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**Section: Senior**

**Name of the student:**

**Group-14**

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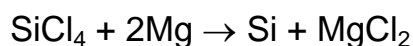
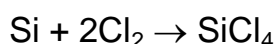
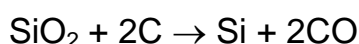
**I.D.No:**

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**Isolation/Extraction**

**Silicon**

- ❖ Si is extracted from silica by carbon reduction. It is purified by converting it to  $\text{SiCl}_4$  followed by reduction with Mg.



- ❖ Ultra pure Si is made by zone refining.
- ❖ Semiconductor quality Si can also be made by sodium reduction of  $\text{Na}_2[\text{SiF}_6]$ , which is a by-product from making phosphate fertilizers from fluoroapatite.

**STRUCTURE AND ALLOTROPY OF THE ELEMENTS:**

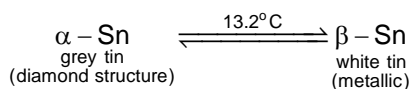
**Carbon**

- ❖ Diamond has a cubic unit cell.
- ❖ Graphite is composed of flat two-dimensional sheets of carbon atoms.
  - In  $\alpha$ -graphite, the layers are arranged in the sequence ABAB... with the third layer exactly above the first layer.
  - In  $\beta$ -graphite, the order of layers is ABCABC...
  - Heating turns  $\beta$  into  $\alpha$ , and grinding turns  $\alpha$  into  $\beta$ .
  - In both forms the C – C bond lengths within a sheet are 1.41 Å (similar to the C – C distance of 1.40 Å in benzene). The distance between layers is 3.35 Å.
  - This interlayer distance is large – appreciably more than twice the covalent radius of carbon ( $2 \times 1.54 \text{ Å} = 3.08 \text{ Å}$ ). Thus bonding between layers is weak.
  - Graphite cleaves easily between the layers, which accounts for the remarkable softness of the crystals.
  - Graphite is used as a lubricant..

- In graphite, the fourth electron of carbon forms a  $\pi$  bond. The  $\pi$  electrons are delocalized over the whole sheet, and as they are mobile, graphite conducts electricity.
- Conduction can occur in a sheet, but not from one sheet to another.
- Graphite is thermodynamically more stable than diamond, and its free energy of formation is  $1.9 \text{ kJ mol}^{-1}$  lower at room temperature and ordinary pressure.
- ❖ Thermodynamically it is favourable for diamonds to turn into graphite. They do not normally do so because there is a high energy of activation for the process.
- ❖ Graphite can be converted to synthetic diamonds at  $1600^\circ\text{C}$  by a pressure of 50,000 – 60,000 atmospheres.
- ❖ Carbon also exists as fullerenes, the molecular forms of carbon.

### Other elements

- Silicon & Ge exist in diamond form.
- Tin has a diamond form called  $\alpha$ -Sn and a metallic form called  $\beta$ -Sn.



- Pb has only a metallic form. .
- Ge is unusual because the liquid expands when it forms the solid.

### PHYSICAL PROPERTIES:

#### Melting points:

- ❖ The melting point decrease on descending the group because the M – M bonds become weaker as the atoms increase in size.
- ❖ Sn and Pb are metallic, and have much lower melting points. MP of Sn < Pb.

#### Metallic and Non-metallic character:

- ❖ C & Si are non-metals, Ge has some metallic properties while Sn and Pb are metals.

#### Chemical Reactivity:

- ❖ The  $M^{II}$  oxidation state becomes increasingly stable on descending the group.
- ❖ Pb often appears more noble (unreactive) than expected from its standard electrode potential of  $-0.13$  volts.

The unreactiveness is partly due to a surface coating of oxide, and partly due to the high overpotential for the reduction of  $H^+$  to  $H_2$  at a Pb surface.

