Sec-B Unit- V

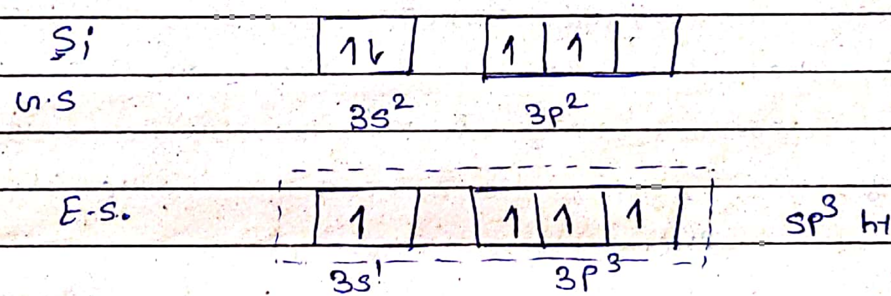
chemistry of Non-transition elements

a) Silicates :-

- Silicates are compounds of silicon & oxygen with various metals.
- Fusion of silica with metal oxides, hydroxides or carbonates leads to the formation of wide range of silicates
- The earth crust is very largly composed of silica & silicates which form the principal constituents of all rocks & sands.

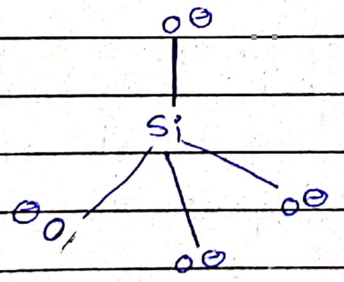
Basic unit of silicates :-

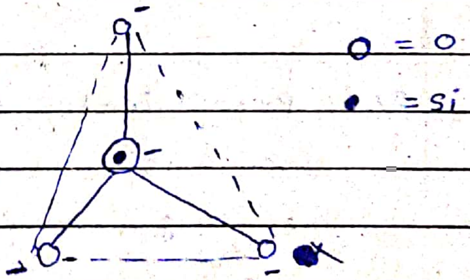
The basic unit in most silicates is SiO_4^{4-} tetrahedron. The SiO_4^{4-} unit is formed by sp^3 hybridisation of si



The sp^3 hybridised Si forms four bonds with oxygen atoms yielding SiO_4^{4-}

E.N.
O = 3.5
Si = 1.9
1.6
Si-O covelent





- In some cases, several $(SiO_4)^{4-}$ units are bridged together through oxygen atom of the unit
- The oxygen that forms bridge bet^n two SiO_4 unit is called bridging oxygen atom.
- The oxygen that does not form a bridge carries -ve charge.

There fore various metal cations such as $Li^+, K^+, Ca^{2+}, Al^{3+}$ are present in silicates. These serve to hold the solid together by ionic attraction.

⊙ classification of silicates :-

The way in which the $(SiO_4)^{4-}$ tetrahedral units are linked together provides a convenient classificatⁿ of silicates They are classified as.

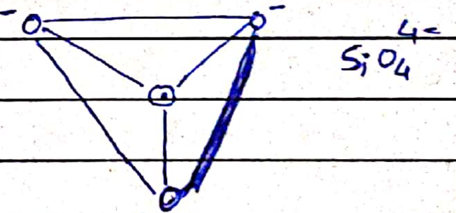
① orthosilicates
② pyro silicates
③ chain silicates
④ cyclic silicates
⑤ sheet silicates
⑥ Three dimensional silicates

1) Ortho silicates :

It contain discrete $(SiO_4)^{4-}$ units i.e. SiO_4 tetrahedre with no shared corners.

