

## Set I

MJ -1 (Chemistry)

Full Marks: 60

Time: 3 Hours

*Answer the questions as per instruction given.*

*The figures in the right-hand margin indicate marks.*

*Candidates are required to give answers in their own words as far as practicable.*

### Group A

#### (Short Answer Type Questions)

Answer all the following questions.

1. Answer the following questions in a few words or maximum in one sentence. (5x1=5)
  - a) Maximum how many electrons can be accommodated in a d-atomic orbital?
  - b) Which element has the highest electronegativity?
  - c) Which element is the most abundant in the earth's crust?
  - d) How many unpaired electrons are present in O<sub>2</sub> molecule?
  - e) How does the solubility of sulphates of alkaline earth metals in water vary on moving down the group?
2. Draw molecular orbital energy level diagram for N<sub>2</sub> and calculate the bond order. (5)
3. How linear silicone polymers can be prepared? (5)

### Group B

#### (Long/Descriptive Answer Type Questions)

Answer any three of the following questions.

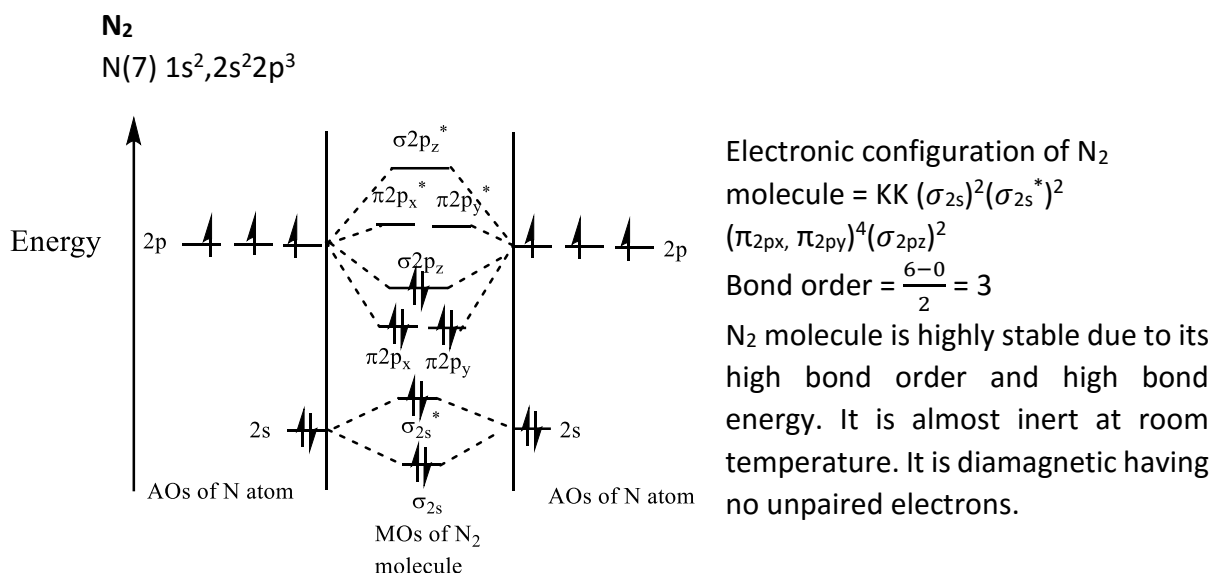
4.
  - a) What is de Broglie theory?
  - b) Derive de Broglie equation.
  - c) Calculate the wavelength of the matter wave associated with an electron moving with a velocity of  $10^7$  cm s<sup>-1</sup>. (5+5+5)
5.
  - a) Define ionisation energy and illustrate with an example.
  - b) Discuss the variation of ionisation energy in the periodic table.
  - c) The ionisation energy of nitrogen is greater than that of oxygen, why? (5+5+5)
6.
  - a) What is valence shell electron pair repulsion theory? Illustrate briefly.
  - b) Explain the shape of XeF<sub>4</sub>, SF<sub>4</sub>, NH<sub>3</sub> and ClF<sub>3</sub> molecules with the help of VSEPR theory. (7+8)
7. a) Explain the molecular orbital theory/ band theory of metals.