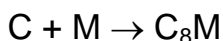
- ❖ C, Si and Ge are unaffected by water.
- ❖ Sn reacts with steam to give  $\text{SnO}_2$  and  $\text{H}_2$ . Pb is unaffected by water.
- ❖ Pb does not dissolve in dilute  $\text{H}_2\text{SO}_4$  because a surface coating of  $\text{PbSO}_4$  is formed.
- ❖ Graphite reacts with hot concentrated  $\text{HNO}_3$ , forming mellitic acid, and with a mixture of hot concentrated  $\text{HF}/\text{HNO}_3$ , forming graphite oxide (has no fixed formula, not to be confused with mellitic anhydride).
- ❖ Pb does not dissolve in concentrated  $\text{HCl}$  because a surface coating of  $\text{PbCl}_2$  is formed.
- ❖ Si reacts slowly with cold aqueous solutions of  $\text{NaOH}$ , and readily with hot solutions forming silicates.
- ❖ Sn and Pb are slowly attacked by cold alkali, and rapidly by hot alkali, giving stannates  $\text{Na}_2[\text{Sn}(\text{OH})_6]$  and plumbates  $\text{Na}_2[\text{Pb}(\text{OH})_6]$ . Thus Sn and Pb are amphoteric.
- ❖ Diamond does not react with the halogens, but graphite reacts with  $\text{F}_2$  at  $500^\circ\text{C}$ , forming intercalation compounds or graphite fluoride  $(\text{CF})_n$  and/or non-stoichiometric  $\text{CF}_n$ ;  $n = 0.7$  to  $0.98$ .

#### **Inert Pair Effect:**

- ❖  $\text{Ge}(+\text{II})$  is a strong reducing agent whereas  $\text{Ge}(+\text{IV})$  is stable.
- ❖  $\text{Sn}(+\text{II})$  exists as simple ions which are strongly reducing but  $\text{Sn}(+\text{IV})$  is covalent and stable.
- ❖  $\text{P}(+\text{II})$  is ionic, stable and more common than  $\text{Pb}(+\text{IV})$  which is oxidizing.
- ❖ The lower valencies are more ionic.

#### **GRAPHITE COMPOUNDS:**

- ❖ When graphite is heated to about  $300^\circ\text{C}$  with the vapours of the heavier Group 1 metals K, Rb and Cs, it absorbs metal, forming a bronze coloured compound  $\text{C}_8\text{M}$ .



- ❖ The crystal structure  $\text{C}_8\text{K}$  can conduct electricity, but the electrical resistance is appreciably lower than for  $\alpha$ -graphite, i.e.  $\text{C}_8\text{M}$  conducts better than graphite.
  - Graphite is diamagnetic, and  $\text{C}_8\text{K}$  is paramagnetic.
  - The presence of the invading species forces the graphite sheets apart from their usual distance of  $3.35 \text{ \AA}$  upto a distance as great as  $10 \text{ \AA}$ .

#### **CARBIDES:**

##### **Salt-like or ionic carbides:**

- ❖ Methanide:  $\text{Al}_4\text{C}_3$ ,  $\text{Be}_2\text{C}$ ; these compounds give methane on hydrolysis

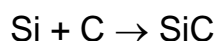
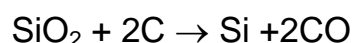
- ❖ Ethynides: They give ethyne on hydrolysis. Eg.  $\text{CaC}_2$ ,  $\text{SrC}_2$ ,  $\text{BaC}_2$ , Group 1 ( $\text{M}_2\text{C}_2$ )
- ❖ Propynide:  $\text{Mg}_2\text{C}_3$  gives propyne on hydrolysis

### **Interstitial/Metallic carbides:**

- ❖ These are formed mostly by transition elements, and some of the lanthanides and actinides.
- ❖ The Cr, Mn, Fe, Co and Ni groups form a large number of carbides with a wide range of stoichiometries. Carbon occupies voids without disturbing the structure of metal lattice.
  - They are harder than the metals.
  - They are infusible or have high melting points.
  - They conduct electricity by metallic conduction.
  - They have metallic luster.
  - They are quite unreactive and are unaffected by water.