- They have general formula $M_2^{II}SiO_4$ or $M^{IV}SiO_4$ where M_2^{II} & M^{IV} are the metals with +2 & +4 oxidⁿ

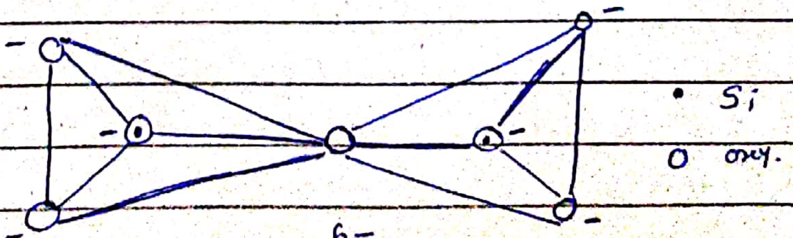
e.g. $ZrSiO_4$ = zircon, willemite (Zn_2SiO_4)
Phenacite (Be_2SiO_4)



SiO_4^{4-}

2) Pyrosilicates :-

It contain disilicate ion $(Si_2O_7)^{6-}$ as the basic unit. Two tetrahedral units are joined by the oxygen atom at one corner gives $(Si_2O_7)^{6-}$



$Si_2O_7^{6-}$

The oxygen atom that does not form a bridge has to pick up an $\bar{e}$ from metal to complete It's octate.

e.g. Thortvetite $[Sc_2(Si_2O_7)]$, hemimorphite $[Zn_4(OH)_2Si_2O_7]$

3) Chain silicates :-

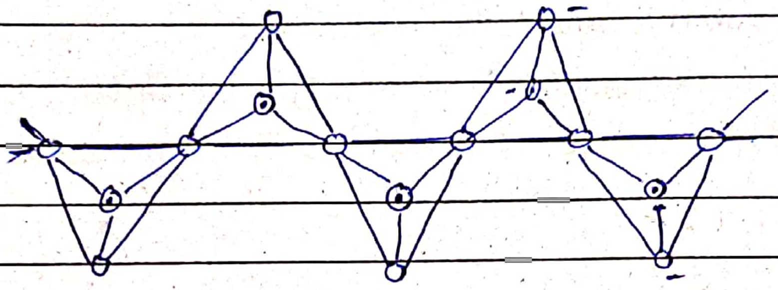
Chain silicates are g two types

a) Simple chain silicates ② Double chain silicates

a) Simple chain silicates or Pyroxenes :-

These are formed by the sharing g the two oxygen atoms g SiO_4 tetrahedra.

Linear chain silicates have formula $(SiO_3)_n^{2n-}$



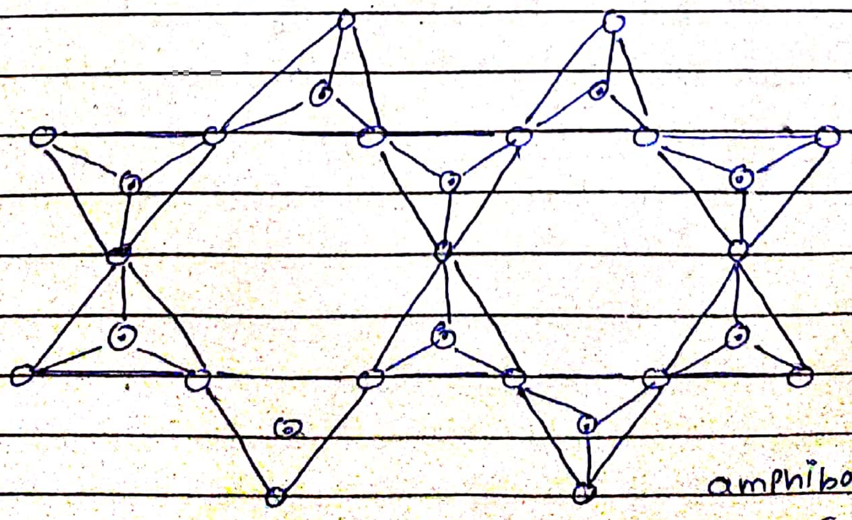
e.g. Spodumene $LiAl[(SiO_3)_2]$, enstatite $Mg_3[(SiO_3)_3]$

diopside $CaMg(SiO_3)_2$

b) Double chain silicates :-

- Two linear chain silicates may be linked side by side into a double chain silicate.
- If some tetrahedra share three oxygen then a double chain is observed. Double chain silicates are called as amphiboles. The general formula of double chain silicate is

