SILICON AND ITS COMPOUNDS

Properties & Compounds of Silicon

Silicones,Tetrachlorosilicon ($SiCl_4$)

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.

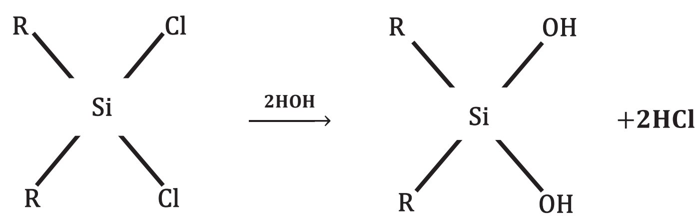
(a) $RCl + Si \xrightarrow[300°C]{Cu} R_3SiCl + R_2SiCl_2 + RSiCl_3$

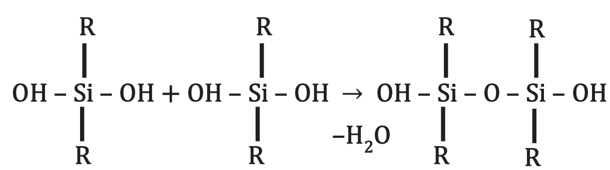
(b) $RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$

$2RMgCl + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$

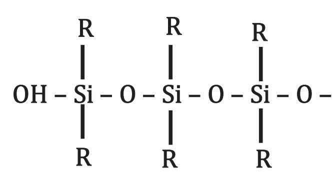
$3RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$

Following fractional distillation, the silane derivatives undergo hydrolysis, and the resulting 'hydroxides' promptly combine through intermolecular removal of water. The ultimate product is determined by the initial quantity of hydroxyl groups linked to the silicon atom.





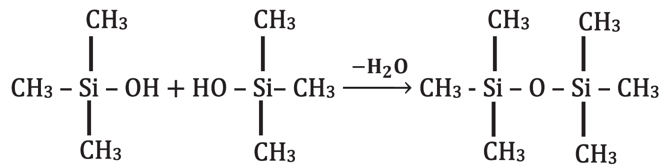
In this manner several molecules may combine to form a long chain polymer who's both the ends will be occupied by –OH groups. Such compounds are generally represented from the following formula.



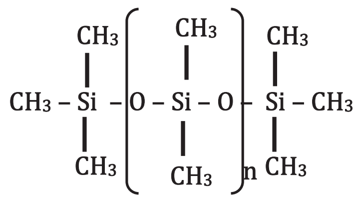
The polymer chain depicted above is terminated by incorporating a small quantity of the Mon chlorosilane derivative into the hydrolysis mixture.

- Silicones can be prepared from the following types of compounds only.
  - (i) R_3SiCl
  - (ii) R_2SiCl_2
  - (iii) $RSiCl_3$
- Silicones from the hydrolysis of $(CH_3)_3$ Sic

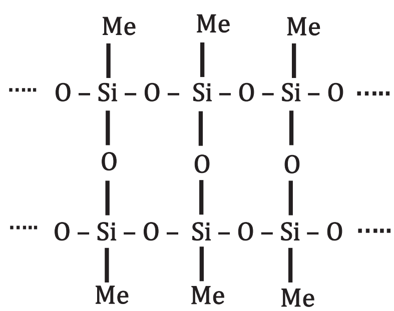
$$(CH_3)_3SiCl \xrightarrow{H_2O} (CH_3)_3Si(OH)$$



- Silicones from the hydrolysis of a mixture of $(CH_3)_3$ SiCl & $(CH_3)_2$ $SiCl_2$
  The dichlorvos 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-chlor derivative.



- Silicones from the hydrolysis of trichloro derivative.
  When a compound like CH_3SiCl_3 undergoes hydrolysis, a complex cross-linked polymer is obtained as chain can grow in three places as.



- The hydrocarbon layer along the silicon-oxygen chain makes silicones water-repellent.
- Silicones find a variety of applications because of their chemical inertness, water repelling nature, heat resistance and good electrical insulation property.

Silicones have the capability to generate products with attributes resembling oils, rubber, and resins. Silicone varnishes, in particular, stand out as superb insulators with exceptional heat resistance. Their use in insulating wiring has allowed motors to withstand overloads that would have ignited previously employed insulation materials. Silicone fluids find application in aircraft hydraulic systems due to their thermal stability and minimal viscosity change with temperature fluctuations. Silicone rubbers are a preferred alternative to conventional rubber, as they maintain their elasticity even at significantly lower temperatures.

SiH_4 (monosilane)

- small scale preparation:

$$SiO_2 + LiAlH_4 \xrightarrow{160^{\circ}C} SiH_4$$

- Hydrolysis of Magnesium silicide

$$Mg_2Si + H_2O \longrightarrow \text{mixture of silanes}$$

- Reduction of chlorosilanes by $LiAlH_4$ to produce silane
- Photolysis of SiH_4–H_2 mixture can make higher silanes
- Among silanes only SiH4 & Si_2H_6 are indefinitely stable at 25°C.

