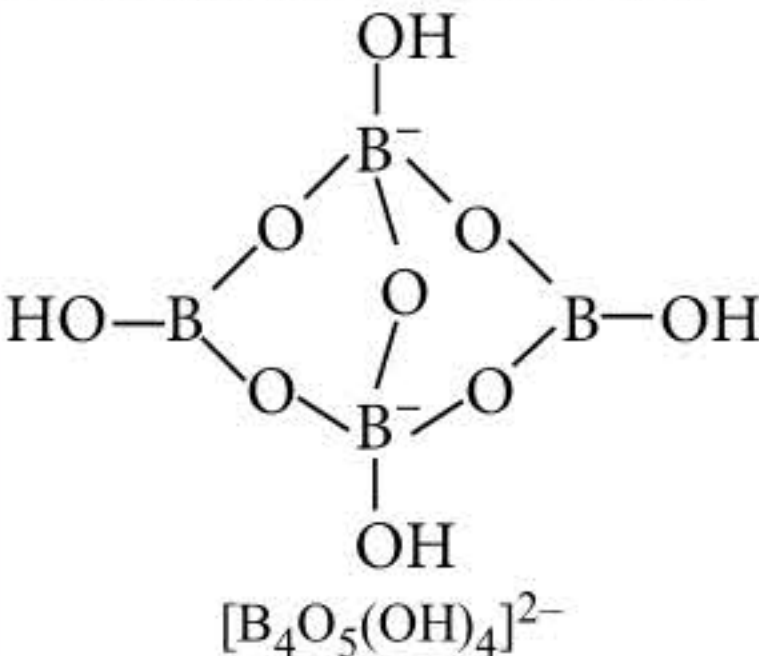
Anomalous Properties of Boron

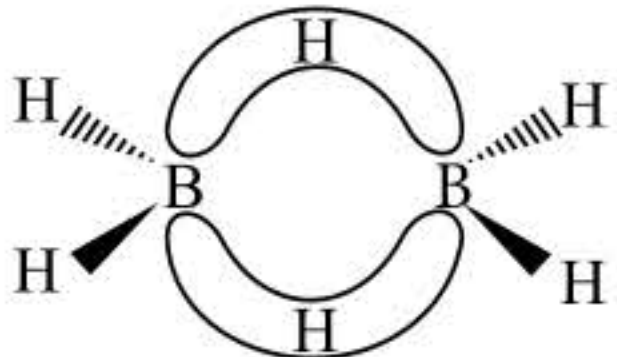
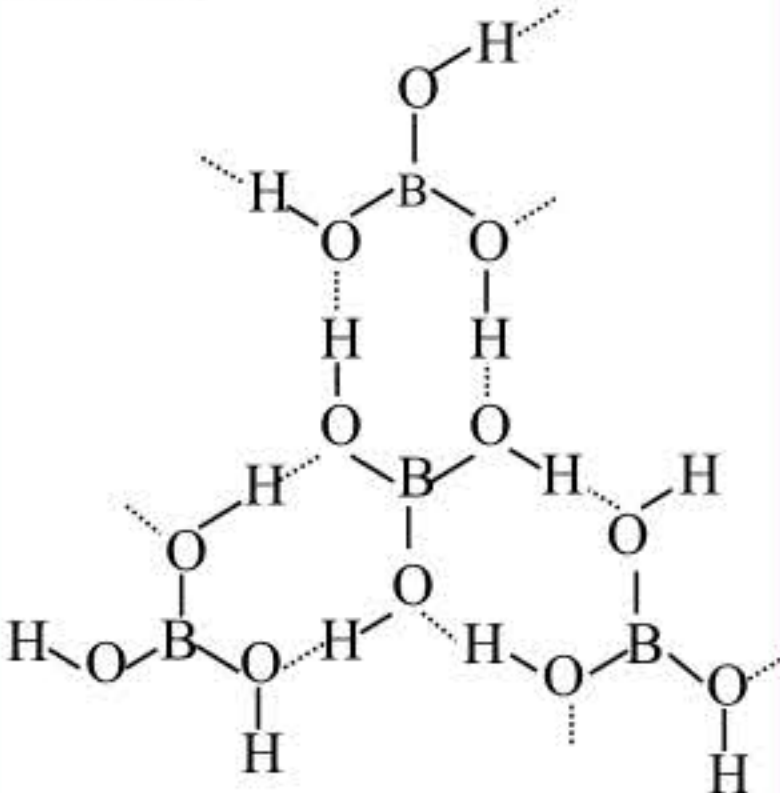
- Due to the smallest size, high ionisation energy, absence of vacant *d*-orbitals and high electronegativity boron shows anomalous behaviour as compared to other members of the group.