### **Covalent carbides:**

- ❖ SiC and  $\text{B}_4\text{C}$  are the most important.
- ❖ Silicon carbide is hard (9 – 9.5 on Mohs' scale) infusible and chemically inert.
- ❖ It is widely used as an abrasive called **carborundum**.

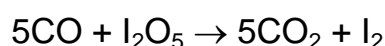
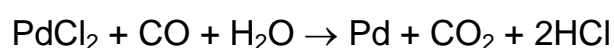


- ❖ SiC is very unreactive. It is unaffected by acids (except  $\text{H}_3\text{PO}_4$ ), but it does react with NaOH and air (to give  $\text{Na}_2\text{SiO}_3$  &  $\text{CO}_2$ ), and with  $\text{Cl}_2$  at  $100^\circ\text{C}$  (to give  $\text{SiCl}_4$  + C).
- ❖ Boron carbide is even harder than silicon carbide and is used both as an abrasive and as a shield from radiation.

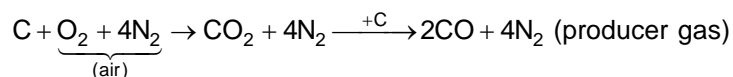
### **OXYGEN COMPOUNDS:**

#### **Carbon Monoxide CO:**

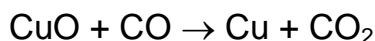
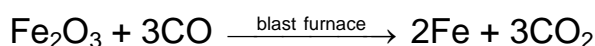
- ❖ Prepared by the dehydration of formic acid.
- ❖ CO reduces an aqueous  $\text{PdCl}_2$  solution to metallic Pd, and when passed through a solution of  $\text{I}_2\text{O}_5$  it liberates  $\text{I}_2$ , i.e., it reduces  $\text{I}_2\text{O}_5$  to  $\text{I}_2$ .
- ❖ The latter reaction is used to estimate CO quantitatively.
- ❖ The  $\text{I}_2$  is titrated with  $\text{Na}_2\text{S}_2\text{O}_3$



- ❖ *Water gas*: an equimolar mixture of CO and H<sub>2</sub>.
- ❖ *Producer gas* : a mixture of CO and N<sub>2</sub>
- ❖ *Coal gas* : a mixture of CO, H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>. This was the 'town gas'.
- ❖ Water gas is made by blowing steam through red or white hot coke.
- ❖  $\text{C} + \text{H}_2\text{O} \xrightarrow{\text{red heat}} \text{CO} + \text{H}_2$  (water gas)       $\Delta H^\circ = +131 \text{ kJ mol}^{-1}$   
 $\Delta S^\circ = +134 \text{ kJ mol}^{-1}$
- ❖ Water gas has a high calorific value, because both CO and H<sub>2</sub> burn and evolve heat.
- ❖ Producer gas is made by blowing air through red hot coke.



- ❖ The overall reaction is exothermic.



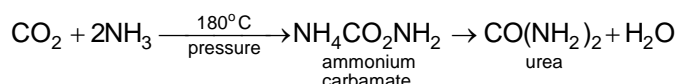
- ❖ In the Mond process (now obsolete) for purifying nickel, nickel carbonyl Ni(CO)<sub>4</sub> was made from Ni and CO at 50°C.
  - Ni(CO)<sub>4</sub> is a gas and can be separated from other metals and impurities.
  - The Ni(CO)<sub>4</sub> gas was then decomposed at 230°C.

### **CO as a Ligand:**

- ❖ The carbon-metal bond in carbonyls may be represented as the donation of an electron pair from carbon to the metal  $\text{M} \leftarrow \text{C} \equiv \text{O}$ .
  - This original  $\sigma$  bond is weak.
  - A stronger second bond is formed by back bonding, sometimes called dative  $\pi$  bonding.
  - This arises from sideways overlap of a full  $d_{xy}$  orbital on the metal with the empty antibonding  $\pi^* 2p_y$  orbital of the carbon, thus forming a  $\pi \text{ M} \rightarrow \text{C}$  bond.
  - The total bonding is thus  $\text{M} = \text{C} = \text{O}$ .
  - *The filling, or partial filling, of the antibonding orbital on C reduces the bond order of the C > O bond from the triple bond in CO towards a double bond.*
  - This is shown by the increase in C – O bond length from 1.128 Å in CO to about 1.15 Å in many carbonyls.
  - The drift of  $\pi$  electron density from M to C makes the ligand more negative, which in turn enhances its  $\sigma$  donating power.

