Silicones

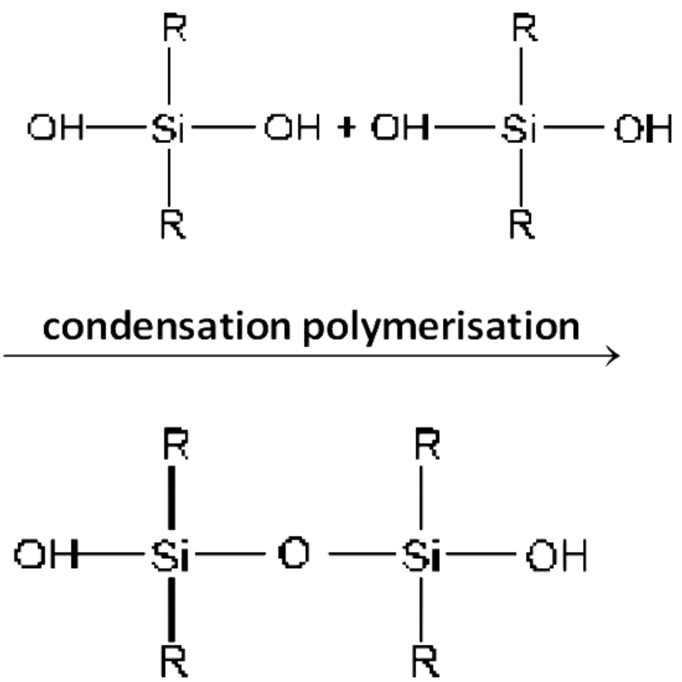
Silicones are synthetic organosilicon compounds having repeated -(-R_2SiO-)- units held by Si – O – Si linkages. These compounds have the general formula $(R_2SiO)n$ where R = alkyl or aryl group.

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.

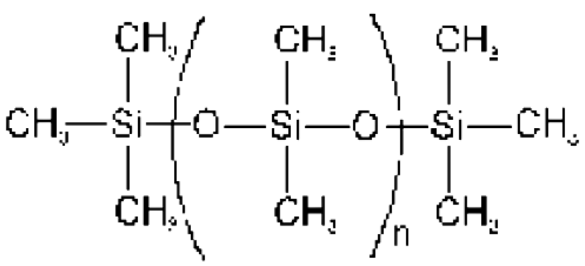
$$CH_3Cl + Si \xrightarrow{\text{Cu Powder(570K)}}$$

$$(CH_3)_2SiCl_2 \xrightarrow{+2H_2O\ \&\ -2HCl}$$

$$(CH_3)_2Si(OH)_2$$



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.



Property & Use:

Water repelling in nature, high thermal stability, chemical inert in nature, used as electrical insulator and water proofing fabric. Silicones are biocompatible so used in surgical and cosmetic plants.

Q. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are

[IIT-JEE Advanced, 2015]

A. CH_3SiCl_3 and $Si(CH_3)_4$

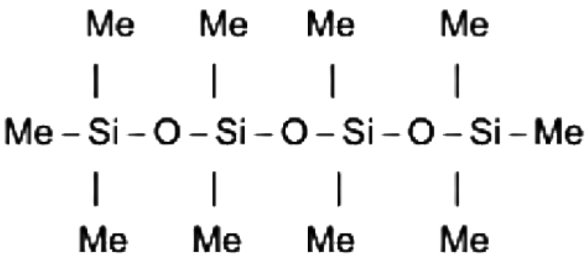
B. $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$

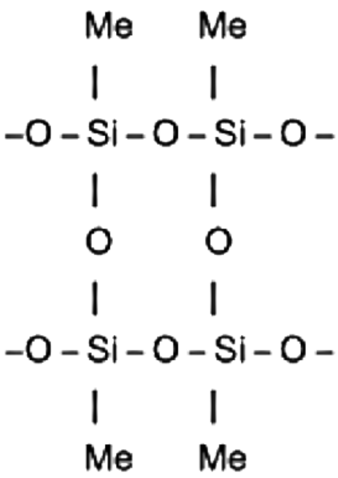
C. $(CH_3)_2$ $SiCl_2$ and CH_3SiCl_3

D. $SiCl_4$ and $(CH_3)_3$ $SiCl$

Q.