b) Explain insulators, semiconductors and conductors on the basis of band theory. (9+6)

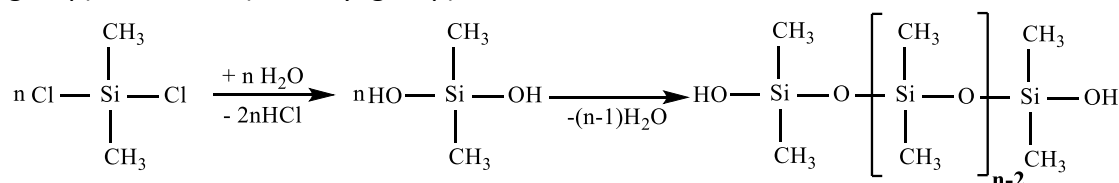
8. What are silicates? How silicates are classified? Give one example of each class of silicate? (3+12)

Answer:

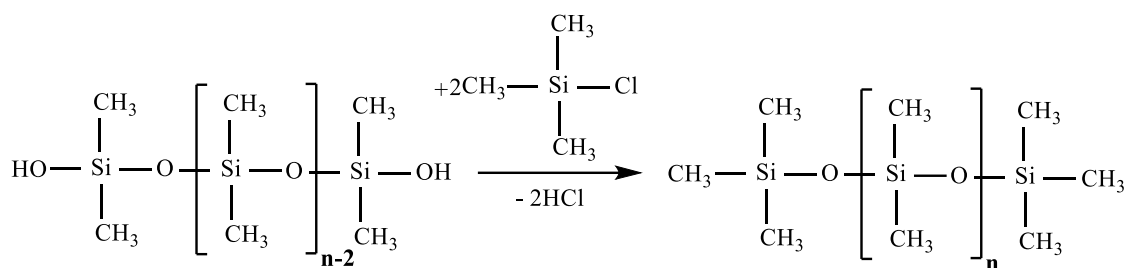
- 2
  - Fluorine
  - Oxygen
  - 2
  - The solubility of sulphates of alkaline earth metals in water decreases on moving down the group.
- The molecular orbital energy level diagram for N<sub>2</sub> molecule is given below:



- The linear silicone polymers can be prepared by the hydrolysis of R<sub>2</sub>SiCl<sub>2</sub> (R = Alkyl group) or Ar<sub>2</sub>SiCl<sub>2</sub> (Ar = Aryl group).



The molecular weight/chain length of the linear silicone polymer is controlled by adding calculated amount of R<sub>3</sub>SiCl.



#### 4. a) de Broglie theory:

Light has dual character. It behaves like a wave and like a particle. Relying on this fact, de -Broglie presented a theory in 1924 which is known as de-Broglie's theory. According to this theory,

“Any extremely small fast-moving material particle such as an electron is associated with a wave which is called matter wave and thus such particle also has dual character.”

The wavelength of the matter is given by the expression:

$$\lambda = \frac{h}{mv} \quad (i)$$

Here,  $\lambda$  = Wavelength of the matter wave

$m$  = Mass of the particle

$v$  = Velocity of particle

$h$  = Planck's constant ( $6.626 \times 10^{-34}$ Js)

We know that

$$m \times v = p(\text{momentum}) \quad (ii)$$

From equations (i) and (ii), we have

$$\lambda = \frac{h}{p} \quad (iii)$$

Equations (i) and (iii) are called de-Broglie's equations. It is obvious that the wavelength of matter wave associated with a particle is inversely proportional to its momentum.