~~$(\frac{SiO_4}{11})$~~ $(Si_4O_{11})_n^{6n-}$



amphiboles $= (Si_4O_{11})_n^{6-}$

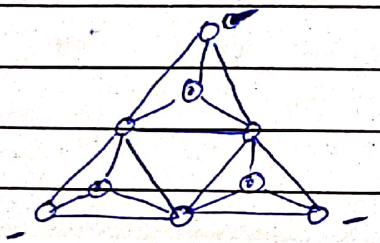
4) Cyclic Silicates:

Instead of forming long chain structures the ends of chain may join together to form cyclic silicates.

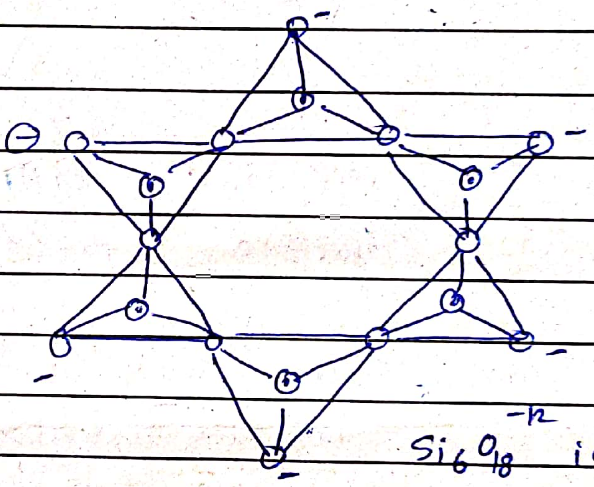
Thus cyclic silicates are formed by sharing of two oxygens per Si tetrahedron resulting in the formation of a cyclic structure.

In this str. each silicon has 2 terminal oxygens & 2 bridging oxygens & the charge density is -2 per silicon ato

- The primary unit in this case is also $(SiO_3)^{2-}$
- It contains 3, 4, 6 & 8 tetrahedral units are known but those with three $(SiO_3)_3^{6-}$ & six $(SiO_3)^{-12}$ are most common