Silicates

Compounds formed between silicon and oxygen are termed silicates, and they typically include other metals within their structures.

(i) The Si-O bond can be viewed as approximately 50% ionic and 50% covalent due to the electronegativity difference of about 1.7 between O and Si.

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

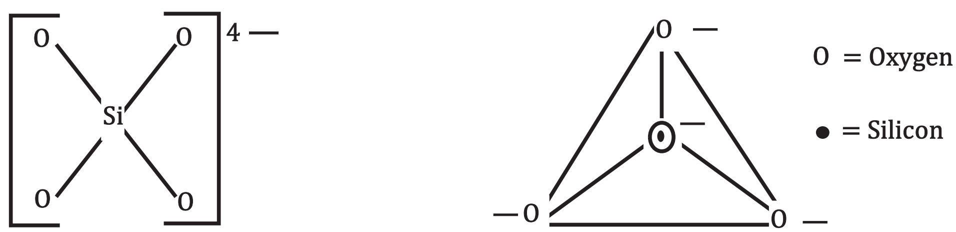
It suggests that the coordination number of silicon must be 4 and from VBT point of view we can say that Si is sp^3 hybridized. Therefore, silicate structures must be based upon SiO_4^{4-} tetrahedral units.

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

Classification of Silicates

(A) Orthosilicates

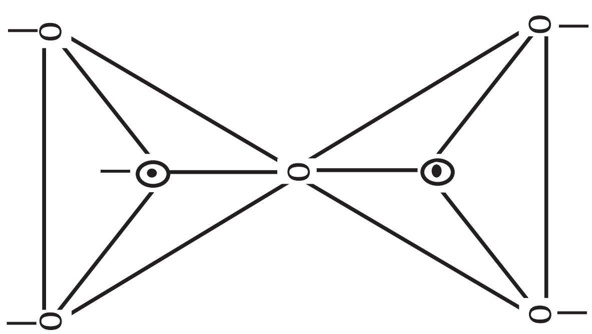
These contain discrete $[SiO_4]^{4-}$ units i.e., there is no sharing of corners with one another as shown is figure.



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

(B) Pyro silicate

In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving $[Si_2O_7]^{6-}$ units.

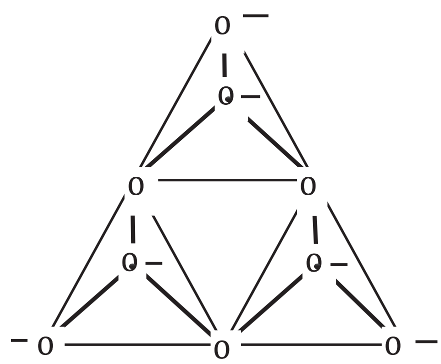


e.g. Thorteveitite ($Sc_2Si_2O_7$), Hemimorphite ($Zn_3(Si_2O_7)\ Zn(OH)_2H_2O$)

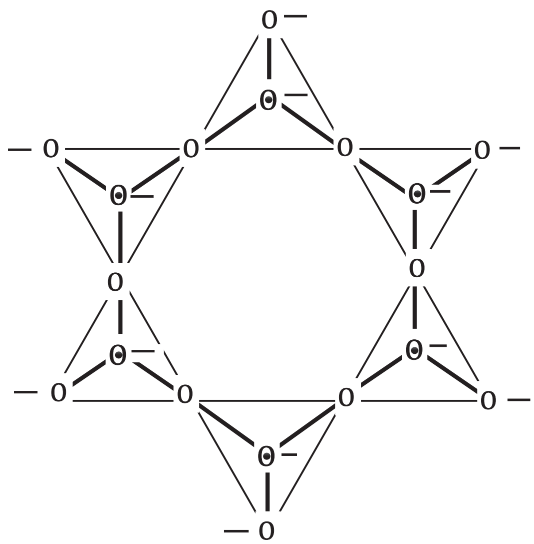
➢ (–) charge will be present on the oxygen atoms which is bonded with one Si atom.

(C) Cyclic silicates:

If two oxygen atoms per tetrahedron are shared to form closed rings such that the structure with general formula $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ is obtained, the silicates containing these anions are called cyclic silicates. $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ anions are the typical examples of cyclic silicates.