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 ($Na_2B_4O_7 \cdot 10H_2O$)  $[B_4O_5(OH)_4]^{2-}$	<ul style="list-style-type: none"> $Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$ Colemanite Borax Cal. carbonate Metaborate $4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$ $4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + CO_2 \uparrow + 6H_2O$ 	<ul style="list-style-type: none"> $Na_2B_4O_7 + 7H_2O \rightleftharpoons 2NaOH + 4H_3BO_3$ Strong alkali Weak acid $Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$ $Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$ (Glassy mass) $CuSO_4 \longrightarrow CuO + SO_3 \uparrow$ $CuO + B_2O_3 \longrightarrow Cu(BO_2)_2$ (Bluish green bead) 	<ul style="list-style-type: none"> 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.

<p>Diborane (B₂H₆)</p>  <p>Four 2c-2e B-H terminal bonds Two 3c-2e B-H bridging bonds</p>	<ul style="list-style-type: none"> • $4\text{BF}_3 + 3\text{LiAlH}_4 \xrightarrow[\text{ether}]{\text{Diethyl}}$ $2\text{B}_2\text{H}_6 + 3\text{LiF} + 3\text{AlF}_3$ • Laboratory Method $2\text{NaBH}_4 + \text{I}_2 \longrightarrow \text{B}_2\text{H}_6 + 2\text{NaI} + \text{H}_2$ • Industrial Method $2\text{BF}_3 + 6\text{NaH} \xrightarrow{450\text{ K}}$ $\text{B}_2\text{H}_6 + 6\text{NaF}$ 	<ul style="list-style-type: none"> • $\text{B}_2\text{H}_6 + 3\text{O}_2 \longrightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O}$ • $\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \longrightarrow 2\text{H}_3\text{BO}_3 + 6\text{H}_2$ • $\text{B}_2\text{H}_6 + 6\text{CH}_3\text{OH} \longrightarrow 2\text{B}(\text{OCH}_3)_3 + 6\text{H}_2$ • $\text{B}_2\text{H}_6 + 2\text{NMe}_3 \longrightarrow 2\text{BH}_3 \cdot \text{NMe}_3$ • $\text{B}_2\text{H}_6 + 2\text{CO} \longrightarrow 2\text{BH}_3 \cdot \text{CO}$ 	<ul style="list-style-type: none"> • for preparing a number of borohydrides such as LiBH₄, NaBH₄, etc. • as a reducing agent in organic reactions.
<p>Orthoboric acid (H₃BO₃) or B(OH)₃</p> 	<ul style="list-style-type: none"> • From borax : $\text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{BO}_3 + 2\text{NaCl}$ $\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{SO}_4 + 5\text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{BO}_3 + \text{Na}_2\text{SO}_4$ • By hydrolysis of boron compounds : $\text{BCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{BO}_3 + 3\text{HCl}$ $\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \longrightarrow 2\text{H}_3\text{BO}_3 + 6\text{H}_2$ $\text{BN} + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{BO}_3 + \text{NH}_3$ 	<ul style="list-style-type: none"> • It is a weak monobasic acid. It is not a protonic acid but acts as Lewis acid. $\text{B}(\text{OH})_3 + 2\text{HOH} \longrightarrow [\text{B}(\text{OH})_4]^- + \text{H}_3\text{O}^+$ • Action of heat : $\text{H}_3\text{BO}_3 \xrightarrow{370\text{ K}} \text{HBO}_2 + \text{H}_2\text{O}$ Boric acid Metaboric acid $4\text{HBO}_2 \xrightarrow[-\text{H}_2\text{O}]{410\text{ K}} \text{H}_2\text{B}_4\text{O}_7$ Metaboric acid Tetraboric acid $\xrightarrow[\text{heat}]{\text{Red}}$ $2\text{B}_2\text{O}_3 + \text{H}_2\text{O}$ Boron trioxide 	<ul style="list-style-type: none"> • 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 <i>boric lotion</i>.