$Si_3O_9^{6-}$ ion



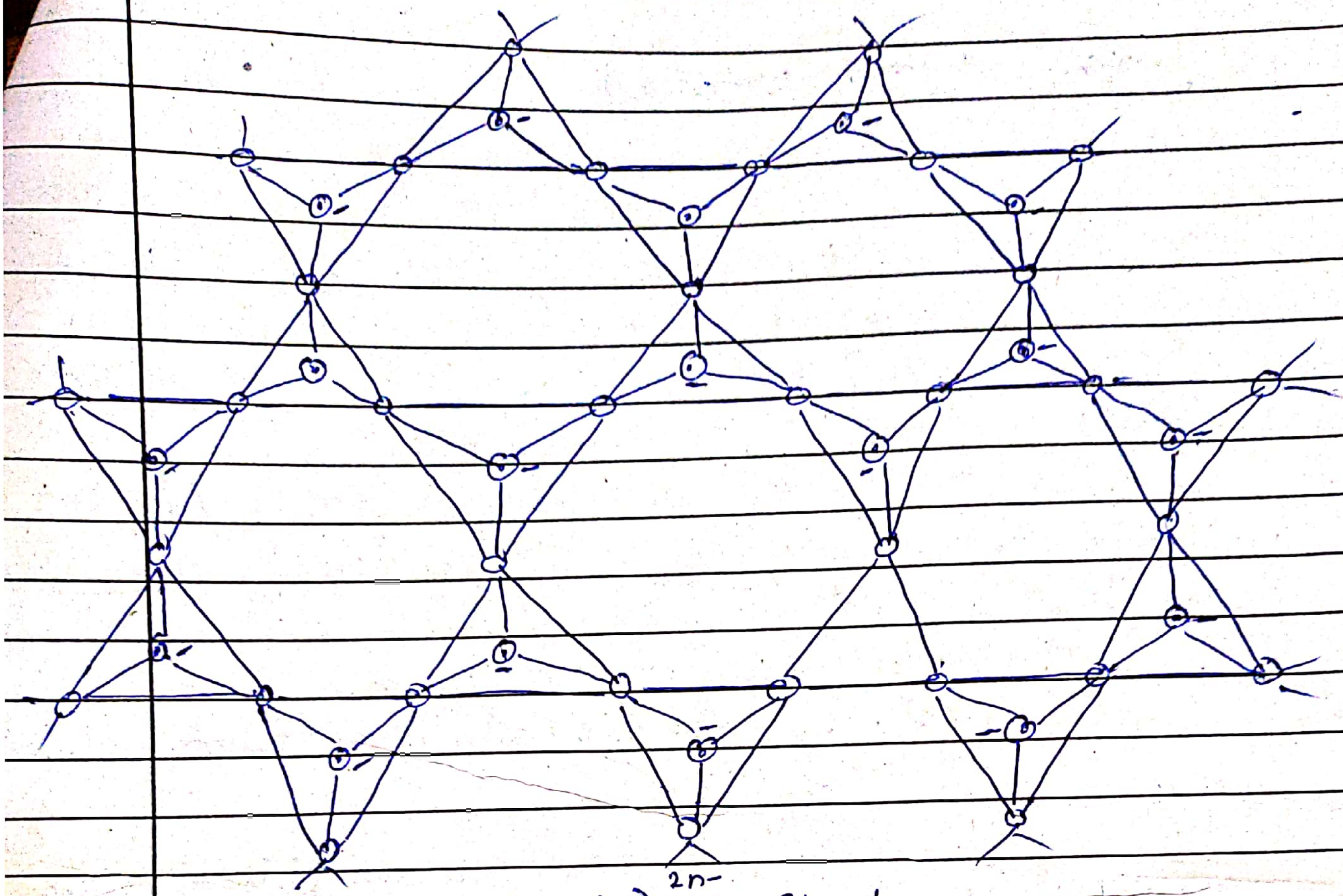
$Si_6O_{18}^{-12}$ ion.

cyclic trimer ion $(Si_3O_9)^{6-}$ occurs in wallastonite $Ca_3[Si_3O_9]$ & in benitoite $BaT[Si_3O_9]$

⑤ Sheet Silicates :- when side by side linking of linear chain silicates is continued ~~[illegible]~~ indefinitely it forms two dimensional network of Sheet Silicate.

- In sheet silicates, each SiO_4 tetrahedron shares three oxygen's with its neighbours, producing a sheet-like structure.

Sheet silicates have the empirical formula $[Si_4O_{10}]_n^{4n-}$



$(Si_2O_5)_n^{2n-}$ Sheet

The oxygen atom shown around silicon atom is the one that does not form the bridge & hence carries a -ve charge - This oxygen lies below the plane g the paper.

The minerals containing sheet silicate str are

micas - muscovite & biotite

clay minerals - montmorillonite, kaolinite, china clay & vermiculite.

Talc - $Mg_3(OH)_2Si_4O_{10}$ - it is soft & smooth.

⑥ Three dimensional silicate :- Three dimensional silicate form when silicon is joined to 4 other silicon atoms via bridging oxygen gives 3-d polymeric structure. Thus these consist of SiO_4 tetrahedra in which every oxygen is shared with an adjacent tetrahedra. Because g ~~these~~ this sharing there is overall one Si atom for every two oxygen so the formula g these is SiO_2.

e.g. Quartz, tridymite & cristobalite.