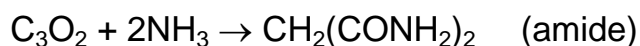
- CO forms weak bonds to Lewis acids such as  $\text{BF}_3$  as only  $\sigma$  bonding is involved while it forms strong bonds to transition metal where both  $\sigma$  and  $\pi$  bonding can occur.
- CO may stabilize metal clusters by the C forming a multi-centre bond with three metal atoms, and the  $\pi^*$  orbitals in CO may be involved in bonding to other metal atoms. Eg.  $\text{Fe}_2(\text{CO})_9$ .

## **CO<sub>2</sub>:**



## **Carbon suboxides:**

- ❖ Carbon suboxide  $\text{C}_3\text{O}_2$  is a four-smelling gas, boiling point  $6^\circ\text{C}$ . It is made by dehydrating malonic acid with  $\text{P}_4\text{O}_{10}$ .



- ❖ The only other stable suboxide is  $\text{C}_{19}\text{O}_9$ . This is a white solid, and is the anhydride of mellitic acid  $\text{C}_6(\text{COOH})_6$ .

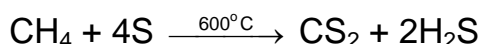
## **CARBONATES:**

- ❖ The  $\text{CO}_4^{4-}$  ion does not exist, even though  $\text{SiO}_4^{4-}$  does. This is probably because C is too small, and the situation is analogous to the formation of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  in Group 15.
- ❖  $\text{Ag}^+$  salts are typically white,  $\text{Ag}_2\text{CO}_3$  is yellow due to the strong polarizing effect of  $\text{Ag}^+$
- ❖  $(\text{NH}_4)_2\text{CO}_3$  and Group 1 carbonates are readily soluble in water, except  $\text{Li}_2\text{CO}_3$  which is only slightly soluble.
- ❖  $\text{Ti}_2\text{CO}_3$  is moderately soluble, but the other group 13 carbonates are sparingly soluble or insoluble.
- ❖ Carbonates all react with acids, liberating  $\text{CO}_2$ .
- ❖ Group 1 carbonates are stable to heat, and melt without decomposing.
- ❖ Group 2 carbonates all decompose if heated sufficiently strongly.
  - Their stability increases as the size of the metal ion increases.
- ❖ Most other carbonates decompose easily.
- ❖ The only solid bicarbonates known are those of the group 1 metals and of  $\text{NH}_4^+$ .

- These are colourless solids, and are somewhat less soluble than the corresponding carbonates.
- They decompose easily on heating.
- The solid structures of these contain polymeric chains of  $\text{HCO}_3^-$  groups hydrogen bonded together.

### **SULPHIDES:**

- ❖ Carbon disulphide  $\text{CS}_2$  has a very low flash point ( $30^\circ\text{C}$ ) and it ignites spontaneously at  $100^\circ\text{C}$ .

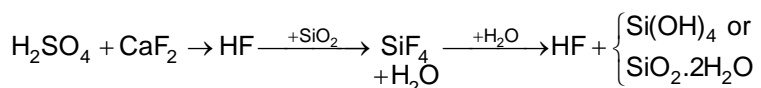


- ❖ It is used in the manufacture of viscose rayon (artificial silk) and cellophane.
- ❖ Smaller amounts are used as a solvent for S in the cold vulcanization of rubber.
- ❖  $\text{CS}_2$  forms complexes more readily than  $\text{CO}_2$ .
- ❖ The  $\text{CS}_2$  acts as a bidentate ligand with one C atom and one S atom bonded to the metal, and the  $\text{CS}_2$  molecule is bent.

