MIND MAP

p-block (13-14)

13	14	15	16	17	18
					2 He
5 B	6 C	7 N	8 O	9 F	10 Ne
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

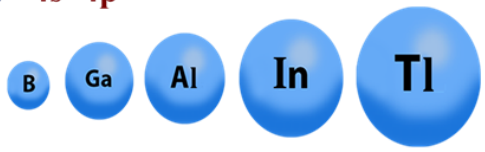
Valence shell electronic configuration of p - block elements is $ns^2 np^{1-6}$. (except for He)

The Boron Family

- 5 B → $1s^2 2s^2 2p^1$
- 13 Al → [Ne] $3s^2 3p^1$
- 31 Ga → [Ar] $3d^{10} 4s^2 4p^1$
- 49 In → [Kr] $4d^{10} 5s^2 5p^1$
- 81 Tl → [Xe] $4f^{14} 5d^{10} 6s^2 6p^1$

Atomic and Ionic radii order
B < Ga < Al < In < Tl

- 13 Al → [Ne] $3s^2 3p^1$
- 31 Ga → [Ar] $3d^{10} 4s^2 4p^1$



Atomic radius of Ga is less than that of Al due to poor shielding of 3d electrons in Ga.

Boiling point order

B.P. B > Al > Ga > In > Tl

Electronegativity

B > Tl > In > Ga > Al

Density of the elements increases down the group from boron to thallium.

B < Al < Ga < In < Tl

Melting point order

M.P. B > Al > Tl > In > Ga

Ionization Enthalpy

B > Tl > Ga > Al > In

Electropositive Character

$$\frac{\text{B}}{\text{Non metal}} < \frac{\text{Al} < \text{Ga} < \text{In} < \text{Tl}}{\text{Metals}}$$

Chemical Properties

(i) Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds.

Preparation of Boron compound

(i) Preparation of B_2O_3 from Borax or Colemanite

$Na_2B_4O_7 + HCl/H_2SO_4 \longrightarrow NaX + H_2B_4O_7$

$H_2B_4O_7 + 5H_2O \longrightarrow 4H_3BO_3$

$\xrightarrow{\Delta} B_2O_3 + H_2O$

Borax

$2CaO.3B_2O_3 + 2Na_2CO_3 \longrightarrow 2CaCO_3\downarrow + Na_2B_4O_7 + 2NaBO_2$

Colemanite

↓ Filtered - $CaCO_3$ (as residue)

$Na_2B_4O_7 + NaBO_2$ (in solution)

Concentrated and allowed to crystallise out and filtered

$NaBO_2$ (in filtrate) + $Na_2B_4O_7 \cdot 10H_2O$ (as residue)

↓ CO_2 Passed and crystallise out again

$[4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3]$

$Na_2B_4O_7 . 10H_2O \downarrow$

MIND MAP

p-block (13-14)

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

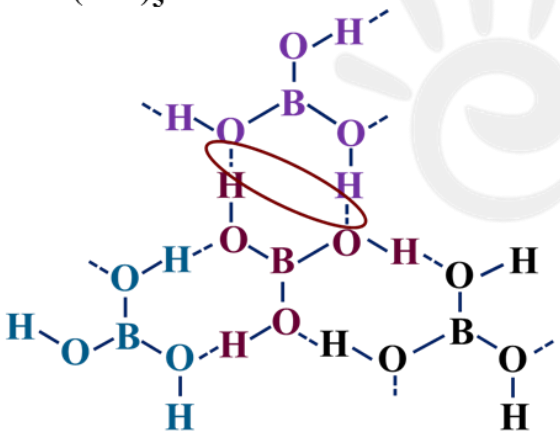
[Heating effect]

Orthoboric acid

Preparation

(i) It can be prepared by acidifying an aqueous solution of borax.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4B(OH)_3$$