If we start with $MeSiCl_3$ as the starting material, silicones formed is:

(A) 

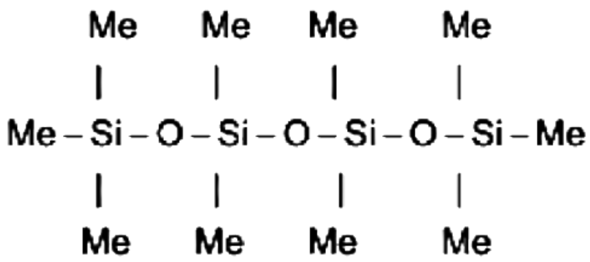
(B) 

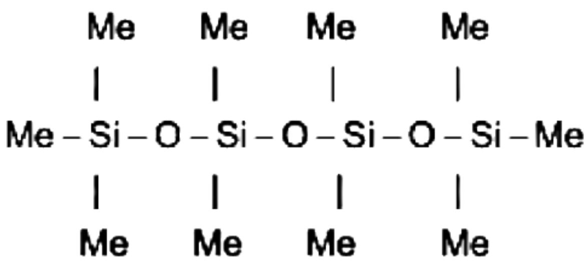
(C) Both of the above

(D) None of the above

Q.

If we mix Me_3SiCl with Me_2SiCl_2, we get silicones of the type:

(A) 

(B) 

(D) none of the above

(C) both of the above

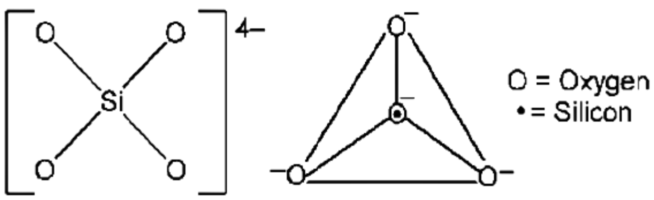
Silicates :

SiO_4^{-4} tetrahedral units may exist as discrete units or may polymerise into larger units by sharing corners.

Classification of Silicates

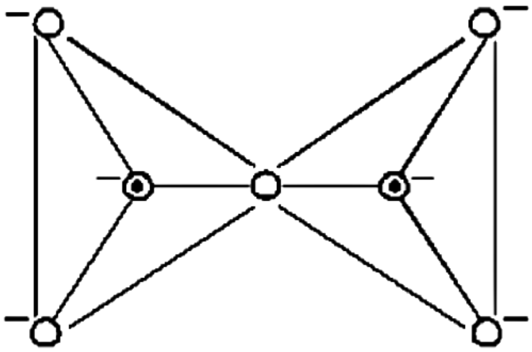
Orthosilicates (neso - silicates):

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



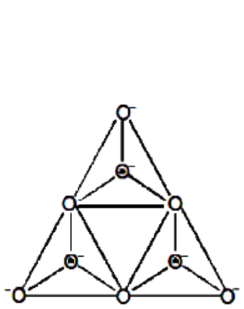
Pyrosilicate (soro-silicates, disilicates) :

In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving $[Si_2O7]^{6-}$ units.

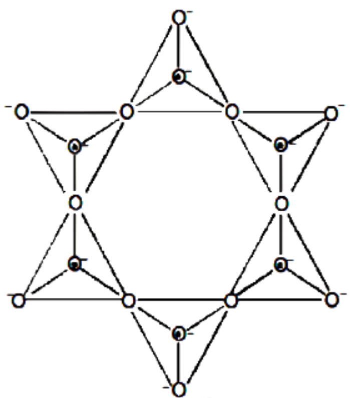


Cyclic silicates

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. Si3O96– and $Si_6O_{18}^{12-}$ anions are the typical examples of cyclic silicates.