[illegible] ~~[illegible] [illegible] compounds~~

These contain no metal ions, but 3-D structure can form the basis of silicate str. If there is isomorphous replacement ~~yields~~ of some of the Si^{+4} atoms by Al^{+3} plus additional metal atoms. This results in formn of aluminosilicates.

- For ~~so~~ each Si^{+4} ion replaced by an Al^{+3}, the charges must be balanced by having other +ve ions such as Na^+, K^+, & Ca^{2+} ion.

The typical alluminosilicates are

Ⓐ Feldspar ($KAlSi_2O_8$) Ⓑ Zeolites Ⓒ Ultramarines.

$[NaAlSi_2O_6 \cdot H_2O]$

★ Zeolite :- microporous, aluminosilicate minerals used as adsorbents & catalyst.

General formula is $M^{n+}_{x/n}(Al_x Si_y O_{2x+2y})^{x-} \cdot zH_2O$

Zeolites are alluminosilicates that have porous structure. Zeolites are found in certain rocks.

- About 40 natural zeolites are known & 150 zeolites have been synthesized.
- Zeolites are formed when some of the Si^{+4} ion in 3d silicates are replaced by Al^{+3} ions.

∵ Silicon typically exists in a +4 oxidn state, the Si – O tetrahedra are electrically neutral.

⇒ However in zeolites, aluminium typically exists in the +3 oxidn state so that Al – O tetrahedra form centers that are electrically deficient of one e. Thus, zeolite frameworks are typically anionic & charges compensating cations populate the pores to maintain electrical neutrality. These cations can participate in ion-exchange processes & this yields some imp properties for zeolites.

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zeolites are microporous, alluminosilicate minerals commonly used as adsorbents & catalysts.

It was first coined by swedish mineralogist Axel Fredrik Cronstedt in 1756

- The porous structure of zeolite can be accomodate by a wide variety of cations such as $Na^+, K^+, Ca^{2+}, Mg^{2+}$ & othere.
- natural zeolites are form where volcanic rocks & ash layers react with alkaline groundwater.

-

uses/ Applicat^n :-

① They are widely used as ion-exchange beds in water purification, softening

② ~~Ex~~ zeolites are used to separate molecules. (only molecules of certain size & shape can pass ~~through~~)

③ used as catalyst & sorbents, in Petrochemical ind

④ used as specific separation of gases.

ines

A semiprecious deep-blue gem lapis lazuli has been known from ancient times & is available in synthetic forms under the name ultramarine.

- The Lapis Lazuli has the composition of $Na_8[(AlSiO_4)_6]S_2$ in which colour is produced by poly sulphide ion.

- The ultramarine are a group of related compounds, that contains anions such as Cl^-, SO_4^{--} & S_2^{2-}

e.g.

ultramarine	$Na_8[(AlSiO_4)_6]S_2$
Sodalite	$Na_8[(AlSiO_4)_6]Cl_2$
Nosean	$Na_8[(AlSiO_4)_6]SO_4$.

③ Carbide :-

The compounds in which carbon is combined with elements of similar or lower electro-vity are called as carbides.

There are three types g carbides :-

1) salt like carbide (saline carbide)
2) covalent carbide
3) Interstital carbide. (metallic carbides)

① salt like carbide :-

These are compounds g c with more electro +ve elements i.e. with metals of group I, II & III.

e.g. CaC_2, Al_4C_3

Prep^n :- They are obtained by heating metal or its oxide or hydride with carbon atom in an electric arch.

e.g

$$2BeO + 3C \xrightarrow{1900°C} Be_2C + 2CO$$

Properties :- 1) They exist as transparent crystal

2) They are non-conducter of ~~be~~ electricity in the solid state.