Structure of boric acid; the dotted lines represent hydrogen bonds

Heating of Boric acid

$$\underset{\text{Metaboric acid}}{H_3BO_3} \xrightarrow{100^\circ C} \underset{\text{Tetra boric acid}}{HBO_2} \xrightarrow{140^\circ C} H_2B_4O_7 \xrightarrow[\text{red hot}]{\Delta} \underset{\text{Glassy mass}}{B_2O_3}$$

$$H_3BO_3 + H_2O_2 \longrightarrow (H_2O) + (HO)_2B{-}O - O - H \xrightarrow{NaOH}$$

$$Na_2\left[(HO)_2B\begin{matrix}O-O\\O-O\end{matrix}B(OH)_2\right].6H_2O$$

Sodium peroxy borate used in washing powder as brightener

Diborane, B_2H_6

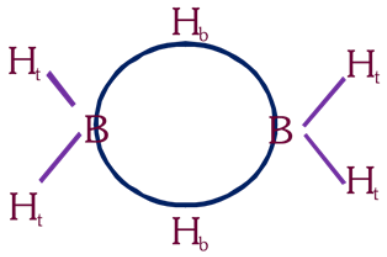
The simplest boron hydride known as diborane.

Preparation

It is prepared by treating boron trifluoride with LiAlH4 in diethyl ether.

$$3LiAlH_4 + 4BF_3 \longrightarrow 3LiF + 3AlF_3 + 2B_2H_6$$

or $LiBH_4$ or $3(BF_3)$



B_2H_6

MIND MAP

p-block (13-14)

The terminal B–H bonds are normal 2C-2 electron bonds but the two bridge bonds are 3C-2 electron bonds. The 3-centred-2 electron bridge bonds are also referred to as banana bonds.

Some Important Compounds of Aluminium

Al_2O_3 Preparation

(i) $2Al(OH)_3 \xrightarrow{300°C} Al_2O_3 + 3H_2O$

(ii) $Al_2(SO_4)_3 \xrightarrow{\Delta} Al_2O_3 + 3SO_3$

(iii) $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \xrightarrow{\Delta} Al_2O_3 + 2NH_3 + 4SO_3 + 25H_2O$

$AlCl_3$ Preparation

$2Al + 6HCl\ (vap.) \longrightarrow 2AlCl_3 + 3H_2$

(over heated) (dry)

$Al_2O_3 + 3C + 3Cl_2 \xrightarrow[1000°\ C]{\Delta} 2AlCl_3\ (vap.) + 3CO$

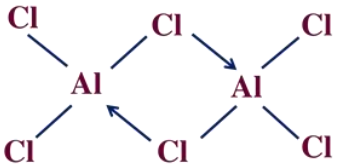
Cooled ↓

Solid anh. $AlCl_3$

Properties

(i) Its anhydrous form is deliquescent and fumes in air.

(ii) It sublimes at 180°C.



Alumns

$M_2SO_4 . M'_2(SO_4)_3 \cdot 24\ H_2O$

$M_2SO_4 . M'_2(SO_4)_3 \cdot 24\ H_2O$

where

$M = Na^+, K^+, Rb^+, Cs^+, As^+, Tl^+$,

$M' = Al^{+3}, Cr^{+3}, Fe^{+3}, Mn^{+3}, Co^{+3}$

Uses

(i) Acts as coagulant

(ii) Purification of water

(iii) Tanning of leather

(iv) Mordant in dyeing

(v) Antiseptic

Group 14 Elements

5 C	$1s^2\ 2s^2\ 2p^2$
13 Si	$[Ne]\ 3s^2\ 3p^2$
31 Ge	$[Ar]\ 3d^{10}\ 4s^2\ 4p^2$
49 Sn	$[Kr]\ 4d^{10}\ 5s^2\ 5p^2$
81 Pb	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$

Covalent Radius

Covalent radii C < Si < Ge < Sn < Pb

Melting and Boiling Points

M.P. C > Si > Ge > Pb > Sn

B.P. C > Si > Ge > Sn > Pb

Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13.

Electronegativity

The electronegativity values for elements from Si to Pb are almost the same.

Chemical Properties

Reactivity Towards Oxygen

All members when heated in oxygen form oxides.