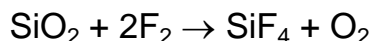
### **OXIDES OF SILICON:**

- ❖  $\text{SiO}_2 + \text{Si} \rightarrow 2\text{SiO}$  (at high temperatures)
- ❖ Silicon dioxide  $\text{SiO}_2$  is commonly called silica, and it is widely found as sand and quartz.
- ❖  $\text{SiO}_2$  forms an infinite three-dimensional structure, and  $\text{SiO}_2$  is a high melting solid.
- ❖  $\text{SiO}_2$  exists in at least 12 different forms.
- ❖ The main ones are quartz, tridymite and cristobalite.
- ❖  $\alpha$ -Quartz is by far the most common, and is a major constituent of granite and sandstone.
- ❖  $\alpha$ -Quartz is the most stable form at room temperature and in this the tetrahedral form helical chains. These are interlinked. Since the helix may be left or right handed, they cannot be superimposed, so it exists as d and l optical isomers.
- ❖ Tridymite has wurtzite structure and cristobalite has zinc blende structure.
- ❖ Silica in any form is unreactive. However, it does react with HF, forming silicon tetrafluoride  $\text{SiF}_4$ .

This reaction is used in qualitative analysis to detect silicates.



- ❖  $\text{SiO}_2$  is an acidic oxide: it dissolves slowly in aqueous alkali, and more rapidly in fused alkalis  $\text{MOH}$  or fused carbonates  $\text{M}_2\text{CO}_3$ , forming silicates. This reaction accounts for glass stoppers sticking in reagent bottles containing  $\text{NaOH}$ .
- ❖ Of the halogens, only fluoride attacks  $\text{SiO}_2$ .



- ❖ Silica gel is amorphous and very porous. It is obtained by dehydrating silicic acid, and contains about 4% water.

It is widely used as a drying agent, a catalyst, and in chromatography.

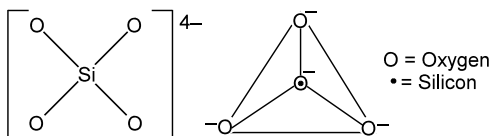
## SILICATES:

### Soluble silicates:

- ❖  $\text{Na}_2\text{CO}_3 \xrightarrow{1400^\circ\text{C}} \text{CO}_2 + \text{Na}_2\text{O} \xrightarrow{+\text{SiO}_2} \text{Na}_4\text{SiO}_4, (\text{Na}_2\text{SiO}_3)_n$  and others
  - The product is called water glass.
  - It is dissolved in hot water under pressure, and is filtered from any insoluble material.
- Nesosilicates (lone tetrahedron) -  $[\text{SiO}_4]^{4-}$ , e.g. olivine.
- Sorosilicates (double tetrahedra) -  $[\text{Si}_2\text{O}_7]^{6-}$ , e.g. epidote,
- Cyclosilicates (rings) -  $[\text{Si}_n\text{O}_{3n}]^{2n-}$ , e.g. tourmaline group.
- Inosilicates (single chain) -  $[\text{Si}_n\text{O}_{3n}]^{2n-}$ , e.g. pyroxene group.
- Inosilicates(double chain) -  $[\text{Si}_{4n}\text{O}_{11n}]^{6n-}$ , e.g. amphibole group.
- Phyllosilicates (sheets) -  $[\text{Si}_{2n}\text{O}_{5n}]^{2n-}$ , e.g. micas and clays.
- Tectosilicates (3D framework) -  $[\text{Al}_x\text{Si}_y\text{O}_{2(x+y)}]^{x-}$ , e.g. quartz, feldspars, zeolites.