3) These carbides are readily hydrolysed in water yielding different hydrocarbons.

The salt like carbides are further classified according to the hydrocarbon that they produce on hydrolysis.

They are classified as :

$CaC_2 + H_2O$
↓
$CH \equiv CH + Ca(OH)_2$

ⓐ Acetylides : The carbides that produce acetylene on hydrolysis are known as acetylides e.g MgC_2, BeC_2, CaC_2

ⓑ methanides : The carbides that produce methane on hydrolysis are known as methanides e.g. $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

ⓒ Allylide = ~~Which~~ carbides that produce Allylene on hydrolysis is called Allylides

(e.g.) $Mg_2C_3 + 4H_2O \xrightarrow{\cancel{e.g}} (CH_3-C\equiv CH)$, [illegible] , $+ 2Mg(OH)_2$

2) Covalent carbides :-

Carbides that contain carbon covalently bonded with the elements, which have the same electro-vity as carbon or higher value are called covalent carbides.

e.g. CH_4, SiC, CCl_4, B_4C.

Prepn :- These carbides are prepared by direct union of the elements with carbon at high temp.

They are classified in to two categories depending upon their volatility

(1st) - Consist of covalent carbide which contain small discrete molecule e.g. CH_4, CCl_4.

These includes carbides which are formed betn carbon & H or elements of gr. $\frac{VI}{16}$ or gr. $\frac{VII}{17}$. These carbides are either gases or volatile liquids. ~~This category consist of gaint molecules~~.

~~B_4C, SiC~~

~~They are~~

(II) The 2nd category consist of gaint molecules by linking together of a large number of simpler units.

e.g Boron carbide B_4C, SiC. These are thermally stable, hard & chemically inert solids.

3) Interstitial Solid :- The comp. of carbon with transition metals such as Ti, Zr, Hf etc called as interstitial carbides.

e.g. WC, Nb_2C.

Prepn. They are obtained by direct combinatn of metal & carbon or by the reduction of metal oxide with carbon at high temp.

Structure :- In these, the metals retain their closed-packed lattice structure & incorporate c in octahedral interstatices. C atom occupy octahedral interstices in closed packed lattice of metal atom. ∴ The size of the metal atoms must be large enough to form octahedral site of sufficient size to accomodate c-atom.

Prop :- They are hard & brittle & good conductors of electricity.

Fullerene:- is an allotrope of carbon in the form of hallow, ellipsoid, tube & many other shapes

Spherical Fullerene → Buckminsterfullerenes or buckyballs

Cylindrical Fullerene → carbon nanotubes (buckytubes)

Fullerene are simillar in structure to graphate which is composed of stacked graphene sheet of linked hexagonal rings.

Cyliendrical → must contain Pentagonal (or sometimes heptagonal) rings.

Property : These are stable but not totally unreactive

- It show electrophilic addn reacn.
- It is spirangly soluble in toluene, CS_2 & most of the solvents

Types : Bucky ball cluster

- Smallest member is C_{20}

2) Nanotubes - Hallow tubes of very small dimension

3) megatubes - larger in diameter than nanotubes

SP^2 - hybridised

C_{2n} $(n = 30-48)$

The structure of C_{60} is truncated isocahedron which resembles an association football - made up of 20 Hexagon & 12 Pentagons. with C-atom at the vertices of each Polygon

2 types of C-C bond length
C_{60} = 1.48 A° & 1.38 A°
C_{70} = 1.39 A° & 1.54 A°

Production / Preparatn :- ~~Synthes~~ vaporising graphite rod in inert atmospheres

Large amt of current is passed
↓
Plasma $\xrightarrow[\text{cool}]{}$ Sooty residue → C_{60}, C_{70}, C_{72}

Applicatn = extensively used in several biomedical applicatn

- HP MRI contrast agent
- drug & gene delivery
- Tumor research
- X-ray Imaging contrast agent
- Photodynamic therapy