There are mainly two types of oxides, i.e., monoxide and dioxide of formula MO and MO_2 respectively.

SiO only exists at high temperature.

Reactivity Towards Halogen

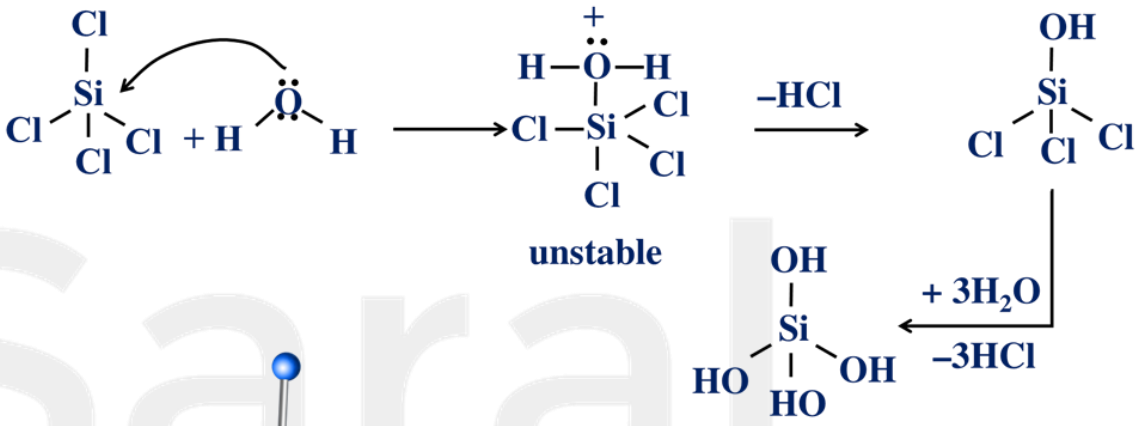
(i) These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl, Br, I).

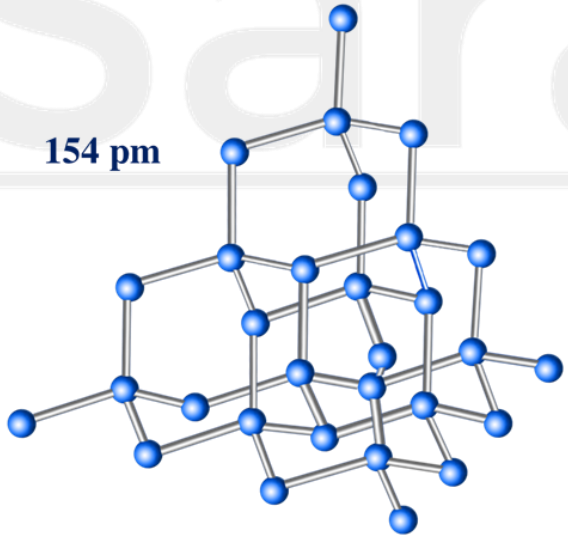
(ii) Except carbon, all other members react directly with halogen.

MIND MAP

p-block (13-14)

Hydrolysis of $SiCl_4$ (Mechanism)





Uses

It is used as an abrasive for sharpening hard tools,

And in the manufacture of tungsten filaments for electric light bulbs.

MIND MAP

p-block (13-14)

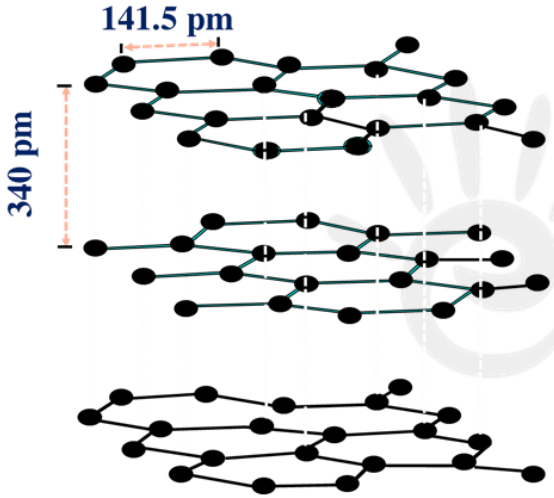
Graphite

(i) Graphite has layered structure.