#### b) Derivation of de Broglie equation:

There are several experimental facts, which suggest that light has dual character. It behaves both like a wave and like a particle. The particle character of light is supported by

i) Photoelectric effect

ii) Compton effect

The wave character of light is supported by

i) Interference

ii) Diffraction

If light behaves like a particle, its energy can be given by

$$E = mc^2 \quad (iv)$$

If light behaves like a wave, its energy can be given by

$$E = hv$$

$$\text{or, } E = h \frac{c}{\lambda} (v) (\because c = v\lambda, \therefore v = \frac{c}{\lambda})$$

The energy of light should be the same whether it behaves like a wave or like a particle.

$$\therefore mc^2 = h \frac{c}{\lambda}$$

$$\text{or, } mc = \frac{h}{\lambda}$$

$$\text{or, } \lambda = \frac{h}{mc} (vi)$$

Equation (v) has been derived for light. de-Broglie suggested that equation (vi) can be applied to extremely small fast-moving particle also. On doing so, equation (vi) becomes

$$\lambda = \frac{h}{mv} (vii)$$

Equation (vii) is nothing but de-Broglie's equation.

c) We know that

$$\lambda = \frac{h}{mv}$$

Here,

Mass of electron,  $m = 9.109 \times 10^{-31} \text{ kg}$

$v = 10^7 \text{ cm s}^{-1} = 10^5 \text{ ms}^{-1}$

$$\text{or, } \lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{9.109 \times 10^{-31} \text{ kg} \times 10^5 \text{ ms}^{-1}}$$

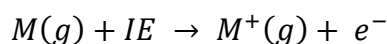
$$\text{or, } \lambda = 7.27 \times 10^{-9} \text{ m} = 72.7 \text{ \AA}$$

$$\text{or, } \lambda = 72.7 \times 10^{-10} \text{ m}$$

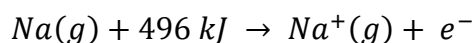
$$\text{or, } \lambda = 72.7 \text{ \AA}$$

## 5. a) Ionisation energy:

The minimum amount of energy required to remove the most loosely bound electron *i.e.*, the outermost electron from an isolated gaseous atom in its ground state to produce gaseous cation is called its ionisation energy. It is abbreviated as IE and its unit is  $\text{kJ mole}^{-1}$ .



An illustrative example is given below:



It is obvious that the ionisation energy of sodium is  $496 \text{ kJ mole}^{-1}$ .

b) On moving down a group in the periodic table, the  $Z_{\text{eff}}$  remains almost constant but atomic radius increases. As a result, the electrostatic attractive force acting on the outermost electron becomes increasingly weaker and hence the ionisation energy goes on decreasing as illustrated below:

Group 1	
Elements	IE(kJ/mole)
Li	520
Na	496
K	419
Rb	403
Cs	376

On moving from left to right in a period in the periodic table, the atomic radius decreases and the  $Z_{\text{eff}}$  increases. As a result, the electrostatic attractive force acting on the outermost electron becomes increasingly stronger and hence the ionisation energy goes on increasing as illustrated below:

Period	Elements	Li	Be	B	C	N	O	F	Ne
2	IE(kJ/mole)	520	<b>899</b>	801	1086	<b>1403</b>	1314	1681	2080

c) The half-filled or full-filled subshell is relatively more stable and it is more difficult to remove electron from such subshell.

N (7)  $1s^2, 2s^2 2p^3$

O (8)  $1s^2, 2s^2 2p^4$

In the case of N- atom, the electron is to be removed from extra stable half-filled  $2p^3$  subshell while the removal of one electron from O- atom produces such subshell. This is why the ionisation energy of nitrogen is greater than that of oxygen.

#### 6. a) Valence shell electron pair repulsion (VSEPR) theory:

The valence shell electron pair repulsion theory has been proposed to explain the shapes of covalent molecules and ions. The main points of this theory are given below:

- The electron pairs present in the valence shell of the central atom of a molecule/ion arrange themselves in the space in such a way that there is maximum distance among them and there is minimum repulsion among them so that the molecule may have minimum energy and maximum stability.
- If the central atom of a molecule or ion is surrounded only by bond pairs and no lone pair, the molecule has regular geometry.
- The bond pair is attracted by two nuclei while the lone pair is attracted by only one nucleus. Therefore, the lone pair occupies greater angular space than the bond pair around the central atom

Therefore, the lone pair causes greater repulsion than the bond pair. The order of repulsion between various electron pairs is in the order:

$$\text{BP-BP} < \text{BP-LP} < \text{LP-LP}$$

This is why the presence of lone pair in the valence shell of the central atom of a molecule produces distortion in the bond angle from the regular geometry.