$Si_3O_9^{6-}$

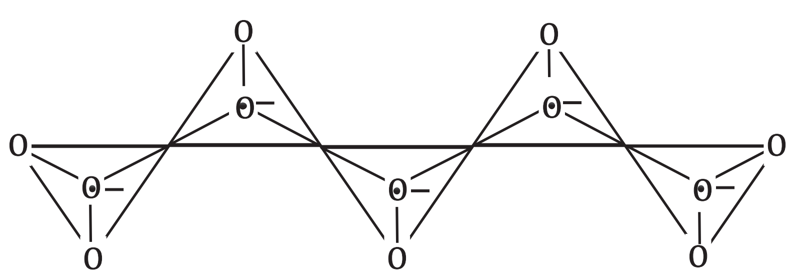


$Si_6O_{18}^{12-}$

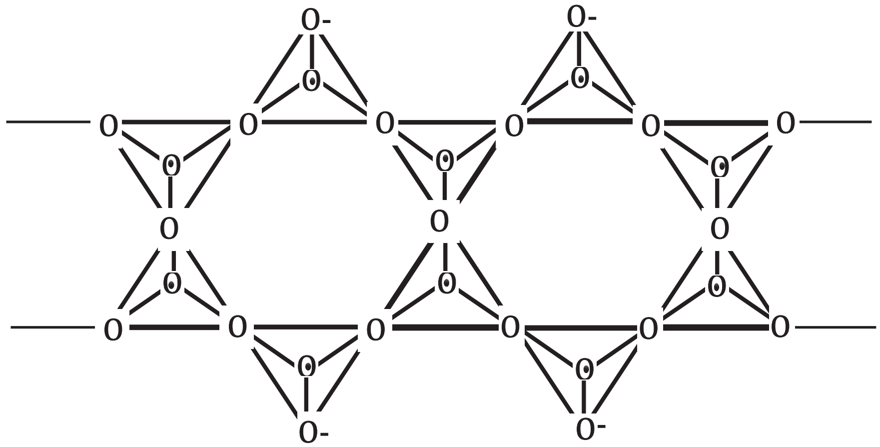
(D) **Chain Silicates**

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. $(SiO_3)_n^{2n-}$



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 $(Si_4O_{11})_n^{6n}$ e.g., Synthetic silicates (Li_2SiO_3, Na_2SiO_3), Spodumene ($LiAl(SiO_3)_2$), Enstatite ($MgSiO_3$), Diopside ($CaMg(SiO_3)_2$), Tremolite ($Ca_2Mg_5(Si_4O_{11})_2(OH)_2$), etc.

(E) Two-Dimensional Sheet Silicates

In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedra's. Such sharing forms two-dimension sheet structure with general formula $(Si_2O_5)_n^{2n-}$ e.g. Talc ($Mg(Si_2O_5)_2\,Mg(OH)_2$, Kaolin $Al_2(OH)_4\,(Si_2O_5)$

(F) Three Dimensional 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.

Organosilicon Compounds and the Silicones

(1) Organosilicon Compounds

Organosilicon compounds, classified as organometallic compounds, are characterized by the presence of silicon-carbon bonds. Consequently, these compounds fall under the category of organic compounds. Additionally, they exhibit typical traits associated with organic compounds, including flammability, hydrophobicity, and a colorless appearance. Notably, organosilicon compounds display stability under normal atmospheric conditions.

$$(CH_3)_2SiCl_2 + CH_3MgCl \rightarrow (CH_3)_3SiCl + MgCl_2$$

$$(CH_3)_3SiCl + CH_3MgCl \rightarrow (CH_3)_4Si + MgCl_2$$

$$CH_3SiCl_3 + CH_3MgCl \rightarrow (CH_3)_2SiCl_2 + MgCl_2$$

(2) Carborundum (SiC)

Preparation:

$$SiO_2 + 3C \xrightarrow[2000°C]{\text{electric furnace}} SiC + 2CO$$

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.

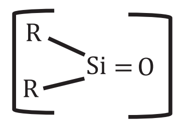
$$SiC + 2NaOH + 2O_2 \xrightarrow{\Delta} Na_2SiO_3 + CO_2 + H_2O \quad ; \quad SiC + 4Cl_2 \xrightarrow{\Delta} SiCl_4 + CCl_4$$

- 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.

(3) Silicones

Silicones belong to the category of organosilicon polymers and are characterized by the overall formula (R_2SiO), with R representing any organic group. A prominent example within this category is poly-dimethyl siloxane, which serves as an exemplary illustration of the essential characteristics of organic silicon compounds.

Contrary to the anticipated silicon compound



the hydrolysis of alkyl-substituted (-R) chlorosilanes leads to the creation of a lengthy chain polymer known as silicones. In silicones, carbon atoms are substituted by silicon, resulting in the presence of R_2SiO units.

The primary source of silicones is metallic silicon, initially obtained from silica sand. Commercially available silicones predominantly consist of methyl derivatives, with phenyl derivatives being less common. These silicone substances are known for their chemical inertness, heat resistance, water repellent properties, and effective insulation against electricity.