(ii) Layers are held by vander Waals forces and distance between two layers is 340 pm.

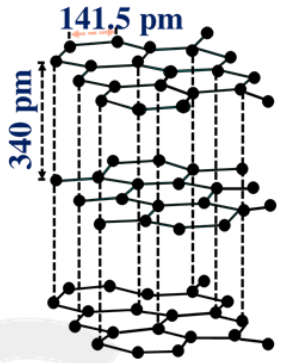
(iii) Each layer is composed of planar hexagonal rings of carbon atoms.

C—C bond length within the layer is 141.5 pm.



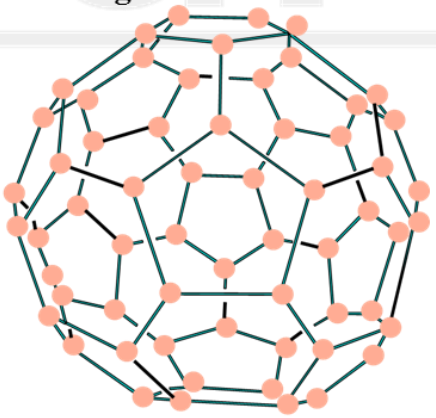
The Structure Of Graphite

(iv) Each carbon atom in hexagonal ring undergoes sp2 hybridisation and makes three sigma bonds with three neighbouring carbon atoms.



Fullerenes

(i) Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon.



The material formed by condensation of vapourised C_n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above.

Carbide

(i) Ionic and salt like

Classification on basis of no. of carbon atoms present in hydrocarbon found on their hydrolysis.

(a) C_1 unit

(b) C_2 unit

(c) C_3 unit

C_1 unit

Be_2C , Al_4C_3

$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$

$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

C_2 unit

CaC_2, BaC_2

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + CH \equiv CH$

C_3 unit

Mg_2C_3

$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3-C \equiv CH$

Propyne

(ii) Covalent carbide

CH_4, CO_2, CS_2 can be consider as covalent carbide and SiC & B_4C also consider as covalent carbide.

(iii) Interstitial carbide

Transition element or inner transitional elements forms this kind of carbide. Interstitial carbide formation doesn't affect the metallic luster and electrical conductivity.

Carbon Monoxide

Prepration

(i) Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.

$$2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$$

This property of CO is used in the extraction of many metals from their oxides ores.

$$Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$$

$$ZnO(s) + CO(g) \xrightarrow{\Delta} Zn(s) + CO_2(g)$$

Carbon Dioxide

Prepration

(i) It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.t

MIND MAP

p-block (13-14)

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$$

$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$$

(iii) With water, it forms carbonic acid, H_2CO_3 which is a weak dibasic acid and dissociates in two steps

$$H_2CO_3(aq) + H_2O(l) \leftrightharpoons HCO_3^-(aq) + H_3O^+(aq)$$

$$HCO_3^-(aq) + H_2O(l) \leftrightharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

It is the process by which green plants convert atmospheric CO_2 into carbohydrates such as glucose. The overall chemical change can be expressed as

$$6CO_2 + 12H_2O \xrightarrow[\text{Chlorophyll}]{hv} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

Harmful Effect of CO_2

Unlike CO, it is not poisonous.

But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO2 content of the atmosphere.

(ii) Gaseous CO_2 is extensively used to carbonate soft drinks.

Being heavy and non-supporter of combustion it is used as fire extinguisher.

Silicon (Si)

All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or iron.

Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

(i) Feldspar $K_2O.Al_2O_3.6SiO_2$

(ii) Kaolinite $Al_2O_3.2SiO_2.2H_2O$

(iii) Asbestos $CaO.3MgO.4SiO_2$

Preparation

(i) From silica (sand)

Elemental silicon is obtained by the reduction of silica (SiO_2) with high purity coke in an electric furnace.

$$SiO_2(s) + 2C(s) \xrightarrow{\text{High temperature}} Si(s) + 2CO(g)$$

MIND MAP

p-block (13-14)

Chemical Properties

Silicon is particularly unreactive at room temperature towards most of the elements except fluorine.

Reaction with halogensc

It burns spontaneously in fluorine gas at room temperature to form silicontetrafluoride (SiF_4).

$$Si(s) + 2F_2(g) \xrightarrow{\text{Room Temperature}} SiF_4(l)$$

Compounds of Silicon

Silane

$Si_nH_{2n+2} \rightarrow SiH_4$ & Si_2H_6

Only these two are found

Types of Silicones

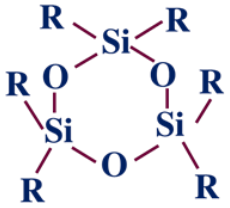
(ii) Linear Silicones

$$R_2SiCl_2 + H_2O \xrightarrow[-2HCl]{} R_2Si(OH)_2 \xrightarrow[-H_2O]{\Delta}$$

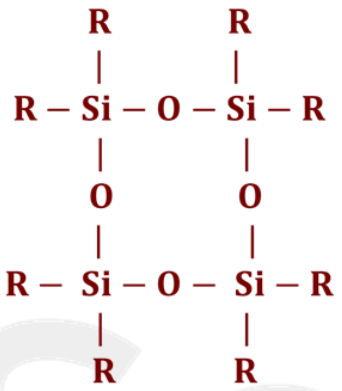
Linear Silicones

(iii) Cyclic Silicones

Silicones may have the cyclic structure also having 3, 4, 5 and 6 silicon atoms within the ring.



cyclic silicone non planar

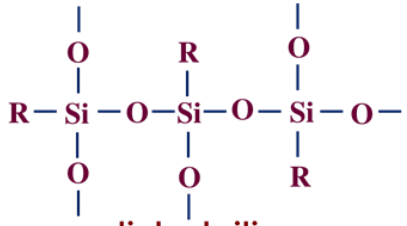


Note

This end of the chain can't be extended hence R_3SiCl is called as chain stopping unit

(iv) Crossed Linked Silicones

$$RSiCl_3 + H_2O \longrightarrow R\text{-}Si(OH)_3 \xrightarrow{\Delta}$$



cross linked silicone

3 dimensional network

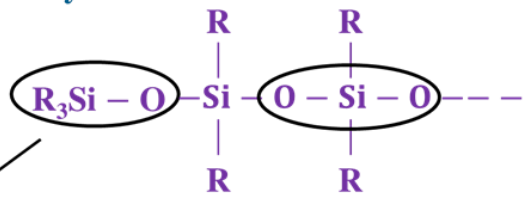
Silicates

Silicates are metal derivatives of silicic acid, H_4SiO_4 or $Si(OH)_4$.

Silicates are formed by heating metal oxide or metal carbonates with sand, e.g.,

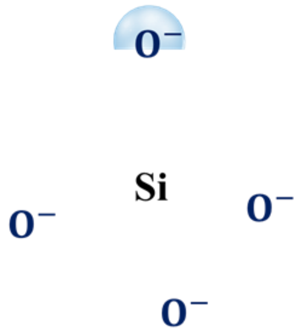
$$Na_2CO_3 \xrightarrow[SiO_2]{\text{Fused with sand}} Na_4SiO_4,\ Na_2(SiO_3)_n,\ \text{etc.}$$

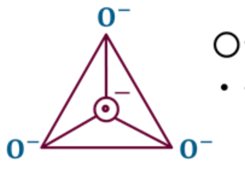
$$R_2SiCl_2 + R_3SiCl \xrightarrow[\text{hydrolysis}]{H_2O} R_2Si(OH)_2 + R_3SiOH \xrightarrow[\text{Heating}]{-H_2O}$$



MIND MAP

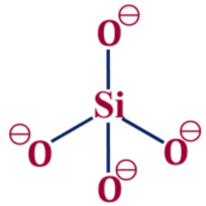
p-block (13-14)

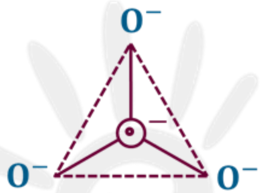




○ → Oxygen
• → Silicon

Ortho silicates (Ex. Zircon, Willemite)
Minerals in which $SiO_4{-}^4$ anion is present in discrete form (not in polymeric form) are called Orthosilicate.