- All the bond pairs do not occupy the same angular space around the central atom. The bond pair attached to the less electronegative substituent occupies

greater angular space around the central atom than the bond pair attached to the more electronegative substituent. Therefore, the bond angle decreases with increase in the electronegativity of substituents or decrease in the electronegativity of the central atom.

- v) Two electron pairs of a double bond cause greater repulsion than one electron pair of a single bond. Similarly, three electron pairs of a triple bond cause greater repulsion than two electron pairs of a double bond.

b)

**SF<sub>4</sub>:**

Central atom = S

No. of electrons in the valence

shell of S atom in SF<sub>4</sub> molecule = 6(S)+1x4(F)=10

No. of electrons pairs=10/2 =5

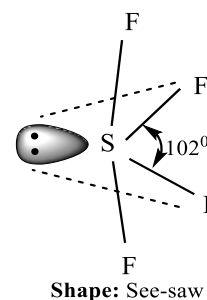
No. of bond pairs=4

No. of lone pairs = 1

BP+LP = 5

Geometry= Trigonal bipyramidal with one equatorial corner occupied by lone pair.

Shape = See-saw



**XeF<sub>4</sub>**

Central atom = Xe

No. of electrons in the valence

shell of Xe atom in XeF<sub>4</sub> molecule = 8(Xe)+1x4(F)=12

No. of electrons pairs=12/2 =6

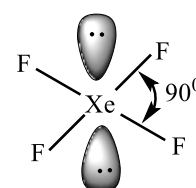
No. of bond pairs=4

No. of lone pairs = 2

BP+LP = 6

Geometry= Octahedral with two axial corners occupied by lone pairs.

Shape = Square planar



**Shape:** Square planar

**NH<sub>3</sub>**

Central atom = N

No. of electrons in the valence

shell of N atom in NH<sub>3</sub> molecule = 5(N)+1x3(H)=8

No. of electrons pairs=8/2 =4

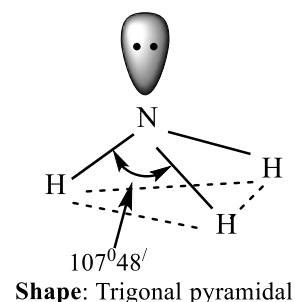
No. of bond pairs=3

No. of lone pairs = 1

BP+LP = 4

Geometry= Tetrahedral with one corner occupied by lone pair.

Shape = trigonal pyramidal



### ClF<sub>3</sub>

Central atom = Cl

No. of electrons in the valence

shell of N atom in ClF<sub>3</sub> molecule = 7(Cl)+1x3(F)=10

No. of electrons pairs=10/2 =5

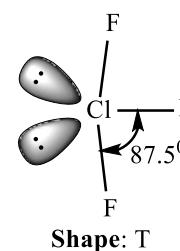
No. of bond pairs=3

No. of lone pairs = 2

BP+LP = 5

Geometry= Trigonal bipyramidal with two equatorial corners occupied by lone pairs.