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	₆ C	[He]2s ² 2p ²
Silicon	₁₄ Si	[Ne]3s ² 3p ²
Germanium	₃₂ Ge	[Ar]3d ¹⁰ 4s ² 4p ²
Tin	₅₀ Sn	[Kr]4d ¹⁰ 5s ² 5p ²
Lead	₈₂ Pb	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²
Flerovium	₁₁₄ Fl	[Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p 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 H₂ at a lead surface.

Reagent	Reactivity
H ₂ O	C, Si, Ge, Pb are unaffected by H ₂ O. $\text{Sn} + 2\text{H}_2\text{O} \longrightarrow \text{SnO}_2 + 2\text{H}_2$ (steam)

Dilute acids	C, Si, Ge are unaffected by dilute acids.
	Pb does not dissolve in dilute H ₂ SO 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 ₄ O 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 sp³ hybridised carbon atoms, hardest substance known and used as an abrasive.
- **Graphite** : Most stable allotrope, having layered structure in which each layer has sp² 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 C₆₀, have shape like soccer ball (also called Buckminsterfullerene) which contains 20 six-membered rings and 12 five-membered rings and all carbon atoms are sp² hybridised.

Amorphous Allotropes of Carbon

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

Important Compounds of Carbon and Silicon

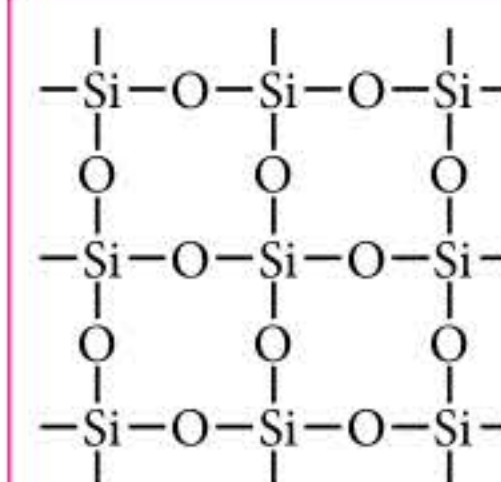
Compound	Preparation	Properties	Structure
Carbon monoxide (CO)	$2C_{(s)} + O_{2(g)} \xrightarrow{\Delta} 2CO_{(g)}$ $HCOOH \xrightarrow[Conc. H_2SO_4]{373 K} H_2O + CO$ <p>Commercial Preparation :</p> $C_{(s)} + H_2O_{(g)} \xrightarrow{473 - 1273 K} \underbrace{CO + H_2}_{\text{Water gas}}$ $2C + O_2 + 4N_2 \xrightarrow{473 - 1273 K} \underbrace{2CO + 4N_2}_{\text{Producer gas}}$	$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}; \Delta H = -12.68 \text{ kcal}$ $3CO_{(g)} + Fe_2O_{3(s)} \xrightarrow{\Delta} 2Fe_{(s)} + 3CO_{2(g)}$ $CO_{(g)} + ZnO_{(s)} \xrightarrow{\Delta} Zn_{(s)} + CO_{2(g)}$ $4CO + Ni \xrightarrow{80^\circ C} [Ni(CO)_4]$ $5CO + Fe \xrightarrow{180^\circ C} [Fe(CO)_5]$ <p>Highly poisonous due to the formation of a complex with haemoglobin (Hb) which is 300 times more stable than O₂-Hb complex thus, prevents Hb in the RBCs from carrying O₂ around the body.</p>	$:C \equiv \ddot{O} : \leftrightarrow \cdot \ddot{O} : C^{\oplus}$ <p>or $:C \equiv \ddot{O} :$</p>
Carbon dioxide (CO₂)	$C_{(s)} + O_{2(g)} \xrightarrow{\Delta} CO_{2(g)}$ $CH_{4(g)} + 2O_{2(g)} \xrightarrow{\Delta} CO_{2(g)} + 2H_2O_{(g)}$ <p>Laboratory Method :</p> $CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$	$CO_2 + Mg \rightarrow 2MgO + C$ $CO_2 + H_2O \rightleftharpoons H_2CO_3$ $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$ <p style="text-align: center;">(Insoluble)</p> $CO_2 + CaCO_3 + H_2O \rightarrow Ca(HCO_3)_2$ <p style="text-align: center;">Soluble</p> $CO_2 + C \rightarrow 2CO$ $6CO_2 + 6H_2O \xrightarrow{hv} C_6H_{12}O_6 + 6O_2$	$\ddot{O} = C = \ddot{O} :$ \updownarrow $:\ddot{O} \equiv C - \ddot{O}^-$