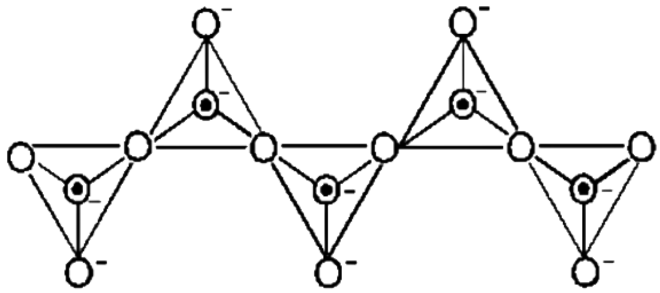
$Si_3O_9^{6-}$



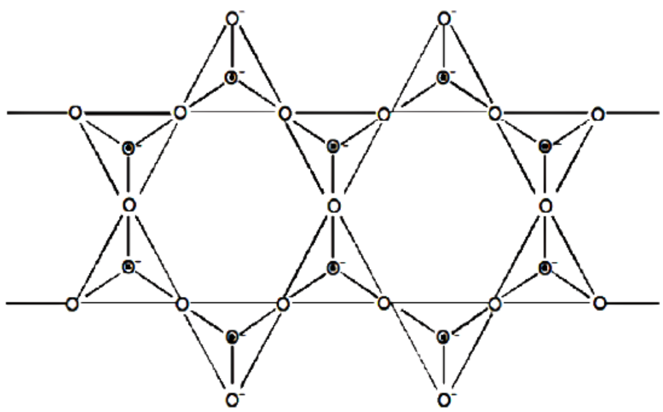
$Si_6O_{18}^{12-}$

Chain silicates

Chain silicates may be further classified into simple chain (pyroxenes) & double chain (amphiboles) 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. Two dimensional sheet silicates

(phylo-silicates):

In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedrals. Such sharing forms two dimension sheet structure with general formula $(Si_2O_5)_n^{2n-}$

e.g. mica, white asbestos

F. Three dimenstional sheet silicates :

These silicates involve all four oxygen atom in sharing with adjacent SiO_4^{4-} tetrahedral units.

e.g. Quartz, Tridymite, Crystobalite, Feldspar, Zeolite and Ultramarines.

Three – dimensional Sheets:

Sharing all 4 corners of SiO_4 unit. These contains no metal ions.

Replacing 1/4th of the Si^{4+} in SiO_2 with Al^{3+}, generally larger metal cations is used such as K^+, Na^+, Ca^{2+}, Ba^{2+}. Smaller cations such as Fe^{3+}, Cr^{3+}, Mn^{2+} is not used due to large cavities in lattice.

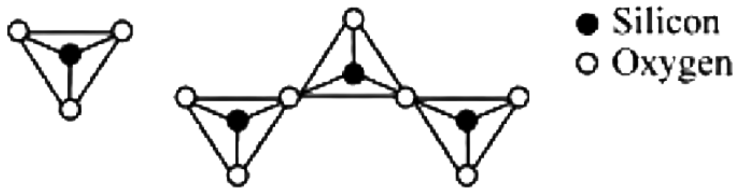
Replacements of ions mainly produce three type of mineral:

1. Feldsprs

2. Zeolites

3. Ultramarines

Q. The following pictures represent various silicate anions. Their formulae are respectively:



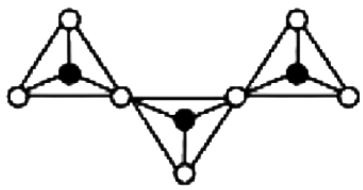
(A) SiO_3^{2-} $Si_3O_7^{2-}$

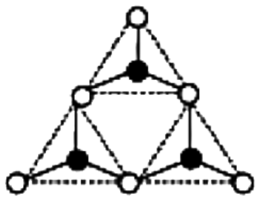
(B) SiO_4^{4-} $Si_3O_{10}^{8-}$

(C) SiO_4^{2-} $Si_3O_9^{2-}$

(D) SiO_3^{4-} $Si_3O_7^{8-}$

Q. $Si_3O_9^{6-}$ (having three tetrahedral) is represented as:

(A) 

(B) 

(C) both

(D) none

Q. By referring to Table 1, predict the structure of each of the following silicate minerals (double chains, sheets, networks, and so forth).

A. $Ca_3Fe_2(SiO_4)_3$

B. $Na_2ZrSi_4O_{10}$

C. $Ca_2ZnSi_2O_7$

D. $Mg_3Si_2O_5(OH)_4$