Shape = T-shaped



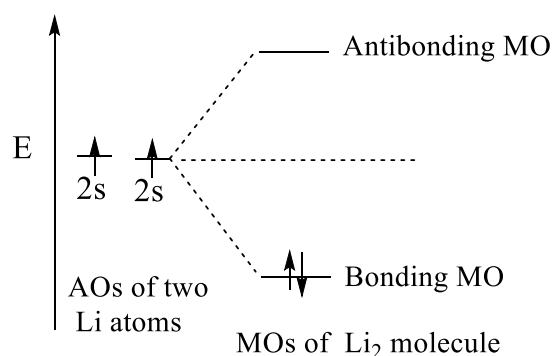
### 7. a) Molecular orbital theory/ band theory of metals:

The electrical properties of solids can be explained on the basis of band theory which is based on molecular orbital theory whose main points are given below:

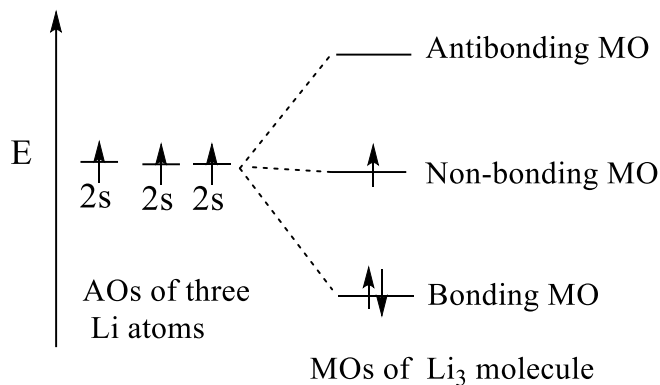
- The molecular orbitals (MOs) are produced by the linear combination of atomic orbitals (LCAOs) of comparable energies lying on two or more atoms – same or different.
- The electron of the atomic orbital is influenced by only one nucleus while the electron of the molecular orbital is influenced by more than one nucleus.
- The atomic orbital is monocentric while the molecular orbital is polycentric.
- The AOs taking part in the linear combination should have the same symmetry property about the internuclear axis.
- The number of MOs produced is always equal to the number of AOs taking part in the linear combination.
- If two AOs take part in the linear combination, two molecular orbitals are produced. One of these, MOs have lower energy than both the atomic orbitals. It is called bonding MO. The other MO has higher energy than both the AOs. It is called antibonding MO.
- If an electron enters bonding MO, the energy of the system decreases and its stability increases while when an electron enters antibonding MO, the energy of the system increases and the stability decreases.

Let us consider lithium molecules with different atomicities.

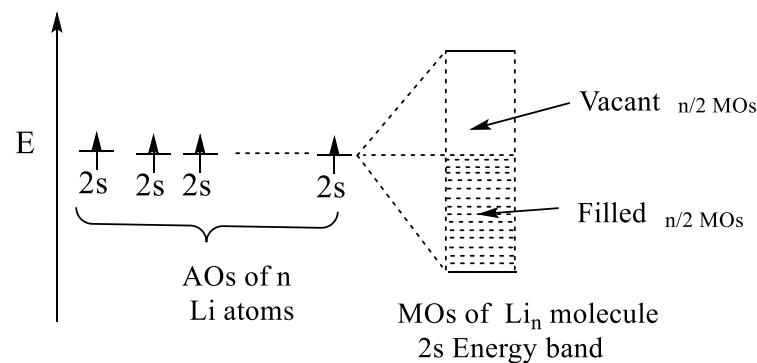
Li<sub>2</sub> molecule:



### Li<sub>3</sub> molecule (hypothetical)



- It is obvious that the energy difference between two consecutive MOs goes on increasing with the increase in the number of atoms in the lithium molecule.
- In actual practice, the lithium crystal is a single molecule containing a large number of Li atoms (about  $10^{20}$ ).
- The MOs produced by the linear combination of such a large number of Li atoms become so closely spaced that they constitute a quasi-continuous energy band which is called 2s energy band which is half-filled. The electrons can be promoted to higher energy levels by providing very small amount of energy.



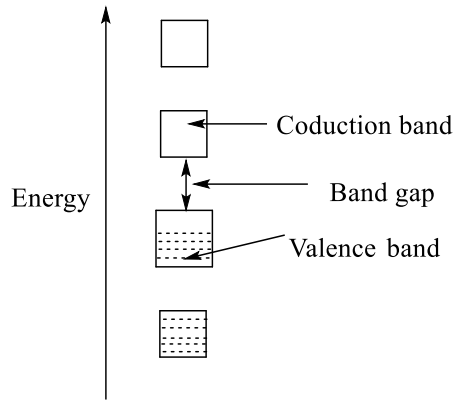
The electrons can move throughout the 2s energy band which is spread over the entire lithium crystal and hence lithium is electrical conductor.

