TDC Part I
Paper I, Group B
Inorganic Chemistry

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TOPIC:- Group 14 Silicates, Organometallic compounds, Complex formation

Silicates

Silicates are important rock forming minerals and comprise of tetrahedral SiO_4 units linked together by sharing corners and edges. Due to the great strength of the Si-O bond, these minerals are insoluble. The main structural principles of silicates have been determined by X- ray crystallography. The electro negativity difference between oxygen and silicon suggests that the bonds are 50% ionic and 50% covalent. The radius ratio Si^{4+}: O^{2-} is 0.29 suggesting that silicon adopts a coordination number of four and is sp^3 hybridized giving SiO_4^{4-} units. These may exist as discrete units or polymerize by sharing oxygen atoms. Some silicon atoms may be replaced by aluminium to give aluminosilicates.

Silicates are classified on the basis of the number of oxygen atoms shared per SiO_4^{4-} tetrahedron. The classification of silicates alongwith some important examples are shown in table 10 while some structures are depicted in Fig 17.

Table 10: Classification of Silicates

Type	**General Formula**	**Examples**	**Remarks**
Orthosilicates	$SiO_4{}^{4-}$	M_2 [SiO_4], M=Zn, Willemite M=Be, Phenacite M=Mg, Forsterite M[SiO_4] M=Zr, Zircon	No corners shared; Discrete tetrahedral units
Pyrosilicates	$Si_2O_7{}^{6-}$	$Se_2Si_2O_7$ Thortveitite	2 tetrahedra linked by one oxygen
Cyclic Silicates	$(SiO_3)_n{}^{2n-}$	$Ca_3[Si_3O_9]$ Wollastonite Ba, Ti [Si_3O_9] Benitonite Be_3Al_2 [Si_6O_{18}] Beryl	2 oxygen atoms per tetrahedron are shared
Chain Silicates a) pyroxene	$(SiO_3)_n{}^{2n-}$	Spodumene LiAl $(SiO_3)_2$ Enstatite Mg_2 $(SiO_3)_2$	2 oxygen atoms per tetrahedron shared – single chain structures
b) Amphibole	$(Si_4O_{11})_n^{6n-}$	Tremolite Ca_2Mg_5 $(Si_4O_{11})_2$ $(OH)_2$ Crocidolite $Na_2Fe_3^{11}Fe_2^{111}$ $(Si_4O_{11})_2$ $(OH)_2$ (Asbestos)	Some tetrahedra share 2 oxygens, some 3; double chain fibrous minerals
Sheet Silicates	$(Si_2O_5)_n^{2n-}$	Clay, White asbestos, Mica, Talc	3 oxygen atoms per tetrahedron shared minerals are soft & cleave into sheets
3 dimensional silicates	-	Feldspar, Zeolite, ultramarine	4 oxygen atoms per tetrahedron shared. Some Si atoms replaced by Al