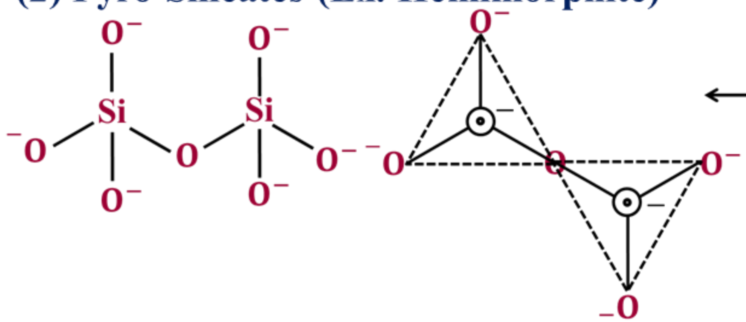




Si = sp^3 hybridisation
Tetrahedral in shape

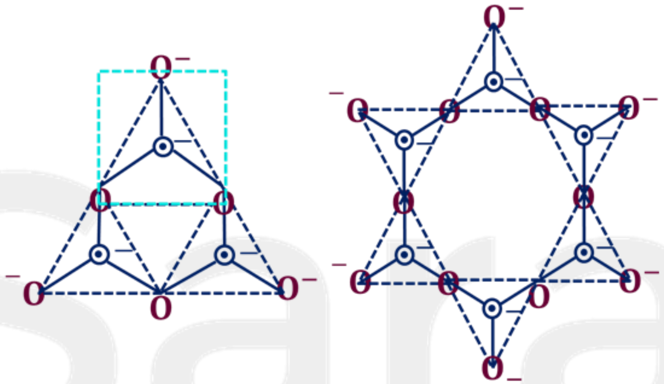
• → Silicon
○ → Oxygen

(2) Pyro Silicates (Ex. Hemimorphite)

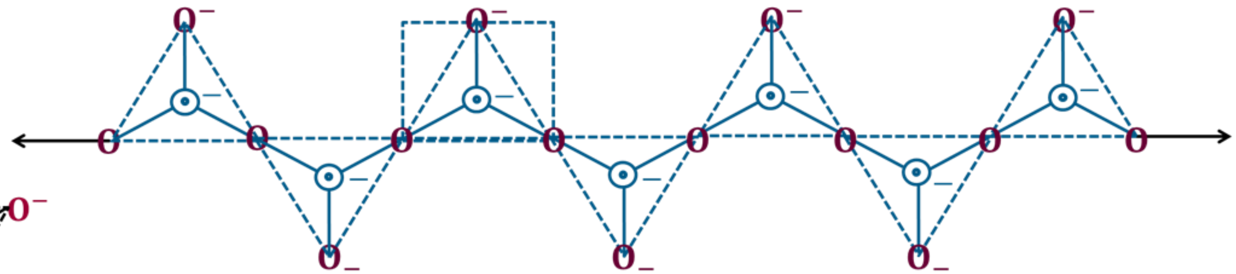


(3) Cyclic Silicate (Wollastonile, Benitotite, Beryl, Emrald)