**b) Explanation of insulators, semiconductors and conductors on the basis of band theory.** Before it let us consider some important terms:

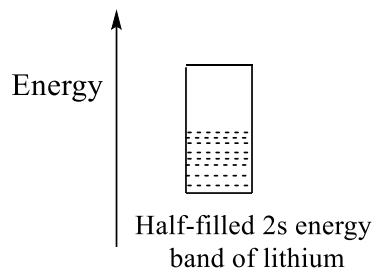
- i. **Valence band (VB)** : The highest occupied energy band is called valence band.
- ii. **Conduction band (CB)**: The lowest unoccupied energy band is called conduction band.
- iii. **Band gap ( $E_g$ )** : The energy difference between the valence band and the conduction band is called band gap.

These three terms have been explained diagrammatically below:



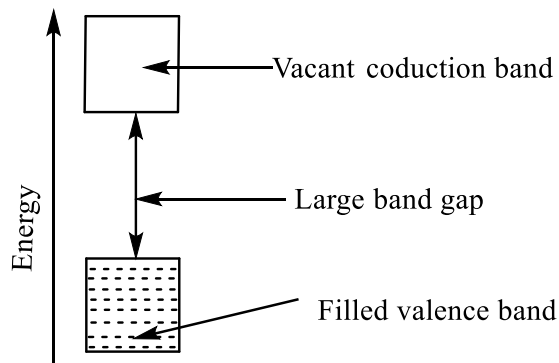


**Conductor:** The conductor has partially filled valence band in which the electrons can move freely.

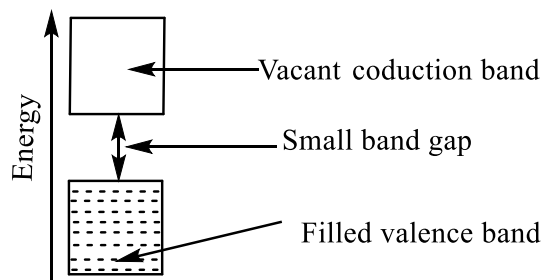


**Insulator:** The insulator contains full-filled valence band and vacant conduction band with a large band gap. The electrons cannot move in the valence band because it is full-filled. The electrons cannot be promoted from the valence band to the conduction band due to large band gap, hence such solid is electrical insulator.

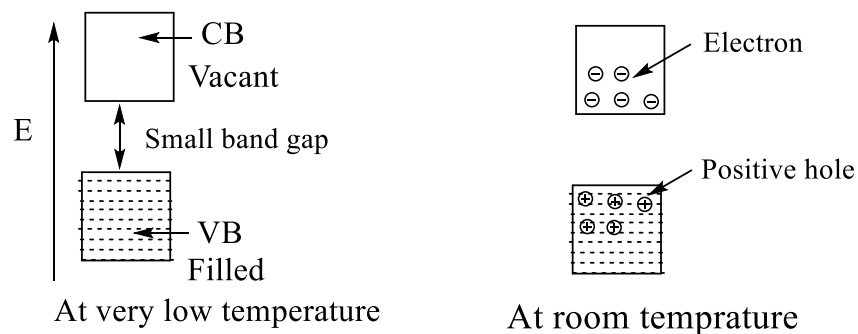
The band gap or the energy gap in diamond is 579 kJ/mole.



**Semiconductor:** The semiconductors have full-filled valence band and vacant conduction band with small band gap.



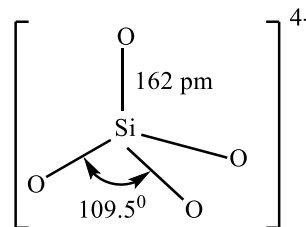
As temperature increases, some electrons are promoted from the filled valence band to the vacant conduction band creating positive holes (vacancy for electrons) in the valence band.