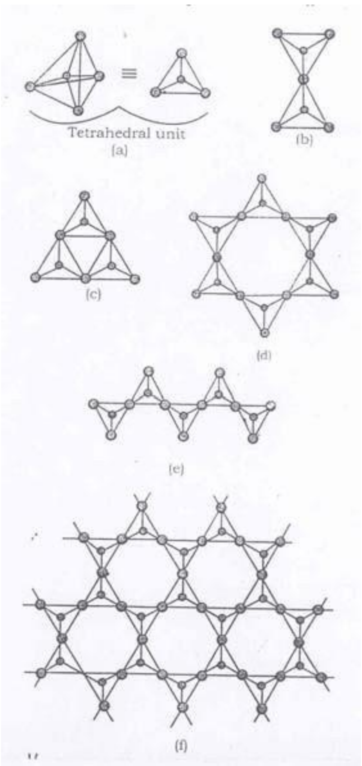


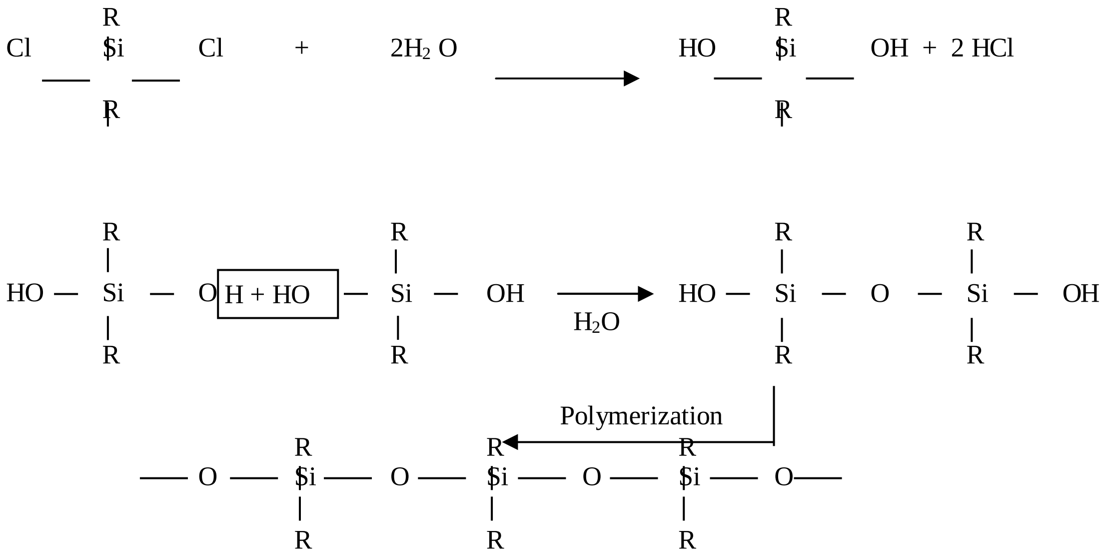
Fig.17: Some typical silicate structures (a) Orthosilicate SiO_4^{4-} (b) Pyrosilicate $Si_2O_7^{6-}$ (c-d) Cyclosilicates $(SiO_3)_n^{2n-}$ (e) Chain Silicate $(SiO_3)_n^{2n-}$ (f) Sheet Silicate $(Si_2O_5)_n^{2n-}$

The importance of silicates becomes apparent if we realize that asbestos, mica, zeolites, igneous rocks are all silicates. The cement, glass and ceramic industry are also based on silicates.

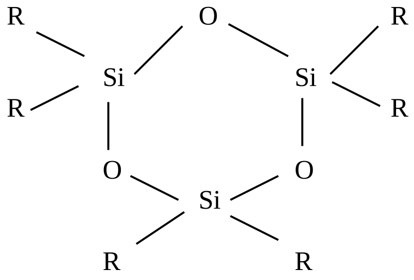
Organometallic compounds.

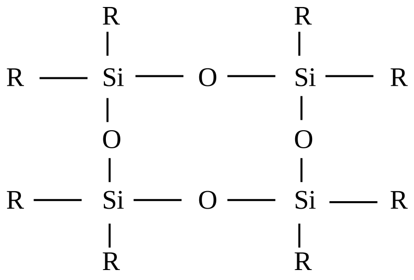
The elements have a fairly extensive organometallic chemistry. Due to inert pair effect the divalent state is more stable for the heavier members, however all organometallic compounds of tin and lead contain the element in the tetravalent state.

Alkyl silicon chlorides ($RSiCl_3$, R_2SiCl_2, R_3SiCl and SiR_4) are well – known. They are starting materials for an important class of organo silicon polymers referred to as silicones. Silicones contain long chains or rings of alternating silicon and oxygen atoms with alkyl or aryl groups attached to silicon. They are prepared by hydrolysis of alkyl substituted chlorosilanes or alkyl silicon chlorides.



The chain size can be limited by adding R_3SiCl. This hydrolyses to give R_3SiOH, which has only one active -OH group. It attaches itself to one side of the chain and since there is no functional – OH group on this side of the chain, the chain cannot grow at this end. Eventually the other end also gets blocked. Hydrolysis under controlled conditions gives cyclic polymers having three to six silicon atoms.





Cross- linked polymers are also known and are obtained when some $RSiCl_3$ is hydrolyzed alongwith R_2SiCl_2.