Uses : It is used

- In the manufacture of soda.
- As carbogen [mixture of O₂ + CO₂ (5-10%)] in artificial respiration especially for pneumonia patients and victims of CO poisoning.
- As a fire extinguisher.

Silicon dioxide (SiO₂)

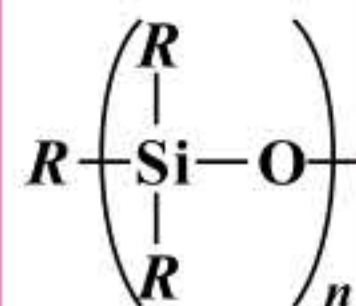
Covalent, three dimensional network solid.
Almost non-reactive due to high Si—O bond enthalpy.
However, it is attacked by HF and NaOH.
SiO₂ + 2NaOH → Na₂SiO₃ + H₂O
SiO₂ + 4HF → SiF₄ + 2H₂O



Uses :

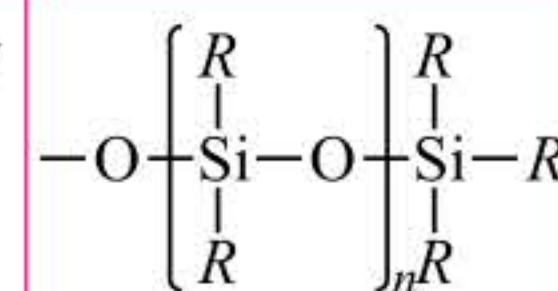
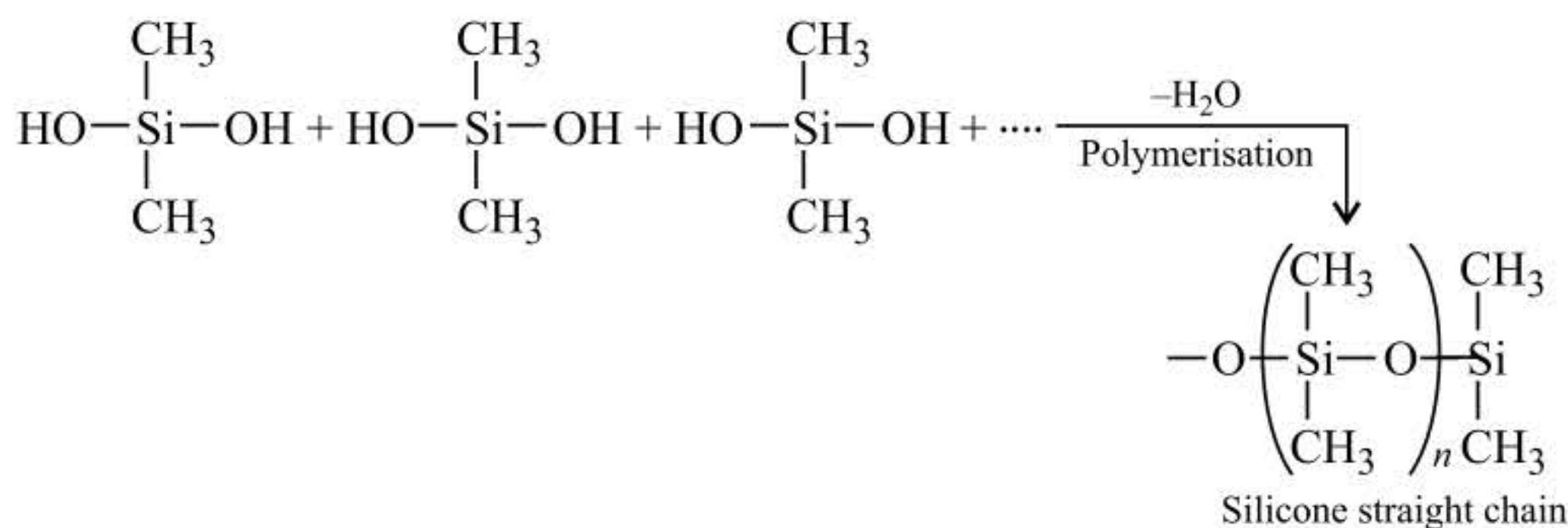
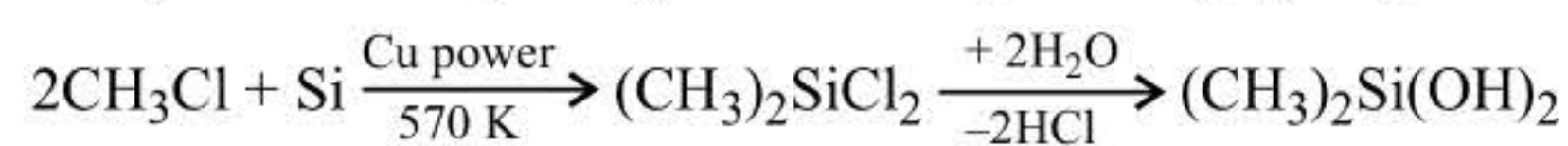
- Quartz is extensively used as a piezoelectric material.
- It has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications.
- Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts.
- Kieselguhr,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

Silicones



where R = alkyl or phenyl group

- Synthetic organosilicon polymers containing repeated R₂SiO units held by Si—O—Si linkage.