Now the electrons can move in the both valence band and in the conduction band and hence such elements conduct electric current to some extent and hence such a substance acts semiconductor.

### 8. Silicates:

The minerals which contain silicon, oxygen and at least one metal in which Si atoms are tetrahedrally surrounded and bonded with four oxygen atoms are called silicates. The electronegativity difference between O and Si atoms is  $3.5 - 1.8 = 1.7$ . It suggests that the Si-O bond has almost 50% ionic character and 50% covalent character. The radius ratio of  $\text{Si}^{4+}$  and  $\text{O}^{2-}$  ions is 0.29 which falls in the range 0.225 to 0.414 for coordination number 4.



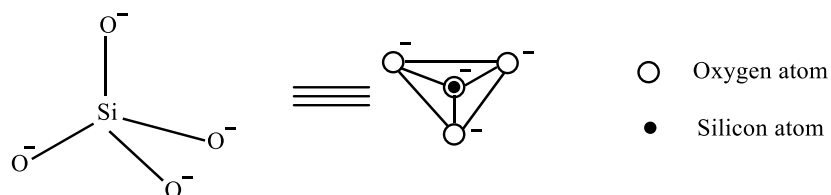
It means, there is tetrahedral arrangement of four O atoms around each Si atom of silicate minerals.

The major portion of earth's crust is made up of silicate minerals. This is why oxygen is the most abundant element in the earth's crust followed by silicon.

#### Classification of silicates:

The silicate minerals are classified on the basis of the way in which tetrahedral  $[\text{SiO}_4]^{4-}$  units are linked together as follows:

a) **Orthosilicates:** These contain discrete tetrahedral  $[\text{SiO}_4]^{4-}$  units.



The oxygen atoms form coordinate bonds to associated metal ions. Various structures are formed depending upon the coordination number of metal ion. Examples:

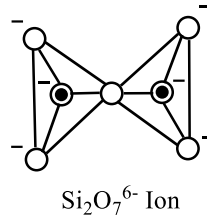
**Willemite-  $Zn_2SiO_4$**  ,  $Zn^{2+}$  is tetrahedrally surrounded by four oxygen atoms.

**Phenacite-  $Be_2SiO_4$**  ,  $Be^{2+}$  is tetrahedrally surrounded by four oxygen atoms.

**Forsterite-  $Mg_2SiO_4$**  ,  $Mg^{2+}$  is octahedrally surrounded by six oxygen atoms.

**Zircon-  $ZrSiO_4$**  ,  $Zr^{4+}$  is surrounded by 8 Oxygen atoms.

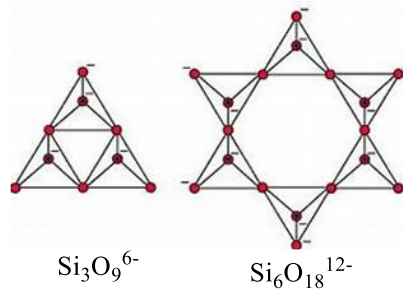
- b) **Pyrosilicates:** In such silicates two tetrahedral  $[SiO_4]^{4-}$  units are linked together by sharing one oxygen atom giving  $Si_2O_7^{6-}$  ion follows:



Example:

**Thortveitite-  $Sc_2Si_2O_7$**

- c) **Cyclic silicates:** In such silicates three or more tetrahedral  $[SiO_4]^{4-}$  units are linked together by sharing two oxygen atoms giving rise to cyclic structures with general formula  $Si_nO_{3n}^{2n-}$  ion.