### Ortho silicates (simple silicates, neso-silicates):

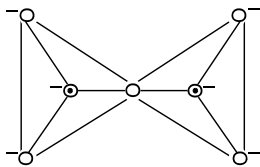
- ❖ A wide variety of minerals contains discrete  $(\text{SiO}_4)^{4-}$  tetrahedral, that is they share no corners.
- ❖ Eg. willemite  $\text{Zn}_2[\text{SiO}_4]$ , phenacite  $\text{Be}_2[\text{SiO}_4]$ , forsterite  $\text{Mg}_2[\text{SiO}_4]$ , Zircon  $\text{ZrSiO}_4$



### Pyrosilicates (soro-silicates, disilicates):

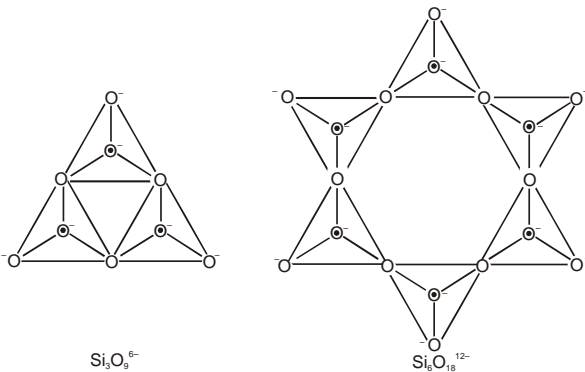
- ❖ Two tetrahedral units are joined by sharing the O at one corner, thus giving the unit  $(\text{Si}_2\text{O}_7)^{6-}$ . Eg. thortveitite  $\text{Sc}_2[\text{Si}_2\text{O}_7]$ .





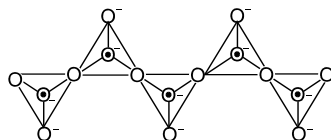
### Cyclic silicates:

- ❖ If two oxygen atoms per tetrahedron are shared, ring structures may be formed of general formula  $(\text{SiO}_3)_n^{2n-}$ .
- ❖ Rings containing three, four, six and eight tetrahedral units are known, but those with three and six are the most common.
- ❖ The cyclic ion  $\text{Si}_3\text{O}_9^{6-}$  occurs in benitoite  $\text{BaTi}[\text{Si}_3\text{O}_9]$ .
- ❖ The  $\text{Si}_6\text{O}_{18}^{12-}$  unit occurs in beryl  $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$
- ❖ Emerald has the same formula as beryl except that it contains 1–2% Cr which gives it a strong green colour.



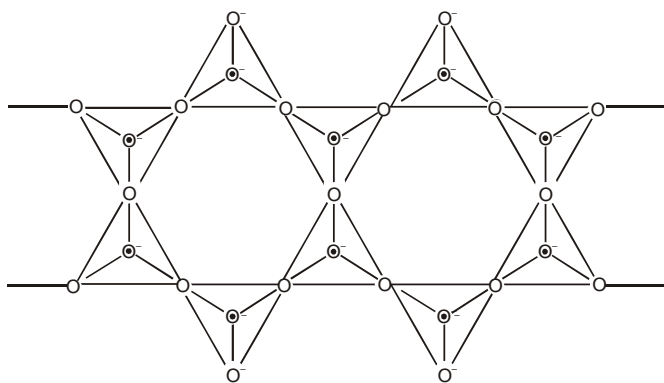
### Chain silicates:

- ❖ **Single chain silicates** or pyroxenes are formed by the sharing of the O atoms on two corners of each tetrahedron with other tetrahedral. This gives the formula  $(\text{SiO}_3)_n^{2n-}$ .  
Eg: spodumene  $\text{LiAl}[(\text{SiO}_3)_2]$



- ❖ **Double chain silicate**,  $(\text{Si}_2\text{O}_5)_n^{2n-}$ ,  $(\text{Si}_4\text{O}_{11})_n^{6n-}$ ,  $(\text{Si}_6\text{O}_{17})_n^{10-}$  and others.

The most numerous and best known amphiboles are the asbestos minerals. These are based on the structural unit  $(\text{Si}_4\text{O}_{11})_n^{6n-}$ .



### Sheet silicates:

- ❖ When  $\text{SiO}_4$  units share three corners the structure formed is an infinite two dimensional sheet of empirical formula  $(\text{Si}_2\text{O}_5)_n^{2n-}$ .