- They are water repelling due to non-polar alkyl groups.



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.

Different Types of Silicates

1. **Orthosilicates :** Basic unit : SiO₄⁴⁻, e.g., Zircon—ZrSiO₄, Forsterite—Mg₂SiO₄
2. **Pyrosilicates or islands :** Basic unit : Si₂O₇⁶⁻, e.g., Thortveitite—Sc₂Si₂O₇, Hemimorphite—Zn₃(Si₂O₇)·Zn(OH)₂·H₂O
3. **Cyclic or ring silicates :** Basic unit : (SiO₃²⁻)_n or (SiO₃)_n²ⁿ⁻, e.g., Wollastonite—Ca₃Si₃O₉, Beryl—Be₃Al₂Si₆O₁₈
4. **Chain silicates :** Basic unit : (SiO₃)_n²ⁿ⁻ or (Si₄O₁₁)_n⁶ⁿ⁻, e.g., Spodumene—LiAl(SiO₃)₂, Diopside—CaMg(SiO₃)₂
5. **Sheet silicates (two-dimensional) :** Basic unit : (Si₂O₅)_n²ⁿ⁻ or (Si₂O₅²⁻)_n, e.g., Kaolin—Al₂(OH)₄(Si₂O₅), Talc—Mg(Si₂O₅)₂Mg(OH)₂
6. **Three-dimensional silicates :** These silicates involve all four oxygen atoms in sharing with adjacent SiO₄⁴⁻ tetrahedra, e.g., Zeolites, Quartz, Feldspar, Ultramarines, etc.