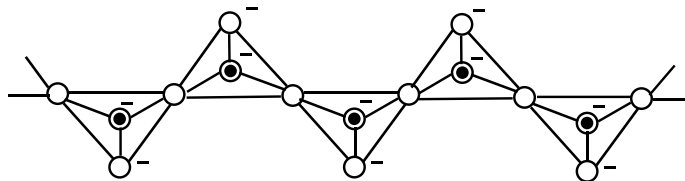


Example:

**Wollastonite-  $Ca_3(Si_3O_9)$**

**Beryl-  $Be_3Al_2(Si_6O_{18})$**

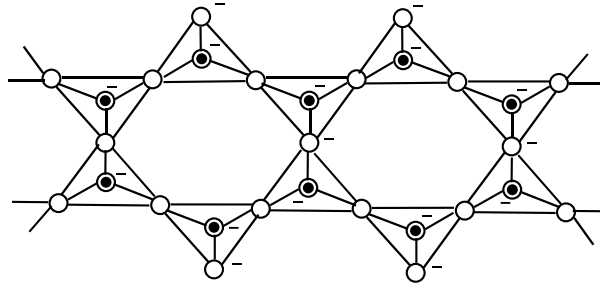
- d) **Chain silicates:** In such silicates a number of tetrahedral  $[SiO_4]^{4-}$  units are linked together by sharing two oxygen atoms giving rise to simple chain structures with general formula  $Si_nO_{3n}^{2n-}$ .



Example:

**Enstatite-  $MgSiO_3$**

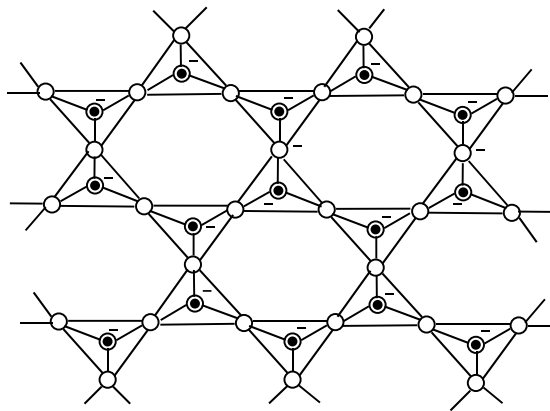
- e) **Double chain silicates:** In such silicates a number of tetrahedral  $[SiO_4]^{4-}$  units are linked together by two/three oxygen atoms giving rise to double chain structures with general formula  $(Si_4O_{11})_n^{6n-}$ .



Example:

**Tremolite  $\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$**

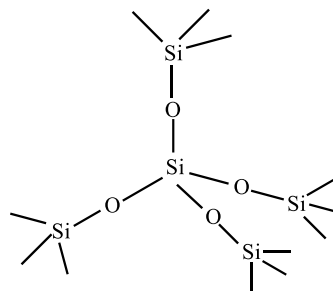
- f) **Sheet-like silicates:** In such silicates a number of tetrahedral  $[\text{SiO}_4]^{4-}$  units are linked together by sharing three oxygen atoms giving rise to sheet-like structures with general formula  $(\text{Si}_2\text{O}_5)_n^{2n-}$ .



Example:

**Talc-  $\text{Mg}_3(\text{OH})_2(\text{Si}_4\text{O}_{10})$**

- g) **Three-dimensional silicates:** In such silicates a number of tetrahedral  $[\text{SiO}_4]^{4-}$  units are linked together by sharing all the four oxygen atoms giving rise to three-dimensional structures with general formula  $(\text{SiO}_2)_n$ .



Three-dimensional silicates with no replacement of Si atoms by metal atoms occur in the amorphous form (sand) and three crystalline forms-quartz, tridymite and cristobalite.

Feldspars and zeolites are three-dimensional silicates in which some Si atoms are replaced by metal atoms.

**Orthoclase (a feldspar)-  $\text{KAlSi}_3\text{O}_8$ :** One  $\text{Si}^{4+}$  ion is replaced by one  $\text{K}^+$  ion and one  $\text{Al}^{3+}$  ion.

**Analcite (a zeolite) –  $\text{NaAlSi}_2\text{O}_6$ :** One  $\text{Si}^{4+}$  ion is replaced by one  $\text{Na}^+$  ion and one  $\text{Al}^{3+}$  ion.