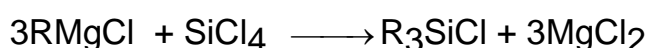
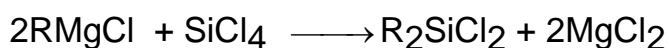
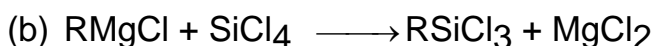
### Three-dimensional silicates:

- ❖ Sharing all four corners of a  $\text{SiO}_4$  tetrahedron results in a three-dimensional lattice of formula  $\text{SiO}_2$  (quartz, tridymite, cristobalite etc.)
- ❖ Zeolites are often used as ion-exchange materials, and as molecular sieves. Natrolite  $\text{Na}_2[\text{Al}_2\text{Si}_3\text{O}_{10}]\cdot 2\text{H}_2\text{O}$  is a natural ion exchanger.
- ❖ The mineral lapis lazuli is a splendid blue colour and was highly prized as a pigment for oil paintings. It contains ultramarine  $\text{Na}_8[(\text{AlSiO}_4)_6]\text{S}_2$ , in which the colour is produced by the polysulphide ion.

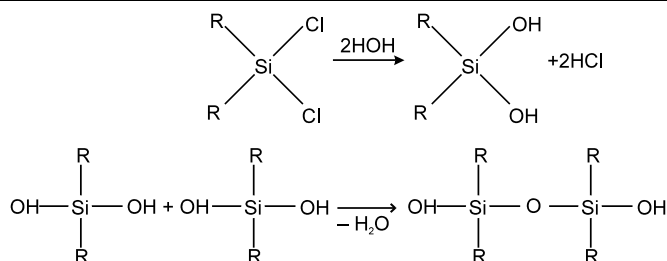
### SILICONES :

Silicones are synthetic organosilicon compounds having repeated  $\text{R}_2\text{SiO}$  units held by  $\text{Si} - \text{O} - \text{Si}$  linkages. These compounds have the general formula  $(\text{R}_2\text{SiO})_n$  where R = alkyl or aryl group.

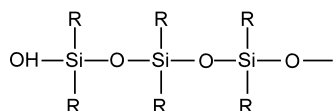
The silicones are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation. The alkyl or aryl substituted chlorosilanes are prepared by the following reactions.



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.

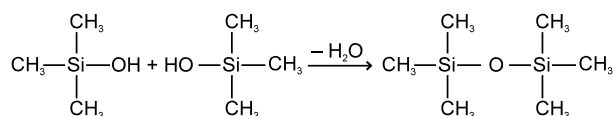
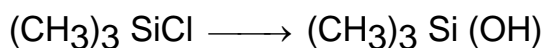


The polymer chain depicted above is terminated by incorporating a small quantity of the monochlorosilane derivative into the hydrolysis mixture.

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

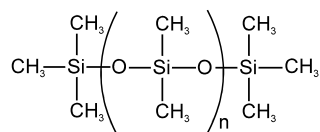
(i)  $\text{R}_3\text{SiCl}$  (ii)  $\text{R}_2\text{SiCl}_2$  (iii)  $\text{RSiCl}_3$

- Silicones from the hydrolysis of  $(\text{CH}_3)_3\text{SiCl}$



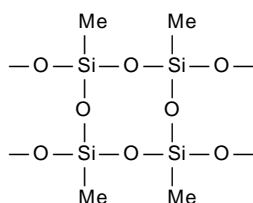
- Silicones from the hydrolysis of a mixture of  $(\text{CH}_3)_3\text{SiCl}$  &  $(\text{CH}_3)_2\text{SiCl}_2$

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  $\text{CH}_3\text{SiCl}_3$  undergoes hydrolysis, a complex cross-linked polymer is obtained as chain can grow in three places as



- Silicones are inert and thermally stable due to strong Si-O and C-Si bonds present in them.

They are water repellent due to the large hydrocarbon content.

- Silicones find a variety of applications because of their chemical inertness, water repelling nature, heat resistance, good electrical insulation property, biocompatibility and antifoaming properties.