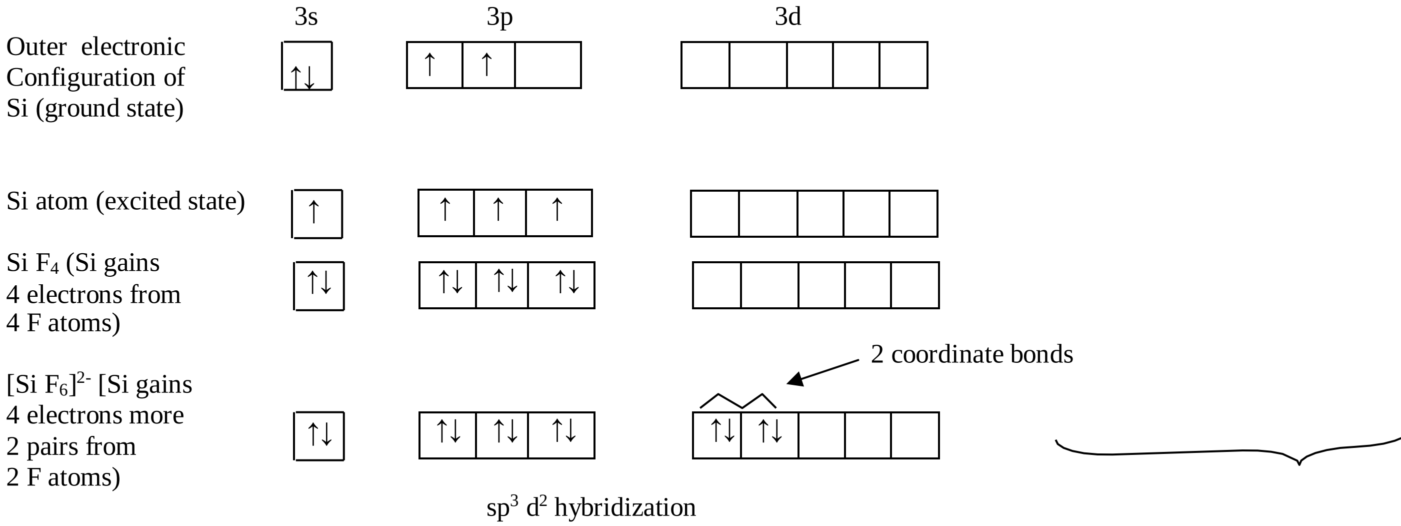
Silicones are thermally and chemically inert due to stable Si-O linkage and a strong Si-C bond. They have oxidative stability, resistance to low and high temperature, excellent water repellency, good dielectric properties, desirable anti-foam and non-stick properties and physiological inertness. They can be made in the form of fluids, greases, emulsions, elastomers and resins (depending on chain length and extent of cross- linkage). They are used as water repellents for treating masonry, buildings and fabrics Due to their anti- foam properties and non- toxicity they are used to reduce the froth in refining of cooking oil, fermentation processes, textile dyeing and sewage disposal. Other applications include their use as hydraulic fluids, light duty lubricants dielectric insulating material and non- stick coating material for utensils. Silicones are the most important inorganic polymers and their worldwide production is about 550,000tons.Over 100 different silicone products are commercially available. Another important organometallic compound is tetraethyl lead $Pb(Et)_4$. This was used as an “anti-knock” agent to increase the octane number of petrol. Its use has been banned now as burning “leaded fuel” releases large amounts of toxic lead salts. Organotin compounds (R_2SnX_2 and R_3SnX) are used to stabilize PVC plastics and as fungicides and pesticides.

Complex formation

Carbon has a maximum coordination number of four and can accommodate eight electrons in the valence shell. It cannot increase its coordination number and forms no complexes. The other members have vacant d orbitals and can increase their coordination number to six and form complexes like

$[SiF_6]^{2-}$, $[GeF_6]^{2-}$, $[GeF_4.(NMe_3)_2]$, $[SnCl_6]^{2-}$ and $[PbCl_6]^{2-}$.

VSEPR theory suggests an octahedral structure based on sp^3d^2 hybridization.



Internal л – bonding using d orbitals

Lateral overlaps of p orbitals give a p л-p л bond. This is common for carbon and we have already seen that a few compounds containing> Si = Si< are known. Under suitable conditions p and d orbitals undergo lateral overlap to give a p л-d л bond. The compounds trimethylamine $(CH_3)_3N$ and trisilylamine $(SiH_3)_3N$ have similar formulae but their shapes are completely different (fig 18). The former has a pyramidal structure based on sp^3 hybridization of nitrogen. The electronic structure of N in trimethylamine is