$Si_3O_9^{-6}$ $Si_6O_{18}^{-12}$

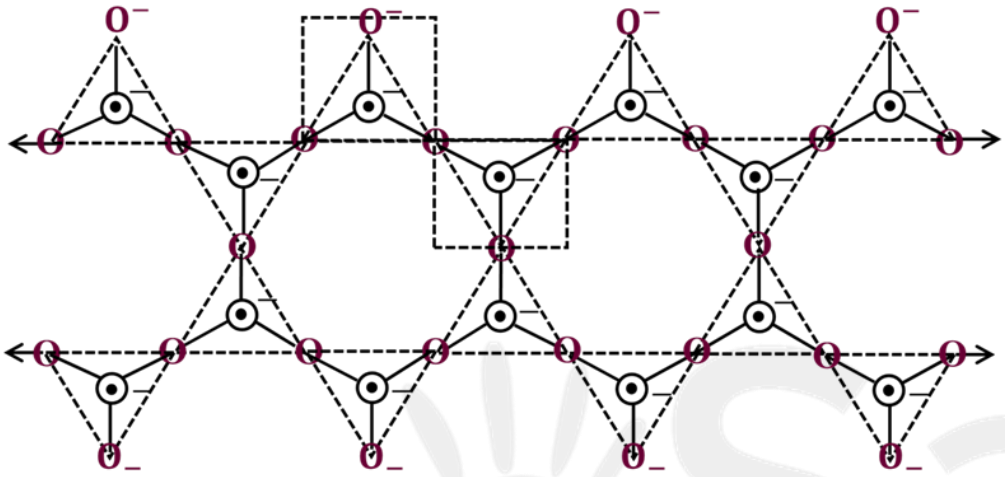


(4) Single chain silicate (Pyroxene Silicate) (Ex. Diopsite)



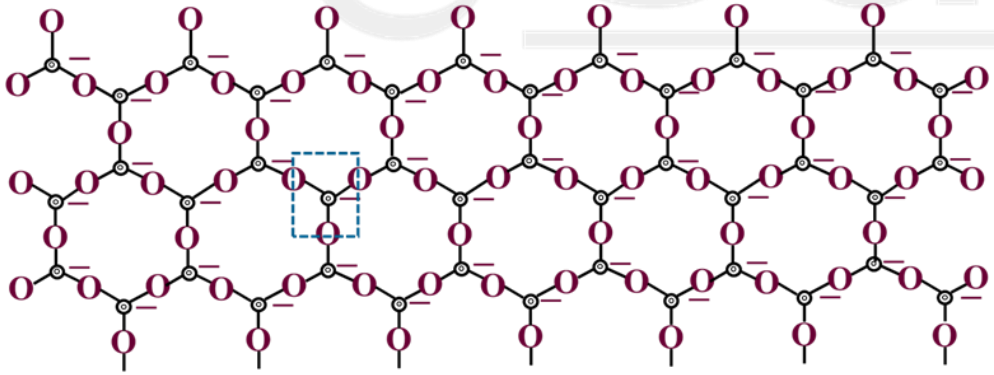
Formula = $(SiO_3)_n^{-2n}$ charge on one unit = –2

(5) Double chain Silicate (Amphiboles)
(Ex. Asbestos)



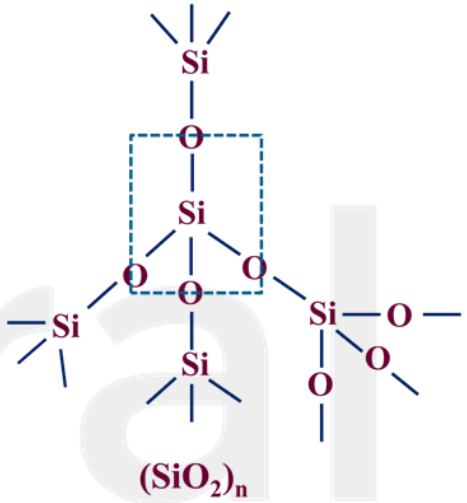
Formula = $(Si_4O_{11})_n^{-6n}$

(6) Sheet Silicate (Ex. Clay talc, Micas)



Formula $(SiO_{2.5})_n^{-n}$ or $(Si_2O_5)_n^{-2n}$

(7) 3-D Silicate (Ex. fledspars,
zeolites, ultramarine, quartz)



$(SiO_2)_n$